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Reaction dynamics of excited states of helium and magneto-optical trapping of helium metastable atoms

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Rice University, 1993
REACTON DYNAMICS OF EXCITED STATES OF HELIUM AND MAGNETO-OPTICAL TRAPPING OF HELIUM METASTABLE ATOMS

by

XIN-XIN ZHAO

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

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HOUSTON, TEXAS

November, 1992
Abstract

Reaction Dynamics of Excited States of Helium
and Magneto-Optical Trapping of Helium Metastable Atoms

Xin-xin Zhao

The temperature dependence of conversion of He(2^3S_1) metastable atoms to He_2(a^3Σ_u^+) metastable molecules in the three-body reaction

He(2^3S_1) + 2He(1^1S_0) ----> He_2(a^3Σ_u^+) + He(1^1S_0)

has been investigated over the temperature range 65K-700K. This reaction is thermally activated as a consequence of a long range repulsive barrier in the He(2^3S_1)-He(1^1S_0) interaction potential. The data reveal that there are two reaction channels with distinctly different activation energies. The temperature dependence of the measured rate coefficient k_b(T) is accurately described by

k_b(T) = [87.4 x 10^{-37} cm^{-6}sec^{-1}]

The first activation energy, 750 ± 70K (63 ± 6meV), is equal to the known He(2^3S_1) - He(1^1S_0) repulsive barrier height. The second activation energy is 17± 2 meV.

The temperature dependences of the rate constants for collision-induced mixing among He(2^3P_{l_m_j}) levels, and for conversion of He(2^3P) atoms to He_2(b^3Π_g) molecules in the three body reaction

He(2^3P)+2He(1^1S) ----> He_2(b^3Π_g) + He(1^1S)

have been investigated over the range 1.4-300K. The measured thermally-averaged cross section for He(2^3P_{l_m_j}) mixing in collisions with ground state helium atoms are described by the function σ_pm(T) = (4.4 + 20.6/T^{1/3}) x 10^{-15} cm^2, and can be understood in terms of Langevin theory. The measured rate coefficients for the three body reaction exhibit a
strong inverse temperature dependence, \( k_p(T) = (0.04 + 2.18/T) \times 10^{-30} \text{ cm}^6 \text{s}^{-1} \), which suggests that, unlike conversion of \( \text{He}(2^3S_1) \) to \( \text{He}_2(a^3 \Sigma_u^+) \), there is no activation energy required for this reaction.

A magneto-optical trap for helium \( 2^3S \) metastable atoms has been designed and constructed, utilizing superconducting magnet gradient coils and a Ti:Sapphire ring laser for pumping the helium \( 2^3S-2^3P \) transition. \( \text{He}(2^3S) \) atoms are produced by a weak discharge in helium gas at temperature 1.3K. The discharge products flow through an orifice into the trap cell, where the \( \text{He}(2^3S) \) atoms are trapped and ground state helium atoms are rapidly cryopumped by zeolite pellets that cover most of the cell bottom. Preliminary experimental results suggest that \( \sim 10^6 \) atoms are trapped, with a trap lifetime of about 0.2 sec limited by \( \text{He}(2^3S) - \text{He}(2^3P) \) Penning reactions. Ultimately, it is estimated that a substantial number of atoms can be trapped and cooled for much longer times in a near-perfect vacuum. Measurements of decay times of the trapped atoms should yield rates for \( ^4\text{He}(2^3S) - ^4\text{He}(2^3S) \) and resonantly-enhanced \( \text{He}(2^3S) - \text{He}(2^3P) \) Penning reactions in the ultra-cold quantum regime, and perhaps the \( \text{He}(2^3S) \) natural lifetime.
Acknowledgements

It is my sincere pleasure to acknowledge the people who have helped make this thesis possible. I would like to express my sincere thanks to Professors King Walters and Barry Dunning for their guidance, encouragement, and patience throughout this work. Their continued support and personal attitude are deeply respected. I would also like to express my sincere thanks to Professor Randall Hulet for his many valuable advices. Thanks are due to Dr. Ali R. Koymen and Dr. Fu-Ching Tang with whom I started on this research, to my fellow graduate students Philip A. Soletsky and Wilkes Bryan for their productive team work, and to fellow graduate student David Oró for his valuable help on the computer interface. I would like to take this opportunity to thank everyone else in this laboratory.

Finally, I would like to thank my family for their constant love and spiritual encouragement throughout my 20 years as a student. My deepest thanks go to my best friend and wife Shaoping for her love and support throughout the thick and thin.
Dedication

To my father
Li-feng Zhao
Dec 24, 1931-Nov 11, 1991
who fighting with cancer for 2 years trying to see this.
Wish him happy now in heaven.
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Chapter One

Introduction

The low-lying excited states of the helium atom, particularly the He(2$^3$S$_1$) metastable state, have been the subject of numerous investigations over the years. He(2$^3$S$_1$) atoms, with their extremely long radiation lifetimes (greater than an hour) and large (19.8eV) internal energies, are important constituents of planetary, astrophysical and laboratory plasmas, and their properties have been exploited in a variety of important scientific and technological applications. In this laboratory optical pumping techniques are routinely employed to polarize He(2$^3$S$_1$) electron spins, enabling powerful spin-sensitive electron spectroscopies for studying dynamics of He(2$^3$S$_1$) reactions with other atomic and molecular species and with metallic surfaces, and as a basis for the development of intense beams of spin-polarized electrons for electron-atom/molecule reaction studies and possibly for accelerator applications in particle physics. When applied to the $^3$He isotope, optical pumping can be used to orient the nuclear spins, and this technique is widely used elsewhere to produce spin-polarized targets for nuclear scattering experiments, and for studies of the $^3$He Fermi quantum fluid at very low temperatures.

Only recently have lasers been developed that operate at wavelengths (~1083nm) required for exciting the He(2$^3$S$_1$) - He(2$^3$P) optical pumping transition. This new laser technology enables the investigation of fundamental reactions involving the helium 2$^3$P state, and open the way to laser cooling and trapping of He(2$^3$S$_1$) and He(2$^3$P) atoms for reaction studies in the ultra-cold (< 1mK) quantum regime.

This thesis reports the progress made in understanding the dynamics of fundamental two-body and three-body reactions involving helium atoms in the excited 2$^3$S$_1$ and 2$^3$P states, as well as the successful development of a magneto-optical trap in which metastable He(2$^3$S$_1$) atoms can be cooled for studies of inelastic atomic collisions in the
ultracold quantum regime. The thesis is arranged as follows: This first chapter gives a brief introduction to the pertinent properties of the excited atomic and molecular states of helium of interest here, and to laser trapping and cooling as applied to He(23S1) metastable atoms. Chapter Two reports the results of both experimental and theoretical (classical) studies of He(23Pj,Mj) state mixing in collisions with ground state helium atoms. Chapter Three reports the results of an experimental investigations of the conversion of He(23S1) and He(23P) atoms to He2(a3Σu+) and He2(b3Πg) molecules in three-body reactions. In Chapter Four the basic principles of laser cooling and trapping are discussed, as they apply to experiments on magneto-optical trapping of He(23S1) atoms. Chapter Five reports the results of experiments on cooling and trapping He(23S1) atoms.

A partial helium energy level diagram are shown in Figure 1.1. Of particular interest in this study are the 23S1 and 23P states with excitation energies 19.8eV and 21 eV respectively. In a collision-free environment, the only decay transition possible for the 23S1 state is to the 11S0 ground state. An examination of the selection rules shows [11], however, that the 23S1 state is metastable and is therefore effectively the ground state of the triplet system. The transition is forbidden for electrical dipole radiation since the parity does not change; electrical quadrupole radiation is also forbidden for a J=1→J=0 transition. Although the transition does satisfy the rigorous selection rules for magnetic dipole radiation, the selection rule ΔS = 0 would be violated. This rule holds well for helium since LS coupling is an excellent approximation. The most probable decay mode for the 23S1 states would therefore appear to be two-photon emission. In fact, for many years after the discovery of forbidden lines, it was thought that the 23S1 → 11S0 transition could occur only by two-photon emission with a transition probability between 10^-8 and 10^-9 s^-1. However, there are spin-dependent relativistic correction operators to the usual magnetic dipole operator which allow a nonzero relativistic magnetic dipole transition to exist directly
Figure 1.1 Helium Energy Level Partial Diagram
between the $2^3S_1$ states and the $1^1S_0$ ground state. The corresponding transition probability for this decay mode has been calculated [2] to be about $10^{-4}$ sec$^{-1}$, and the only experimental measurement of the He($2^3S_1$) life-time [3] agrees with theory within a factor three experimental uncertainty. The success of trapping He($2^3S_{j=1,m=1}$) atoms certainly opens the possibility for an accurate measurement of He($2^3S_1$) metastable radiation lifetime (see Chapter 5).

He($2^3P_{2,1,0}$) states can decay to $2^3S_1$ states through $\sim 1083$nm electrical dipole radiation with natural lifetime $10^{-7}$ sec. Transitions between He($2^3P$) sublevels through non-radiative collisions with He ground state atoms can also occur:

$$\text{He}(2^3P_{1,m}) + \text{He}(1^1S_0) \rightarrow \text{He}(2^3P_{j',m'}) + \text{He}(1^1S_0)$$ (1)

Measurements of the rate coefficient and thermally-averaged cross section for this collision process over the temperature range 1.4 - 300K are presented in Chapter 2 and results can be understood in terms of Langevin theory.

A partial He$_2$ molecular state diagram and interaction potentials are shown in Figure 1.2. The He$_2$(a$^3\Sigma_u^+$) interaction potential function, though highly attractive (-2eV) at shorter range ($\sim 1\text Å$), exhibits a weak repulsive barrier ($\sim 60$meV) at intermediate nuclear separation ($\sim 3\text Å$) and a very shallow ($< 1$meV) van der Waals minimum at large separation ($\sim 6\text Å$). This unusual potential can be interpreted qualitatively in terms of bonding in the short nuclear separation range where the interaction comes mainly from overlapping electron distributions and their consequent rearrangement in molecular orbitals according to the Pauli principle, while at longer range the interaction arises mainly from polarization and distortion of the electron distributions in separate atoms. Because the overlap energy in the molecular bonding range decreases exponentially while the long range van der Waals energy varies as the inverse sixth power of the separation, the latter dominates for most bound diatomic molecules at intermediate and large internuclear
Figure 1.2 Helium Molecular States and Interaction Potential [4]
separations, and the potential remains attractive over that range. However in the case of He$_2$(a$^3\Sigma_u^+$), the atomic polarizabilities are very small and the van der Waals attraction is sufficiently weak that the repulsive electron exchange interaction dominates and leads to a weak potential barrier at intermediate nuclear separation. This potential barrier was first predicted theoretically by Buckingham and Dalgarno [5] in 1952, and subsequently has been investigated by many others. The most recent theoretical calculations of the He$_2$(a$^3\Sigma_u^+$) molecular potential function done by Konowalow and Lengsfiel [6] in 1987 and by Yarkony [7] in 1989 yield He$_2$(a$^3\Sigma_u^+$) potential functions with an attractive minimum at 1.98 a$_0$ (a$_0$=0.51Å, Bohr radius) and a repulsive barrier at 5.1a$_0$ with a height of 65 meV, which is in good agreement with recent scattering experiments[8,9]. This barrier height also agrees with the activation energy measurement [10] reported in chapter 3 for the three-body conversion reaction

$$\text{He}(2^3S_1) + 2\text{He}(1^1S_0) \rightarrow \text{He}_2(a^3\Sigma_u^+) + \text{He}(1^1S_0)$$  \hspace{1cm} (2)

at high temperature; but an unexpected lower activation energy also appears at lower temperature. Latest theoretical calculations of the He$_2$(b$^3\Pi_g$) interaction potential suggest that there is no potential barrier for this state. [4] However earlier experiments[11] on He(2$^3P$) atoms produced in electron-bombarded superfluid liquid helium suggested that they repel ground state helium atoms and create a microscopic void (bubble) in the liquid helium. This was interpreted as evidence for the existence of a repulsive barrier. The experiments reported here provide a more direct test for the possible existence of a potential barrier between He(2$^3P$) and He(1$^1S_0$) ground state, by measuring the rate of three-body conversion

$$\text{He}(2^3P) + 2\text{He}(1^1S_0) \rightarrow \text{He}_2(b^3\Pi_g) + \text{He}(1^1S_0)$$  \hspace{1cm} (3)

over the temperature range 1.4 - 300K. The data suggest that, unlike He(2$^3S_1$) conversion to He$_2$(a$^3\Sigma_u^+$), reaction (3) is not thermally activated. This finding suggests that a new
interpretation is needed for the He(2^3P) bubble states in liquid helium, and this is provided in Chapter 3.

Reactions (2) and (3) are, perhaps, the most fundamental three-body reactions that can be simply studied in the laboratory over an extended temperature range, and their theoretical analysis should significantly advance the understanding of three-body reactions.

1.2. Laser Cooling and Trapping He(2^3S_1)

Laser cooling and trapping of alkali metals, especially of sodium, has been studied extensively. Sodium beams have been decelerated and stopped by frequency chirping of the laser[12-14], or by spatially varying Zeeman tuning [15-17]. Sodium atoms have been trapped at a minimum of the Zeeman potential[18,19] by the dipole force of the laser [20] and also by combinations of spontaneous light force, dipole force, and Zeeman field[21,22]. Because of the unique characteristics of the laser-cooled atomic gases, it is of great interest to extend this technique to other atomic species. Cooling and trapping of neutral helium in its metastable state 2^3S_1 has received considerable attention in recent years. In contrast to trapped alkalis, which are in their electronic ground states, trapping of He(2^3S_1) atoms with 19.8eV excitation energy opens the way to studies of reactive scattering in the ultracold quantum regime where the He(2^3S_1) de Broglie wavelength is much larger than the range of molecular interaction potentials. The de Broglie wavelength can be written

$$\lambda_{\text{del}} = \frac{2.5}{(AT)^{1/2}} \text{ nm}$$

where A is the mass in atomic units, and T the absolute temperature. Thus, for example \(\lambda_{\text{del}} = 200\text{ nm}\), for \(^4\text{He}\) at 30\(\mu\)K, as compared to the \(\sim 1\text{ nm}\) range of the interatomic potential.

If the vacuum is low enough that collisions of the trapped atoms with background gas is negligibly small, as one might reasonably expect to achieve with the trap design discussed in Chapter 5, loss of the trapped atoms would be dominated by the Penning reactions.
\[ \text{He}(2^3S) + \text{He}(2^3S) \rightarrow \text{He}^+ + \text{He}(1^1S) + \text{e}^- \quad (5a) \]

\[ \text{He}(2^3S) + \text{He}(2^3P) \rightarrow \text{He}^+ + \text{He}(1^1S) + \text{e}^- \quad (5b) \]

\[ \text{He}(2^3P) + \text{He}(2^3P) \rightarrow \text{He}^+ + \text{He}(1^1S) + \text{e}^- \quad (5c) \]

Aspect has shown that the resonantly enhanced reaction (5b) with rate \(10^{-7}\text{cm}^3\text{sec}^{-1}\) is one hundred times faster than (5a) and (5c). However, the rates for all the reactions can be greatly suppressed by spin-polarizing the reactants, since in that case a spin flip, hence a magnetic dipole transition, would be required. Further, \(\text{He}(2^3S_1)\) at its Doppler temperature of 30\(\mu\)K can be expected to be well into the quantum threshold range where only \(s\)-wave scattering will make an appreciable contribution to the spin-polarized \(\text{He}(2^3S_1)\)-\(\text{He}(2^3S_1)\) interaction rate. The corresponding rate coefficient for ionization of the spin-polarized \(3^3\text{He}(2^3S_{j=1,m=1})\) isotope should be much smaller compared with that of \(4^3\text{He}(2^3S_{j=1,m=1})\), since this fermion can only collide in \(p\)-waves (and high odd waves) when spin-polarized, and the \(p\)-wave coefficient vanishes in the \(T\rightarrow 0\) limit. Also worthy of note is that a far better, direct measurement of \(\text{He}(2^3S_1)\) radiation lifetime than is currently available might be possible.

In 1989, Kazuko Shimizu and Hiroshi Takuma demonstrated laser trapping of metastable Ne atoms \(^{23}\). They report that \(10^7\) atoms were trapped; however, due to high background density (\(~10^{-7}\)torr) the lifetime of the trap is 150ms which makes reliable measurements of interactions between trapped atoms impossible. In 1991, using a magneto-optical trap (MOT) similar to Shimizu's, Aspect etc were the first to trap \(\text{He}(2^3S_1)\) atoms \(^{24}\); \(10^4\) atoms were trapped, and they found that the rate coefficient for \(\text{He}(2^3S_1) \rightarrow \text{He}(2^3P)\) Penning reactions at ultra-low temperatures is in the order of \(9\times10^{-8} \text{cm}^3\text{s}^{-1}\), which severely limits the trapped \(\text{He}(2^3S_1)\) density and lifetime. To overcome these problem and take advantage of the fact that one can produce \(\text{He}(2^3S_1)\) directly at cryogenic temperatures, Metcalf suggested a possible way to load the trap directly from an electrical discharge at 1.5K \(^{25}\). This technique requires a deep MOT trap and fast removal of \(\text{He}\).
ground state atoms. Unfortunately Metcalf's calculation is based on an one dimensional model which over estimates the effective average trapping depth significantly, and the proposed loading method requires very high helium pumping speed which is very difficult to achieve. For the experiments reported in Chapter 5, a new type of M.O.T for trapping He($^{23}S_1$) atoms was designed. The trap chamber is immersed in liquid helium at 1.3K and utilizes superconducting magnet gradient coils and Ti:Sapphire ring laser for pumping the helium $^{23}S_1$-$^{23}P$ transition. He($^{23}S_1$) atoms are produced by a weak discharge in helium gas at 1.3K. The discharge products flow through an orifice into the trap cell, where the He($^{23}S_1$) atoms are trapped and ground state helium atoms are rapidly cryopumped by zeolite pellets that cover most of the cell bottom. Preliminary experimental results suggest that $\sim 10^6$ atoms are trapped, with a trap lifetime of about 0.2 sec limited by He($^{23}S$) - He($^{23}P$) Penning reactions. Ultimately, it is estimated that a substantial number of atoms can be trapped and cooled for much longer times in a near-perfect vacuum. Measurements of decay times of the trapped atoms should yield rates for $^4$He($^{23}S$) - $^4$He($^{23}S$) and resonantly-enhanced He($^{23}S$) - He($^{23}P$) Penning reactions in the quantum regime, and perhaps the He($^{23}S$) natural lifetime. Because the trap size is limited by the dewar size, larger, deeper and better traps are might be built in the future (see Chapter 5).
Chapter Two
Collisional Mixing of He($2^3P_J$,m_J) States
— He($2^3S^1$)-He($2^3P_J$) Transition Line Shapes

2.1. Excited States Mixing

The effects of excitation transfer between excited states of an atom as a result of collisions are an important process in determining the equilibrium populations of many gaseous systems. These collisional mixing processes are of considerable interest in the analysis of optical pumping experiments and the behavior of gas lasers.

The earliest observation of collisional mixing was made by Mohler and Wood [26] in sodium vapor. In 1967, Schearer [27] using a resonance-fluorescence technique measured the room temperature cross section for the transfer of excitation from the $^3$He($2^3P_0$) to $^3$He($2^3P_{1,2}$) states as a result of collisions with the ground state $^3$He atom.

The usual procedure for observing the effects of mixing is to populate one of the excited levels by irradiation with one of the components of the resonance radiation fine structure levels and then examine the resonance fluorescence in which other fine structure components appear. In helium the resonance radiation connects the metastable $2^3S_1$ level with the $2^3P_{0,1,2}$ levels. Collisional mixing between the $2^3P_J$ levels as a result of collisions with the ground state He atoms modifies the light-induced population therefore changing the transition line shape. We have measured the mixing rate both as function of helium density and temperature by measuring the line shape of the transitions He($2^3S_1$)-He($2^3P_J$).

2.2. Line Shape

Three physical effects determine the line shape function $g(\omega,\omega_0)$, two of them being universal. First, Doppler shifts associated with thermal or any other random motions of the radiating or absorbing atoms always cause some broadening. The Doppler line profile
resulting from thermal motion is Gaussian. Second, there is natural broadening due to the finite radiative lifetime of states involved in the transition. The third contribution arises from the interactions of the radiating systems with the surrounding atoms. Such interactions not only reduce their lifetime through collision-induced transitions but also can shift the atomic energy levels (especially in the cases of liquids, plasmas or quantum gases). The general name for this third effect is pressure broadening. Lifetime and pressure broadening introduce Lorentzian components to the line shape.

Therefore the proper lineshape function for He(2\(^3\)S\(_1\)) - He(2\(^3\)P\(_j\)) transition, is in general neither Gaussian nor Lorentzian but rather a convolution of a Gaussian \(g_G(\omega,\omega_0)\) resulting from Doppler (inhomogeneous) broadening and a Lorentzian \(g_L(\omega,\omega_0)\) representing a combination of spontaneous emission and p-state mixing. The convolution integral is commonly called a Voigt function \(g_V(\omega,\omega_0)\) and given by:

\[
g(\omega,\omega_0) = \int_{-\infty}^{\infty} g_L(\omega,\Omega) g_G(\Omega,\omega_0) d\Omega
\]

(2-1)

with:

\[
g_L(\Omega,\omega_0) = \frac{\Delta \omega_L / 2}{[(\Omega - \omega)^2 + (\Delta \omega_L / 2)^2]}
\]

(2-2)

\[
\Delta \omega_L = 2(A + \sigma_p vN) = 2(A + k_m P)
\]

and

\[
g_G(\Omega,\omega_0) = \left(\frac{4\ln 2}{\pi}\right)^{1/2} \frac{1}{\Delta \omega_G} \exp\left[-4\ln 2 \frac{(\Omega - \omega_0)^2}{\Delta \omega_G^2}\right]
\]

(2-3)

\[
\Delta \omega_G = \frac{2\omega_0}{c} \left[\frac{2k_B T \ln 2}{M}\right]^{1/2}
\]

where \(\sigma_p\) is the p-state mixing cross section, \(k_m\) the p-state mixing rate, \(P\) the helium pressure, \(\omega_0\) the central frequency of the line profile, \(c\) the speed of light, \(v = \frac{16 kT}{\pi M}\) the mean relative velocity of the atoms, \(k_B\) the Boltzmann constant \((8.612 \times 10^{-5} \, \text{eV/K})\), \(T\) the temperature, and \(M\) the atomic mass.
2.3. Experimental Method

The scanning ability of the Ti:Sapphire laser can be used to study the lineshapes of the He(2^3S_1) ↔ He(2^3P_{0,1,2}) transitions. (The Ti:Sapphire laser can be scanned over a range 12 GHz, with center frequency drift ~1MHz/minute when locked to a commercial reference cavity.) As discussed above, the lineshape is not a pure Gaussian, but a convolution of a Gaussian (due to Doppler broadening) and a Lorentzian (representing a combination of spontaneous emission and p-state mixing). This lineshape, the Voigt profile, can be decomposed using a simple graphical analysis method\cite{28} in order to find the widths of the individual Gaussian \[ c \exp(-x^2/\beta_2^2) \] and Lorentzian \[ \frac{c}{1+(x/\beta_1)^2} \] contributions to the lineshape as shown in Figure 2.1, where h is the Voigt profile full width at half peak intensity, \( b_{0.1} \) the width at one-tenth of peak intensity.

A schematic diagram of the apparatus used in this investigation is presented in Figure 2.2. Prior to taking data, the sample cell is cleaned by baking and repetitive discharge cleaning in which helium admitted to the cell is subjected to an intense rf discharge, and then is pumped away. This procedure is terminated when the discharge spectrum observed with a hand-held spectroscope is characteristic of pure helium. If any lines not characteristic of helium are observed, the cell is purged and the cleaning process repeated. This clean sample cell is filled with high purity helium to the desired density, and data acquisition begins.

The sample temperature can be adjusted by immersing the cell in either liquid nitrogen or liquid helium. The helium is excited by an RF discharge that is weak enough to avoid heating the sample gas significantly. The Ti:Sapphire laser is scanned across the desired transition. The scanning width is set so as to assure that the entire lineshape under investigation is observed. The lineshape is monitored by measuring the absorption of the
Figure 2.1 Working Graph of the Parameters

Where $h$ is measured line width, $b_{0.1}$ the width at one-tenth of peak intensity,

$$\beta_1 = \Delta \omega / 4\pi, \quad \beta_2 = \Delta \nu / 1.665.$$
Figure 2.2 System Schematic Diagram
laser light using a silicon photodetector. As the transition is scanned, the signal from the photodetector is digitized and stored by computer. A pulse from the CR899-21 Ti:Sapphire laser control electronics triggers the computer at the beginning of each scan, and scanning is repeated and summed until a good signal to noise ratio is achieved. To check that the measured lineshapes are not distorted by saturation of the transition, the probing laser intensity is reduced by neutral density filters until the measured line shape becomes independent of intensity. Line shapes of the \( \text{He}(2^3S_1) \leftrightarrow \text{He}(2^3P_{0,1,2}) \) transitions were measured as functions of both helium density and temperature. Both Gaussian and Lorentzian components of the \( \text{He}(2^3S_1) \leftrightarrow \text{He}(2^3P_{0,1,2}) \) transition line shape are obtained directly from the data, and the Lorentzian component is used to calculate the \( \text{He}(2^3P_j, m_j) \) mixing rate and thermally averaged cross section.

2.4. Experimental Results

The \( \text{He}(2^3S_1) - \text{He}(2^3P) \) transition lineshapes were measured as a function of gas density at several temperatures (300K, 77K, 4.2K, 1.4K), and representative examples are shown in Figure 2.3. \( \hbar \) and \( b_{0,1} \) were measured for each lineshape. The laser scan width was calibrated to the frequency difference between \( D_1 \) and \( D_2 \) lines (2.33GHz). Both Gaussian and Lorentzian components \( \beta_2 (\Delta \nu_G / 1.665) \) and \( \beta_1 (\Delta \omega_L / 4\pi) \) of each lineshape profile were determined by the graphical decomposition procedure described above. The Gaussian components were checked to be within 10% of the calculated Doppler width at each temperature. (Except for the data at 1.4K, where the measured Gaussian width was much larger than Doppler width, presumably because of fluctuations in the laser frequency.) The expected linear density dependence of the extracted \( \Delta \omega_L \) for 4.2K is shown in Fig 2.4. Thermally averaged collisional mixing cross-sections are obtained using eq(2-2). The results, which are in good agreement with Schearer's measurement at 300K, are shown in Figure 2.5.
Figure 2.3 Representative $^2\text{S} - ^2\text{P}$ Transition Line Shapes. Where Frequency is Calibrated by the Difference Between Centers of $D_1$ and $D_2$ Transitions (2.33 GHz).
Figure 2.4 Density Dependence of $\Delta \omega_L$ at 4.2K

Figure 2.5 Thermally-Averaged P-State Mixing Cross Section
The data show that the cross section for \( \text{He}(2^3P_J, m_J) \) mixing is independent of \( J \) and \( m_J \) (\( D_{0,1,2} \) have the same line widths), which is to be expected since the fine structure splittings are much less than \( kT \) in these experiments, hence \( \sigma_I, m_J/\sigma_I', m_J' \sim \exp[ (E_I, m_J - E_I', m_J')/k_B T] \sim 1. \)

It is clear from Figure 2.5 that \( \sigma_p \) varies as \( (T)^{-1/3} \), which is consistent with the dependence expected from simple two-body Langevin collision theory assuming that \( J, m_J \) mixing is associated with so called "sticky" orbiting collisions. Consider the effective interaction potential as a combination of a (repulsive) centrifugal term \( V_c \) and an (attractive) van der Waals term \( V \) as shown in Figure 2.6:

![Figure 2.6 The Effective Potential Functions Used for Analysis of Scattering in an Attractive Inverse-Sixth-Power Potential Field.](image)

Thus

\[
V_{\text{eff}}(r) = \frac{L^2}{2\mu r^2} \cdot \frac{C}{r^6}
\]

(2-5)

where \( L \) is the angular momentum, \( \mu \) is the reduced mass, and \( C \) is a constant.
This $V_{\text{eff}}(r)$ has a maximum at a distance $r_0$ given by:

$$\frac{dV_{\text{eff}}(r)}{dr} \bigg|_{r=r_0} = -\frac{12}{\mu r_0^3} + \frac{6C}{r_0^2} = 0$$

with the solution:

$$r_0 = \left(\frac{6\mu C}{L^2}\right)^{1/4} \quad (2-6)$$

Let us consider the motion for several different values of the total energy. A particle of energy $E_1 < E_0$ starting at large $r$ and moving toward the center of attraction will evidently be reflected at $r = r_n$ by the potential barrier shown. If, however, the total energy is $E_2 > E_0$, the particle will be able to pass over the potential barrier. It will experience a repulsion only for $r > r_0$ and will sense an attraction thereafter, as its radial distance from the scattering center decreases. When $E > E_0$, the particle actually passes through the center of attraction. A particularly interesting situation develops when the total energy just exceeds $E_0$, the value of $V_{\text{eff}}(r)$ at the peak of the potential curve. In this case the particle will spend a considerable time at a radial distance near the peak, while spiraling inward toward the center. The particle is then said to "orbit" about the scattering center. (This type of collision is sometimes referred to as a "sticky collision"). The angular motion speeds up as $r$ decreases in order to conserve angular momentum, and a large number of revolutions may be made. (This is an unstable orbit, unlike those for which $n < 2$.) Under certain conditions the scattering angle may approach $-\infty$. We see that the orbits may thus be meaningfully classified as spiraling or nonspiraling, and this distinction is frequently encountered in the literature.

Expressing the angular momentum of the system in terms of the impact parameter, $b$, and the kinetic energy of the relative motion, $E_K (= \mu v^2/2 = 3k_B T/2)$:

$$L = \mu b v = b (2\mu E_K)^{1/2} \quad (2-7)$$

allows $r_0$ to be rewritten:

$$r_0 = \left(\frac{3C}{E_K b^2}\right)^{1/4} \quad (2-8)$$
Thus for an orbiting collision to occur, \( b_0 \) must satisfy \( E_K = V_{\text{eff}}(r_0) \):

\[
E_K = V_{\text{eff}}(r_0) = \left(\frac{E_K b^2}{3C}\right)^{1/2} [E_K b^2 - E_K b^2/3] = \left(\frac{E_K b^2}{3C}\right)^{1/2} [2E_K b^2/3]
\]

(2-9)

i.e. \( b_0 = \left(\frac{22C}{4E_K}\right)^{1/6} = \left(\frac{9C}{2k_B T}\right)^{1/6} \)

(2-10)

Orbits for which \( b < b_0 \) would pass through the origin if no repulsive core were present, whereas those orbits for which \( b \geq b_0 \) come no closer than \( r_0 \). Several versions of each type are plotted in Figure 2.7. Langevin suggested that it is reasonable to suppose that there exists a certain critical radius \( r_c \) such that a given type of reaction between the two particles under consideration is impossible if the distance of the closest approach is greater than \( r_c \) and almost certain to occur if it is less than \( r_c \). Then, if \( r_c \) lies between 0 and \( r_0 \), all collisions for which \( b < b_0 \) must lead to this reaction. We may therefore assume the cross section for the reaction is the same as the cross section for orbiting collisions, namely \( \sigma_P = \pi b_0^2 = (T)^{-1/3} \). This is the Langevin cross-section, which predicts a temperature dependence for collisional mixing that agrees well with the experimental results.
Figure 2.7 Representative Trajectories for the Inverse-Sixth-Power Polarization Potential as a Function of the Impact Parameter $b$ for a Given Velocity $v_0$. For Clarity Only the Incoming Branch of Each Spiraling Trajectory Is Shown.
Chapter Three

$\text{He}(2^3S)$ and $\text{He}(2^3P)$ Three-body Conversion

Conversion of $\text{He}(2^3S)$ atoms to $\text{He}_2(a^3\Sigma_u^+)$ molecules by the three-body reaction

$$\text{He}(2^3S_1) + 2\text{He}(1^1S_0) \rightarrow \text{He}_2(a^3\Sigma_u^+) + \text{He}(1^1S_0)\quad (2)$$

where $\text{He}$ is a ground state helium atom, plays a significant role in the kinetics of rf discharges in helium. $\text{He}_2(a^3\Sigma_u^+)$ molecules are also produced in copious quantities in electron-bombarded liquid helium, and have been shown also to be metastable with radiative lifetime $\geq 0.1$ sec. In 1953, Phelps and Molnar reported measurements of rate coefficients for (2) at two temperatures 300K and 77K, that suggested an activation energy of about 30 meV, consistent with earlier predictions of the existence of a long-range repulsive barrier in the $\text{He}(2^3S_1)$ - $\text{He}$ interaction potential. Since that time, experiments and theory have converged on a barrier height of about 60 meV, apparently inconsistent with the Phelps-Molnar experiment. The present experiment was undertaken in an attempt to resolve this discrepancy by measuring the rate coefficient of reaction (2) over a wide temperature range. The recent development of high-intensity lasers capable of producing appreciable steady-state populations of $\text{He}(2^3P)$ atoms by exciting $2^3S_1 - 2^3P$ transitions in the afterglow of a pulsed rf discharge made possible the extension of the investigation to include also the corresponding three-body conversion reaction for $\text{He}(2^3P)$ atoms,

$$\text{He}(2^3P) + 2\text{He}(1^1S_0) \rightarrow \text{He}_2(b^3\Pi_g) + \text{He}(1^1S_0)\quad (3)$$

In this chapter, the dynamics of three-body atom-molecule conversion reactions are discussed qualitatively. This is followed by development of a rate equation model for interpreting the three-body conversion kinetics when the $\text{He}(2^3S_1)$ and $\text{He}(2^3P)$ atoms are coupled by an intense radiation field. A discussion of the experiments and their interpretation complete the chapter.

3.1. Dynamics of Three-body Atom-Molecule Conversion [29]
Let us consider two atoms approaching each other with interaction potential energy as function of internuclear distance shown in Figure 3.1.

![Interaction Potential Between Two Atoms](image)

**Figure 3.1 Interaction Potential Between Two Atoms**

The total energy of the two atoms is represented by the horizontal line AB. At every point the relative kinetic energy of the collision partners is given by the vertical distance of this line to the potential curve. At point A, the kinetic energy is completely converted into potential energy. Classically, it is the turning point for the motion. After reaching it, the potential curve is traversed in the opposite direction, and the two atoms fly apart again.

A permanent recombination of the two atoms will take place only when energy is removed during the short time during which the potential energy is smaller than at infinite separation. This time is of the order of a period of vibration, that is, of the order of $10^{-13}$ sec. (The collision time is somewhat less than the time obtained by dividing the distance $2xAB$ in Figure 3.1 by the average speed of the free atoms, since in the region AB their kinetic energy is increased). The removal of energy may occur in only two ways: either by
collision with a third particle during the collision time (three-body conversion) or by radiation of energy (two-body conversion). Molecular formation in a two-body collision is, however, a very rare process, since the time that elapses on the average before an excited molecule radiates (about 10^{-8} sec) is very long compared to the duration of the collision (10^{-13} sec). As a result, molecular formation in two-body collisions take place only for an extremely small fraction \( \gamma \) of the collisions (about 10^{-5}). This mechanism is important only when the density of atoms is so low that three-body collisions are extremely infrequent, as, for example in the Earth's upper atmosphere or in the interstellar space. On the other hand, molecular formation via three-body collisions dominates at the moderate-to-high gas densities used in the experiment reported here.

3.2. Kinetic Model for Three-body Conversion of Radiation-Coupled He(2^3S) and He(2^3P) States

In the late afterglow of a pulsed rf discharge in helium gas, the residual He(2^3S) population decay exponentially as a result of the three-body reaction (2), and/or diffusion of the He(2^3S) atoms to the container walls where they are deexcited. If the afterglow is illuminated with intense 1083 nm radiation which excites 2^3S - 2^3P transitions, the 2^3P state also has a significant population, and the corresponding 2^3P three-body reaction (3) and diffusion of the He(2^3P) atoms must also be taken into account. The radiative and kinetic processes governing the decay of the coupled He(2^3S) and He(2^3P) system are illustrated in Figure 3.2, and the differential equations describing the He(2^3S) and He(2^3P) populations are:

\[
\frac{dS}{dt} = - [R(g_p/g_s) + \Theta_s/\Lambda^2 + k_sN^2]S + (R + A)P \quad (3 - 1)
\]

\[
\frac{dP}{dt} = R(g_p/g_s)S - [R + A + \Theta_p/\Lambda^2 + k_pN^2]P \quad (3 - 2)
\]

where \( S \) and \( P \) are the He(2^3S) and He(2^3P) populations respectively, \( R \) is the stimulated emission rate, \( g_s \) and \( g_p \) are the statistical weights of the 2^3S and 2^3P sublevels respectively, \( \Theta_s \) and \( \Theta_p \) are the diffusion coefficients for 2^3S and 2^3P atoms respectively,
A is the Einstein coefficient for spontaneous emission, \( \Lambda \) is the lowest mode diffusion length, \( k_s \) and \( k_p \) are the reaction rate constants for three-body conversion of \( ^2S^3 \) and \( ^2P^3 \) respectively, and \( N \) is the He(\( ^1S \)) atom density.

![Figure 3.2 He(\( ^2S^3 \)) and He(\( ^2P^3 \)) Coupled System](image)

Further,

\[
R = (\text{stimulated emission cross section}) \times (\text{photon flux}) \\
= \frac{\lambda^2}{8\pi} A g(\omega, \omega_0)(I_\omega/\hbar \omega)
\]  

(3 - 3)

where \( \lambda \) is the optical pumping wavelength (1.083 \( \mu \)m), \( I_\omega \) is the light intensity at frequency \( \omega \), and \( g(\omega, \omega_0) \) is the Voigt lineshape function of the transition, which is Gaussian in the limit \( N \rightarrow 0 \) and Lorentzian in the limit \( N \rightarrow \infty \).

Solutions to (3 - 1), (3 - 2) are of the form:

\[
S, P \sim \exp(-\alpha_\pm t)
\]  

(3 - 4)

where \( (\alpha_\pm)^{-1} \) are the time constants governing the \( S(t), P(t) \) population.

Substituting (3 - 4) to (3 - 1) and (3 - 2), using approximation that the term \([A + R(1 + g_p/g_s)]\) is much greater than all other terms for all laser intensities employed, we get (see Appendix I):

\[
\alpha_+ = A + R(1 + g_p/g_s)
\]  

(3 - 5)

and

\[
\alpha_- = \frac{(A+R)(k_sN^2 + \Theta_s^0/\Lambda^2N) + R(g_p/g_s)(k_pN^2 + \Theta_p^0/\Lambda^2N)}{A + R(1+g_p/g_s)}
\]  

(3 - 6)
where $\Theta_{S,P}^o = \Theta_{S,P} N$ are density independent \cite{30}, $\alpha_+$ is the characteristic rate at which the S and P states come into equilibrium with one another ($= 10^7$ s$^{-1}$), while $\alpha_-$ is the measured common decay rate of the S and P states.

Substituting (3 - 3) into (3 - 6), in the limit $R << A$ (low laser power), yields:

$$\alpha_- = \left[ k_s N^2 + \Theta_{S}^0 \right] + \frac{g_p}{g_s} \left[ (k_p-k_s)N^2 + \Theta_{P}^0 - \Theta_{S}^0 \right] \frac{\lambda^2}{8 \pi} \frac{g(\omega, \omega_0)}{\hbar \omega} I_\omega \quad (3 - 7)$$

and

$$\frac{d\alpha_-}{dI_\omega} = \frac{g_s}{g_s} \frac{\lambda^2}{8 \pi \hbar \omega} g(\omega, \omega_0) \left[ (k_p-k_s)N^2 + \Theta_{P}^0 - \Theta_{S}^0 \right], \quad (3 - 8)$$

whereas in the limit $R >> A$ (saturation limit)

$$\alpha_- = \frac{g_s}{g_s + g_p} \left[ k_s N^2 + \Theta_{S}^0 \right] + \frac{g_p}{g_s + g_p} \left[ k_p N^2 + \Theta_{P}^0 \right] \quad (3 - 9)$$

From equation (2 - 1), we obtain (Appendix I):

$$g(\omega_0, \omega_0) = \frac{0.939}{\Delta \omega_G} f(N,T) \quad (3 - 10)$$

where $\Delta \omega_G = \frac{2 \omega_0}{c} \left[ \frac{2k_B T \ln 2}{M} \right]^{1/2}$, is the Gaussian width of the transition at temperature $T$ and $f(N,T)$ is numerical factor by which $g(\omega_0, \omega_0)$ deviates from $g_G(\omega_0, \omega_0)$ due to p-state mixing and spontaneous emission; $\omega_0$ is the central frequency of the line profile, $c$ is the speed of light, $k_B$ is the Boltzmann constant ($8.612 \times 10^{-5}$ eV/K), $T$ is the temperature, and $M$ is the atomic mass. The p-state mixing rate coefficients reported in Chapter Two are used to calculate $f(N, T)$ for comparison of the kinetic model predictions with experiment. (For densities less than $3.5 \times 10^{17}$ cm$^{-3}$, the lineshape $g(\omega, \omega_0)$ is Gaussian at all temperatures to within 10%.) Substituting (3 - 10) into (3 - 8) and assuming the laser to be tuned to line center (i.e., $\omega = \omega_0$), we obtain:

$$\frac{d\alpha_-}{dI_\omega} = \frac{g_p}{g_s} \frac{\lambda^2}{8 \pi \hbar \omega} \frac{0.939}{\Delta \omega_G} f(N,T) \left[ (k_p-k_s)N^2 + \Theta_{P}^0 - \Theta_{S}^0 \right] \quad (3 - 11)$$

Figure 3.3 illustrates the dependence of $\alpha_-$ on $I_\omega$. From this figure, we see that the intercept at $I = 0$ yields $k_s$, and the slope yields $(k_p-k_s)$ hence $k_p$, so long as the density $N$
is sufficiently large that diffusion can be neglected. This condition is easy to satisfy experimentally.

In the actual experiment, \( k_s \) was obtained by measuring the He(\( ^2\text{S} \)) metastable decay time as function of He density using a very weak laser probe beam or a helium discharge lamp.\(^{10}\) To measure \( k_p \), the He(\( ^2\text{S} \)) metastable lifetimes were extracted from semi-log plots of the fractional absorption versus time. While maintaining the pressure and temperature constant, the laser intensity \( I_\omega \) was varied using neutral density filters. In this way, plots of \( \alpha \) versus \( I_\omega \) are obtained for several gas densities. For low laser intensities, as is seen from \(( 3 - 11)\), these are linear. Since all other factors are known, \( k_p \) can then be determined from the slope. Repetition of the procedure at various temperatures allows study of the dependence of \( k_p \) on \( T \).

\[
\frac{g_s}{g_s + g_p} \left( k_s N^2 + \frac{\Theta_s^0}{\Lambda^2 N} \right) + \frac{g_p}{g_s + g_p} \left( k_p N^2 + \frac{\Theta_p^0}{\Lambda^2 N} \right)
\]

\[
\frac{d{\alpha}_N}{d\omega} = \frac{g_p}{g_s 8\pi \tilde{\alpha} \omega} g(\omega, \omega_0) \left( (k_p - k_s) N^2 + \frac{\Theta_p^0 - \Theta_s^0}{\Lambda^2 N} \right)
\]

Figure 3.3 Illustration of Decay Rate \( \alpha \) as Function of Laser Intensity \( I_\omega \).

B. Experiments and Results

B1. He(\( ^2\text{S} \)) Three-body Conversion Rate

The temperature dependence for conversion of He(\( ^2\text{S} \)) metastable atoms to He\(_2\)(\( ^3\Sigma_u^+ \)) metastable helium molecules in the three-body reaction (2) was investigated over the temperature range 65-700K.\(^{10}\) A conventional helium discharge afterglow
technique, similar to that of Phelps [30,31] was used to measure the temperature dependence of the volume loss rate of He($^23S_1$) atoms resulting from this reaction. He($^23S_1$) metastable atoms were created in a small Pyrex sample cell by pulsed rf excitation and their subsequent loss monitored by measuring the absorption of 1.083µm $^23S-^23P$ resonance radiation. The experimental apparatus is shown schematically in Figure 3.4. The cylindrical Pyrex sample cell was initially prepared by baking and electrical-discharge cleaning. Helium gas was then admitted to the desired density and the sample temperature adjusted either by immersion in selected cryogenic fluids, or by heating in a simple oven. Helium atoms in the cell were excited to the $^2S$ state by igniting a week electrodeless 3 MHz pulsed electrical discharge of $\approx$ 100 µs duration at a repetition rate

![Figure 3.4 System Schematic Diagram](image)

between 10 and 150 per second depending on sample density and temperature. The He($^23S$) population was monitored during the afterglow period by measuring the absorption of 1.083 µm $^23S-^23P$ resonance radiation from a low-power rf-excited helium lamp. Absorption signals recorded following many rf pulses were accumulated and integrated using a waveform eductor and output to an X-Y plotter. Care was taken to
ensure that the rf pulse discharge energy was low enough to avoid heating the sample gas significantly. The weak discharge pulses also assured that the fractional absorption of 1.083 μm probing radiation was small, always < 5% for T ≥ 200 K and < 2% at lower temperatures. Measurements verified that He(2³S) decay rates were independent of both the rf pulse energy and the intensity of the probing radiation which uniformly illuminated the entire sample cell so as to minimize possible effects associated with local variations in He(2³S) density that can result from rf excitation.

In the early afterglow, immediately following the rf discharge pulse, significant production of He(2³S) metastable atoms can occur as a result of He(2¹S) to He(2³S) conversion in superelastic collisions with electrons, and an important loss channel is Penning ionization in collisions between pairs of He(2³S) atoms that results in ionization of one and deexcitation of the other. Phelps [31] and PM [30], however, demonstrated that both of these processes can be neglected at times sufficiently late in the afterglow that the He(2¹S) → He(2³S) conversion is nearly complete and the He(2³S) density is low. Data acquisition was therefore restricted to times sufficiently late into the afterglow that the He(2³S) population was observed to decay exponentially in time. The differential equation governing the He(2³S) concentration during the time interval over which data were recorded is

\[
\frac{\partial M}{\partial t} = \frac{D_0}{N} \nabla^2 M - k_s N^2 M, \tag{3 - 12}
\]

where M and N are the concentrations of metastable 2³S and ground-state helium atoms (M << N), D₀ is the 2³S diffusion coefficient normalized to unit density, and ksN² is the frequency for destruction of He(2³S) metastable atoms by the ternary reaction (2). Under the assumption of a He(2³S) spatial distribution given by the fundamental diffusion mode, the solution to eq. (3 -12) is

\[
M = M_0 \exp(-t/\tau) \tag{3 - 13}
\]
where the decay rate is

\[ \frac{1}{\tau} = \frac{D_0}{N\Lambda^2} + k_d N^2 \]  \hspace{1cm} (3 - 14) \]

and \( \Lambda \) is the lowest-mode diffusion length of the sample cell. For the cylindrical cell of length \( L = 3.5 \text{ cm} \) and radius \( r = 0.75 \text{ cm} \) used in most of the present work \( \Lambda^2 = \left[ \frac{(\pi/L)^2 + (2.4/r)^2}{\Lambda^2} \right]^{-1} = 0.09 \text{ cm}^2 \). To test that the present data were recorded at gas densities sufficiently high that the He(\( ^2\text{S} \)) loss is dominated by reaction (2) decay rates were measured as a function \( N \). Typical data are presented in Figure 3.5 for several representative sample temperatures and the observed quadratic dependence of the measured rates on \( N \) confirms that He(\( ^2\text{S} \)) loss results from reaction (2).

Further evidence that reaction (2) is responsible for He(\( ^2\text{S} \)) destruction was obtained by monitoring the time development of the He\(_2\)(\( a^3\Sigma_u^+ \)) population in the afterglow by measuring the absorption of the 910 nm band of the He\(_2\)(\( a^3\Sigma_u^+ \rightarrow c^3\Sigma_g^+ \)) system. This time development is shown in Figure 3.6 for temperatures of 77 K (190 Torr) and 300 K (80 Torr) together with the decay of the He(\( ^2\text{S} \)) population under the same experimental conditions. Comparison of these data show that as the \( ^2\text{S} \) atoms are destroyed there is a corresponding build-up of He\(_2\)(\( a^3\Sigma_u^+ \)) molecules confirming that reaction (2) is indeed the dominant He(\( ^2\text{S} \)) destruction mechanism.

![Figure 3.5 Dependence of the Measured Decay Rates on Helium Density at Selected Temperatures.](image)
Figure 3.6 Time Evolution of the He(2^3S) and He_2(a^3Σ_u^+) Populations in the Afterglow.

Data were taken over a temperature range extending from 65 to 700 K. For temperatures below ~300 K, the sample cell was immersed in a cryogenic fluid, specifically liquid nitrogen (65-77 K), argon (87 K), freon-14 (120-144 K), a mixture of freon-11 and dry ice (196 K), or ice water (273 K). The temperature ranges indicated for liquid nitrogen and freon-14 were achieved by reducing and measuring the vapor pressure above the liquid bath. For measurements above 300 K the sample cell was mounted in a heated oven, and the temperature determined by use of a thermocouple.

The measured rate coefficient were displayed in Figure 3.7 where k_f/T is plotted as a function of 1/T. Also shown are the earlier data[30,31] which are in good agreement with our results.
He(\(^{23}\)S) + 2He(\(^{11}\)S) \rightarrow \text{He}_2(\text{a}^3\Sigma_u^+) + \text{He}(\text{1}\text{S})

![Graph showing rate coefficients](image)

\[ k_{s(T)} \times 10^{-37} \text{ cm}^6 \text{ sec}^{-1} \text{ K}^{-1} \]

\(1 / T \text{ (K}^{-1})

\[ 1 \quad 0.01 \quad 0.015 \quad 0.02 \]

\( k_{s(T)} \) present results for \(^4\text{He} \) and \(^3\text{He} \), respectively. \ref{[31]}; \ref{[30]}

Figure 3.7 Measured Rate Coefficients \( k_{s(T)} \) for Reaction (2).
At high temperatures the data are well fit by the function

\[ k_{S1}(T) = 8.1 \times 10^{-36} T \exp(-650/T) \text{ cm}^6 \text{s}^{-1} \]  \hspace{1cm} (3 - 15)

which is shown by the dashed line in Figure 3.7. This behavior is consistent with that expected on the basis of a simple dynamical model in which the ternary collision is pictured as two binary collisions in rapid succession. The He(2^3S) - He(1^1S) barrier is surmounted in the first collision producing a transient He_2(a^3\Sigma_u^+) molecule that is stabilized by a subsequent collision with a second He(1^1S) ground state atom. (Dynamical considerations, however, require that this second He(1^1S) atom initially be close to the other reactants in order to affect stabilization before the transient He_2 (a^3\Sigma_u^+) molecule can dissociate. From the result of He(2^3P) conversion experiment, we will see clearly that this model is not accurate.) On the basis of this model, kinetic theory suggests a rate coefficient \( k_S \) of the form

\[ k_S (T) \propto <v>^2 \exp (-E_0/kT) \]  \hspace{1cm} (3 - 16)

where \(<v>\) is the average thermal velocity and \( E_0 \) is the activation energy \( [32] \). However, \(<v>^2\) is proportional to sample temperature and comparison of eqs. (3 -15) and (3 -16) thus suggests an activation energy \( E_0 = 56 \pm 6 \text{ meV} \) (equivalent to \( 650 \pm 70 \text{ K} \)) which is indeed close to the reported He(2^3S) - He(1^1S) repulsive barrier height.

As the temperature is lowered, the frequency of collisions in which such a barrier can be surmounted decreases rapidly. The rate coefficient therefore decreases, but not as rapidly as expected from equation (3-16). This enhanced reactivity suggests that for certain reaction geometries the barrier height along the He(2^3S) - He(1^1S) reaction path is significantly reduced by the presence of the second He (1^1S) atom. After the reduced barrier is surmounted, the barrier rises again as the perturbing atom recedes thereby stabilizing the He_2 (a^3\Sigma_u^+) product.

In this picture, the barrier perturbation is presumably sensitive to both the distance of closest approach in the He (2^3S) - He (1^1S) interaction (and thus collision energy) and to
the configuration of the three reactants. Nevertheless, the data in Figure 3.7 can be reasonably approximated over their entire temperature range by the sum of two functions of the form given in eq. (3-16), viz.,

\[ k_S(T) = T [8.7 \exp (-750/T) + 0.41 \exp (-200/T)] \times 10^{-36} \text{ cm}^6 \text{ s}^{-1} \]  

(3-17)
suggesting that at low temperatures, where the second term is dominant, the reaction can be adequately characterized by an effective (or average) activation energy of \( \approx 17 \pm 2 \text{ meV} \) (equivalent to \( 200 \pm 20 \text{ K} \)). Eq. (3-17), which is shown by the solid line in Figure 3.7, also suggests that at the higher temperatures an activation energy of \( 64 \pm 6 \text{ meV} \) (corresponding to \( 750 \pm 70 \text{ K} \)) is more appropriate.

It is noteworthy that the numerical coefficient for the first term in eq. (3-17) is much larger than that of the second. This suggests that the \( \text{He}(2^3S) - \text{He}(1^1S) \) barrier reduction proposed to account for the low temperature reactivity is restricted to a rather narrow range of three-body configurations. At high temperatures, however, the configurations that can result in reaction should be relatively unrestricted. This reduces the relative importance of those configurations that are associated with a significant reduction in barrier height and results in an activation energy that is close to the \( \text{He}(2^3S) - \text{He}(1^1S) \) barrier height.

To test the possibility that barrier tunneling somehow masquerading as a thermally activated process enhances the reaction rate at low temperatures, the experiment was repeated at four temperatures using the light \( ^3 \text{He} \) isotope. The results of these measurements are included in Figure 3.7. Since barrier tunneling probabilities depend exponentially on the reduced mass of the system, the tunneling rates for \( ^3 \text{He} \) should be substantially higher than those for \( ^4 \text{He} \). Further, energy levels within the potential well should be quite different for the two isotopes, so that any resonantly enhanced tunneling contributions also would be expected to be isotope sensitive. The data, however, show that the rate coefficients for \( ^3 \text{He} \) are uniformly \( \approx 33\% \) higher than those for \( ^4 \text{He} \) and this
can be entirely accounted for by the increased thermal velocity of the lighter isotope. Thus we conclude that tunneling does not contribute significantly to the measured \( k_8(T) \).

The data show that the kinetics responsible for reaction (2) are quite complex, but can be explained using a dynamical model that suggests that the presence of the second He\((1^1S)\) atom might, for certain reaction geometries, reduce the He \((2^3S) - He(1^1S)\) repulsive barrier by a factor of three or more. While this seems a large effect, the barrier exists as a result of the delicate balance between core attraction and exchange repulsion at intermediate nuclear separations and thus might be quite sensitive to relatively small perturbations. Molecular dynamics calculations can provide a quantitative test of the present model but require He\((1^1S) - He(2^3S) - He(1^1S)\) potential energy surfaces for internuclear separations characteristic of the He\((2^3S) - He(1^1S)\) repulsive barrier.

B2. He\((2^3P)\) Three-Body Conversion Rate

The temperature dependence of He\((2^3P)\) conversion to metastable molecules through a similar three-body reaction:

\[
He(2^3P) + 2He(1^1S_0) \rightarrow He_2(b^3Π_g) + He(1^1S_0)
\]

have been investigated over temperature range 1.6K-300K. The apparatus and sample preparation procedure were the same as those described in the preceding section. The He\((2^3P_2)\) state was populated by 1.083\( \mu \)m Ti: Sapphire laser radiation with the laser frequency tuned to the center of the transition \((\omega = \omega_0)\). The coupled He\((2^3S_1) - He(2^3P_2)\) state population was monitored by measuring the absorption or fluorescence of 1.083 \(\mu\)m He\((2^3S_1) \leftrightarrow He(2^3P_2)\) resonance radiation from Ti:Sapphire laser as function of time in the late afterglow of the pulsed rf discharge. Signals recorded following many rf pulses were accumulated and integrated using a digitizer and averager which were interfaced with a computer and the exponential decay rate was obtained. Laser power was measured both in front the cryostat entrance window and after the exit window, and the laser intensity in the
sample cell was obtained by assuming that all the glass windows have same transmission rate. Laser intensity was varied by using neutral density filters. Decay rates of the coupled He(2$^3$S$_1$) - He(2$^3$P$_2$) system were measured as function of laser intensity, and plots similar to Figure 3.3 were obtained. The decay rate is observed to be proportional to laser intensity at low laser intensities, in agreement with the kinetic model. However the decay rate vs. laser intensity curve starts to deviate from linearly at much lower laser intensity than expected, an effect which we attribute to "hole burning" (i.e. the laser saturates a narrow band of frequencies out of the broader Doppler profile). This effect was not considered in the kinetic model. Typical decay rates vs. laser intensity are presented in Figure 3.8 for several temperatures, and the observed slopes $\frac{d\alpha}{dI_\omega}$ vs. helium density at 292K, 77K are presented in Fig 3.9. The dependence of the measured slopes $\frac{d\alpha}{dI_\omega}$ on N agrees with the kinetic model (3 - 11). The deviation of $\frac{d\alpha}{dI_\omega}$ from quadratic dependence on N at high densities is caused by p-state mixing and accounted by the factor $f(N,T)$ in the kinetic model. Data of 1.62K, 2.6K, and 4.2K were taken at lower helium densities where p-state mixing is small and can be neglected, i.e. $f(N,T) \sim 1$. 
Figure 3.8 Decay Rate as Function of Laser Intensity
Figure 3.9 Dependence of Measured Slope $\frac{d\alpha}{d\omega}$ on Helium Density

Where the Solid Lines are Proportional to $N^2 f(N,T)$, Dashed line Propotional to $N^2$
The reaction rate coefficients $k_p(T)$ obtained from the slopes of $\alpha$ vs. $I_o$ plots are displayed in Figure 3.10, where $k_p(T)$ is plotted as a function of $1/T$. The data can be well fit over the entire 1.6-292K temperature range by the function

$$k_p(T) = (0.04 + 2.18/T) \times 10^{-30} \text{ cm}^6 \text{s}^{-1}, \quad (3 - 18)$$

which is shown by the solid line in Figure 3.10.

![Figure 3.10: Temperature Dependence of the Reaction Rate ($k_p$) for Three-body Conversion of He(2$^3$P) into Metastable Molecules.](image)

The temperature dependence of rate coefficient $k_p(T)$ is dramatically different from He(2$^3$S) conversion rate coefficient $k_s(T)$, and suggest that there is no activation energy associated with the conversion reaction (3). In contrast, earlier experiments$^{[11]}$ on He(2$^3$P) atoms produced in electron-bombarded superfluid liquid helium suggested that they repel ground state helium atoms and create a microscopic void (bubble) in the liquid helium. This was interpreted as evidence for the existence of a repulsive barrier. However, it was recognized that the 2$^3$P bubble must be shaped something like the probability distribution of a 2$^3$P\(_x\) electron orbital, pinched in around the "equator" where the p-electron probability
density is minimum. Hence it is possible that a ground state atom incident in the $^{23}\text{P}$ equational plane experiences no repulsion, even though the interaction is repulsive for other directions of approach.$^{32}$

The observed inverse temperature dependence of $k_p(T)$ can not be explained by a simple dynamical model based on Langevin theory, in which the ternary collision is pictured as two binary collisions in rapid succession; this model gives a temperature dependence of $T^{-1/3}$ as shown in Appendix II. However conventional transition-state theory (CTST) does predicts that for this type of reaction the rate is inversely proportional to temperature for a linear reaction geometry, but predicts a $T^{-0.5}$ dependence for nonlinear geometries.$^{33}$ This suggests that either the He($^{23}\text{P}$) conversion reaction requires a linear geometry or that CTST gives an incorrect temperature dependence if the reaction geometry is non-linear. If non-thermally activated He($^{23}\text{P}$) conversion reactions are restricted to the $^{23}\text{P}$ equational plane for the reasons discussed in the preceding paragraph, then perhaps a linear reaction geometry would be favored. On the other hand, an inverse temperature dependence has also been reported for reaction$^{34}$

$$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He} \quad (3 - 19)$$

for which there would apparently be no such restrictions on the reaction geometry. Thus we regard the proper interpretation of the observed temperature dependence of $k_p$ to remain an open question.

The observed $T^{-1}$ dependence of $k_p(T)$ also raises a question about the linear temperature prefactor assumed on the basis of kinetic theory in the analysis of the thermally activated reaction (2), discussed in the preceding section (see equations 3 - 15, 16, 17). Indeed, if the prefactor for that reaction is taken to be $T^{-1}$ instead of $T$, an equally good fit to the data can be obtained, yielding

$$k_6(T) = \frac{1.2}{T} \times 10^{-29} \exp(-657/T) \text{ cm}^6 \text{ s}^{-1} \quad (3 - 20)$$

at high temperatures and
\[ k_s(T) = \frac{4.6}{T} \times 10^{-32} \exp(-180/T) \text{ cm}^6 \text{ s}^{-1} \]  \hspace{1cm} (3-21)

at low temperatures (Figure 3.11 and 3.12). The activation energies obtained from these fits are 657K and 180K, very close to the values 650K and 200K obtained assuming the prefactor to be T (equations 3 - 15, 17). Clearly, the temperature dependence is so dominated by the exponential terms that the prefactor makes little difference, and cannot be derived from fits to the data.

Figure 3.11 High Temperature \( k_s(T) \), Plotted as \( k_s(T)T \) vs. \( 1/T \)

Figure 3.12 Low Temperature \( k_s(T) \), Plotted as \( k_s(T)T \) vs. \( 1/T \)
C. **Transition Species**

The term "transition species" is defined as molecular entities having configurations intermediate between those of the reactants and products of an elementary reaction. "Transition species" covers a much broader range of configurations than does the term "activated complex," which is defined as existing in an arbitrarily small region of phase space. The distinction is illustrated by the schematic potential-energy profile, shown in Fig.3.13.

![Potential-energy profile](image)

**Figure 3.13** Schematic Potential-energy Profile For a Reaction of the Type A+BC → AB + C*. The Heavy Vertical Line Shows the Emission C* → C + hν; The Dashed Lines Show Emissions From Various Transition Species.

Spectroscopic evidence for intermediates in reactive collisions was not obtained until 1980 when J. C. Polanyi and coworkers investigated the reaction

$$F + Na₂ → F···Na···Na → NaF + Na^*$$

in crossed molecular beams. The product Na* is in an electronically excited state and emits the familiar yellow D-line. On both sides of this line there was "wing" emission, and the
evidence indicated that this was due to the transition species F · · · Na · · · Na. A similar result has been obtained for the Mg + H₂ reaction.[35] The possibility of studying the He · · · He(2³P) · · · He transition species in reaction (3) by means of emission should be considered.

There is also the possibility of detecting transition species by absorption spectroscopy, and this might be done even for a reaction that involves only ground state reactants, or reactants in metastable states such as the helium reaction (2). While the detection of transition species by absorption spectroscopy is difficult owing to the low concentrations involved, but the use of laser techniques makes the detection more feasible.

3.3 Conclusion

In summary we have studied two of the most fundamental three-body reactions that are accessible over an extended temperature range. Dramatic differences in the magnitude and temperature dependences of rates of conversion of He(2³S) and He(2³P) atoms to He₂(a³Σ⁺) and He₂(b³Π₁₂) molecules respectively is interpreted in terms of the existence of a potential barrier in the former case but not in the latter. In the case of He(2³S) three-body molecular conversion, an unexpected second activation energy was observed at lower temperatures. In the case of He(2³P) three-body molecular conversion, a kinetic model based on Langevin theory, which treats the collision as two binary collisions in rapid succession, fails to account for the observed temperature dependence of the reaction rate coefficient. Reaction (2) and (3) are perhaps the most fundamental three-body reactions that can be investigated over an extended temperature range, and perhaps are also among the simpler systems for which accurate potential surfaces and molecular dynamics calculations might be possible. Such theoretical investigation might be expected to advance significantly the understanding of ternary reactions.
Chapter Four

Introduction to Laser Cooling and Trapping of Atoms

4.1. Light Forces, Laser Cooling, and Optical Molasses

Light can exert forces on an atom because photons carry momentum. The exchange of photon momentum with an atom can occur incoherently, as in the absorption and reemission of photons, or coherently, as in the redistribution of the incident field by the atom.

The force arising from the coherent interaction with light is also called the dipole force. The laser field polarizes the atom, and the polarized atom experiences a force in the gradient of the electromagnetic field. Unfortunately, the dipole moments that can be induced on an atom are small, and the force is too feeble even to overcome random thermal motion at room temperature. However once the atoms are cooled by other means to temperatures on the order of 1mK, the electric and magnetic dipole forces can easily overcome thermal motion, and become sufficient to control the atoms.

The incoherent interaction that can alter the momentum of an atom is called the scattering force because it arises from direct photon scattering events as shown in Figure 4.1. Every time an atom scatters a photon carrying momentum \( p = \hbar \lambda \), the atom experiences a small change in velocity. In the case of incoherent scattering, two momentum impulses are delivered to the atom: one along the direction of the incident photon and the other opposite to the direction of the scattered photon. Because the photons are not scattered in a preferred direction, the atom experiences a net average momentum change. Consider an atom with a velocity \( v \) interacting with a laser travelling wave (wave vector \( k \), angular frequency \( \omega_L \)), quasi-resonant with a two-level atomic transition (angular
frequency $\omega_{at}$, transition line width $\Gamma$). The average force that the atom experiences is simply:

$$F = \hbar k \times \text{(photon scattering rate)}$$

or

$$F = \hbar k \frac{\omega_1^2}{2} \frac{\omega_{1}^{2/2}}{\omega_{1}^{2} + \Gamma^{2} + \{\delta - k \cdot \vec{v}\}^2}$$  \hspace{1cm} (4 - 1)$$

where $v$ is the atom velocity, $\delta/2\pi = (\omega_L - \omega_{at})/2\pi$ is the laser detuning from the resonance, and $\omega_1$ is the Rabi frequency characterizing the strength of the interaction between the atom and the laser ($\omega_1^2 = (\Gamma^2/2)$ ($I_L/I_{sat}$), $I_L$ is the laser intensity, and $I_{sat}$ the saturation intensity (the power per unit area required to reduce the population difference to one-half its unsaturated value) at resonance of the atomic transition. This force creates cooling when the laser is tuned below the resonant frequency (but within the Doppler profile) of an atom, and has a heating effect when the laser is tuned above resonance.

![Diagram](image)

Figure 4.1 Laser Scattering Force

To see the strength of this force, let us estimate the laser cooling force for the He(2\(^3\)S) - He(2\(^3\)P\(_2\)) transition. The laser wavelength is 1083 nm, $I_{sat} = 2$ mW/cm\(^2\), and the excited state width $\Gamma = (2\pi)1.6$ MHz = 10 MHz. at resonance. For $I_L \gg I_{sat}$
\[
F \sim \frac{6.64 \times 10^{-34}}{1083 \times 10^{-9}} \frac{10^7}{2} = 3.1 \times 10^{-21} \text{ N}.
\]

For helium with atomic mass 4 (6.7 x 10^{-27} kg), this force is 46400 times the force of gravity. This force is the same as the electric force on a singly charged ion in a field of 1.9 x 10^{-4} V/cm. Therefore, the scattering force can be much greater than the gravitational force, but much weaker compared with typical electric forces.

If initially the He(2^3S) atom has speed 100 m/sec (T ~ 1.5 K), and assuming the laser can maintain resonance while the atom is decelerating, then the number \( n \) of photon scatterings needed to stop the He(2^3S) atom is

\[
n = \frac{m_{\text{He}^+}}{h \kappa} = \frac{6.7 \times 10^{-27} \times 100 \times 1083 \times 10^{-9}}{6.64 \times 10^{-34}} \approx 1100,
\]

with stopping time

\[
t = \frac{m_{\text{He}^+}}{F} = \frac{6.7 \times 10^{-27} \times 100}{3.1 \times 10^{-21}} \text{ sec} \approx 0.22 \text{ msec},
\]

and over a distance:

\[
d = v t / 2 = \frac{100 \times 0.22 \times 10^{-3}}{2} \approx 0.011 \text{ m}.
\]

Three-dimensional laser cooling is accomplished by creating three sets of counterpropagating laser beams along \( x, y, \) and \( z \) axes. When the laser is red detuned relative to an atomic transition, an atom moving against the direction of the laser beam will see the beam Doppler-shifted towards resonance, while the laser beam copropagating with the atom will be Doppler-shifted out of resonance. In addition to cooling the atoms this force also serves as a confining medium. An atom caught in this "molasses" will execute a random walk analogous to the Brownian motion of a dust particle in a fluid; therefore it is not a trap.

4.2. Trapping and Cooling Atoms

The main advantage of the trapped atoms (ions) technique is that the ideal of an unperturbed species at rest in space is approached to a high degree; particles such as electrons, atomic ions and spin polarized hydrogen atoms can be stored for long periods of
time without usual problems associated with wall confinement. These unique properties have been exploited most notably by Dehmelt, et al. and Wineland, et al. and co-workers on electrons and ions, and by Greytak, Kleppner and co-workers on spin polarized hydrogen atoms. There are three basic kinds of traps: ion traps, pure magnetic traps (spin polarized neutral atoms), and magneto-optical traps. A brief introduction of each type of trap follows.

A. Electron and Ion Traps, Sideband Cooling

Four types of traps for ions and electrons have been useful: the rf (or Paul) trap, the Penning trap, and electrostatic(orbitron trap) and magnetostatic traps. The rf and Penning traps and their relevant properties are briefly described here.

The ideal rf or Paul trap uses hyperbolic electrodes in a vacuum apparatus as shown in Figure 4.2. These electrodes are symmetric about the z axis, so the potential can be described in cylindrical coordinates. If an alternating voltage of frequency \( \Omega \) is applied between the endcaps and ring electrode, then the instantaneous potential inside the trap is given by:

\[
\phi(r,z) = A \left( r^2 - 2z^2 \right), \quad A = A_0 \cos \Omega t. \tag{4-2}
\]

![Figure 4.2. rf or Penning Trap](image)

An ion experiences an rf electric field such that its motion (the "micromotion") is 180° out of phase with respect to the electric force. Because the electric field is
inhomogeneous, the force averaged over one period \( T = 2\pi/\Omega \) of the micromotion is in a direction of weaker field amplitude (independent of the sign of the charge), i.e., towards the center of the trap.

The Penning trap \(^{39}\) uses the same electrode configuration as the rf trap (Figure 4.2), but now \( A \) in Eq. (4 - 2) is a constant \( U_0 \) such that the charged species see a static potential well along the \( z \) axis. We have \( \phi_T = U_0(r^2 - 2z^2) \). This causes a repulsive potential in the \( x-y \) plane which can be overcome by superimposing a static magnetic field along \( z \) \( (B = B_0 e_z) \).

Due to the fact that the trapping force is electromagnetic on charged particles, electron (ion) traps are very deep and have long trap lifetimes. Cooling of a trapped electron (ion) is possible by side band rf or laser cooling\(^{36}\), a cooling process in which the electron (ion) absorbs rf photons (photons) deficient in energy with the balance supplied from energy stored in the electron (ion) motion to be cooled. Note, one can cool the trapped ion with a single laser beam tuned below resonance.

**B. Magnetic Traps**

Antecedents for the present study of magnetostatic trapping fields are to be found in discussions of neutron traps, developed primarily by Paul and collaborators\(^{40}\) and discussed also by several other authors,\(^{41,42}\) and from the extensive literature on magnetic confinement of plasmas.\(^{43}\) For all of these techniques, as for neutral-atom traps,\(^{44}\) the confining force originates from the interaction between a magnetic moment and a nonuniform static field. The typical trap depth is only about 1 K, from the relation \( T = \mu\Delta B/k \), where \( \mu \) is the atom's magnetic moment, \( \Delta B \) is the field difference between the lowest escape threshold and the trap minimum, and \( k \) is Boltzmann's constant. As compared with the much deeper ion traps, this interaction is inherently weaker and furthermore depends on the maintenance of a given orientation of the moment with the local
field. For neutrons and for neutral atoms, this implies that the particle remains adiabatically in a given Zeeman sublevel.

Three trap configurations that have been proven successful are the quadrupole trap with bias solenoid \(^{[37]}\), the Ioffe trap, and base ball trap.\(^{[45]}\) In all three configurations, the magnetic field at the trap center is non-zero, therefore minimizing losses due to Majorana transitions (non-adiabaticity). In the absence of dissipative cooling forces, the atoms are trapped through collisions, i.e. only those which lose sufficient energy during collisions to reduce their energies below the trap depth are captured by the trap. This requires that the atoms be cooled cryogenically to temperatures < 1K before loading the trap. However, laser cooling makes it possible to load magnetic traps possible in a room temperature environment.\(^{[46]}\)

C. Magneto-Optical Cooling and Trapping

The operation of the magneto-optical trap (MOT) requires both inhomogeneous magnetic fields and radiative forces. The idea was first suggested by Dalibard for one-dimensional cooling and confinement, and the concept was later extended for three dimensions and demonstrated.\(^{[21]}\) Metcalf first discussed MOT tapping of metastable He\((2^3S)\) atoms, suggesting that they might be produced by an rf discharge in helium gas at liquid helium temperature.

Perhaps one of the most important features of the MOT is its relatively large depth which leads to its insensitivity to experimental imperfections such as optical misalignment and imperfect polarization.\(^{[23]}\) The basic principle of the trap can be illustrated by considering a hypothetical atom with angular momentum \(J = 0\) \((m_J = 0)\) ground state and \(J = 1\) \((m_J = -1, 0, +1)\) excited state. In a weak inhomogeneous magnetic field \(B_z(z) = Bz\), the energy levels are split by an amount \(\Delta E = \mu m_B^s B = \mu B m_z\) as shown in Figure 4.3.
Figure 4.3 Principle of One Dimensional MOT.

Two oppositely directed laser beams of opposite circular polarization, each detuned below the zero-field atomic resonance by $\sigma \gg \Gamma$ ($\Gamma$ is line width of $J = 1$ state) are incident as shown. Atomic resonance can then occur only near the two points $z = \pm z_1$ where the Zeeman tuning of each transition corresponds to the laser frequency (atom at rest), and, because of the polarizations, it can only occur with the $\sigma^+$ beam at $z = -z_1$ and $\sigma^-$ beam at $z = +z_1$. At $z = z_2$, an atom moving to the right sees the $\sigma^+$ beam detuned by $\Delta$, but the $\sigma^-$ beam is almost resonant with the transition to $m = -1$. Consequently, the atom will feel a net time-averaged force toward the origin which is approximately given by

$$F = \hbar k \frac{\omega_0^2/2}{\omega_0^2/2 + \Gamma^2/4}$$  \hspace{1cm} (4 - 3)

where all symbols are defined as in (4 - 1). Substituting $\omega_0^2 = (\Gamma^2/2) (I_L/I_{sat})$ into equation (4 - 3), we obtain:

$$F = \hbar k \frac{\beta}{2 + \beta}$$ \hspace{1cm} (4 - 4)

where $\beta = I_L/I_{sat}$ is the saturation parameter for one beam. Therefore the effective trap depth is simply $T_e = 2z_1 F/k_B$.

This scheme is readily extended to three dimensions with two opposed magnet coils forming a magnetic quadrupole field as shown in Figure 4.4.
Figure 4.4 Three Dimension M.O.T

We can see that MOT trap depth is not spherically symmetric. Trap depth depends on both direction and position of the atom when it enters the trap. Along the central axis, the magnetic field is parallel to the laser beam wave vector, and the trap depth is the same as in the one dimensional case. But in the off-axis case, where the magnetic field and the wave vector of the laser beam are not parallel, \( \Delta m = \pm 1, \mp 1 \text{ and } 0 \) transition are all allowed, and the trap depth is substantially reduced relative to the one dimensional case as has been demonstrated by Lindquist et al. \(^{47}\).

4.3. Application of Cold Trapped Atoms and Ions

Sideband and laser cooling, trapping and related techniques are finding applications in a number of areas. Because the experimental techniques have only recently blossomed, the full range of applications has not yet been realized.

Lasers can cool atoms or ions to very low temperatures, therefore dramatically reducing Doppler effects in high-resolution spectroscopy. This technique should eventually reduce inaccuracies in spectroscopy to 1 part in \(10^{18}\) or better for a single trapped ion.\(^{48}\) More accurate atomic clocks are an obvious prospect.

The low temperatures now accessible with laser cooling allow one to study atomic collisions in a regime where the collision times became long enough so that spontaneous emission can occur during the collision. Thus, ground state-excited state collisions are
significantly modified. An ultracold gas of atoms should also display effects due to the quantum statistics of the gas. Differences in collision cross sections between fermions and bosons in low temperature collisions are expected. Further, if the condition can be achieved that the de Broglie wavelength $\lambda = h/p$ of trapped atoms becomes comparable to the interatomic spacing in the trap, a Bose-Einstein condensation or a degenerate Fermi gas should result, depending on whether the total angular momentum of the atom is integral or half-integral. Such phenomenon may eventually be observed by cooling atoms held in a suitable "trap".
Chapter Five

Cooling and Trapping He(2^3S_1) Metastable Atoms

The metastable He(2^3S) atom has long been recognized as an attractive candidate for laser trapping and cooling experiments because its large internal energy (19.8eV) and reactivity offer the possibility of investigating Penning reactions (5a, 5b, 5c) in the ultracold quantum regime where the de Broglie wavelength is much larger than the range of interatomic potentials. Further, Penning reaction rates are expected to be dramatically reduced for spin-polarized reactions, which should be realizable in a suitably designed magneto-optical trap (M.O.T), because a spin flip would be required to produced the He(1^1S) ground state atom. Also, the Penning rates for spin-polarized metastable ^3He(2^3S) fermions are expected to be much smaller at ultra-low temperatures than those of ^4He(2^3S) bosons because the former cannot react via s-waves.

Experimental problems associated with producing and manipulating the fragile and reactive He(2^3S) atoms have proven to be difficult to overcome. The first successful trapping experiment was very recently reported by Bardou, et al. [24], who laser decelerated a He(2^3S) atomic beam and used a M.O.T to cool about 10^4 atoms to about 1 mK. These authors reported a huge rate coefficient of about 10^{-7} cm^3 s^{-1}, consistent with theoretical expectations, for the resonantly enhanced He(2^3S) + He(2^3P) Penning reactions, which severely limits the density of metastable atoms that can be trapped in the presence of the intense cooling radiation that couples these states. Further, because of residual background helium gas accompanying the He(2^3S) atomic beam, trap lifetimes were measured to be less than one second even at low He(2^3S) densities.

The present experiments were designed to provide substantially enhanced ^3He(2^3S) injection rates and trapping efficiencies, and much longer trap lifetimes. The He(2^3S) atoms are produced by an rf discharge at low temperatures (1.3 - 4.2 K) and injected into a
M.O.T with trap depth comparable to their average kinetic energy, a procedure first suggested by Metcalf [25]. The entire trap and rf discharge source are submerged in liquid helium, and the background helium gas is rapidly cryopumped to produce a near-perfect vacuum in which trap lifetimes of hours or days are expected, long enough for an accurate measurement of the $^4_3\text{He}(^2\text{S})$ radiative lifetime (about $10^4$ second.)

5.1. Apparatus

The apparatus is shown schematically in Figure 5.1. Briefly the temperature is controlled by pumping on the liquid helium in which the apparatus is immersed. The two opposing superconducting current coils produced a quadrupole magnetic field. The coils can be operated either in tunable and persistent current modes. Frequency stabilized, red detuned laser beams which have right hand circular polarization relative to the local magnetic field complete the magneto-optical trap. The laser beams are incident through windows along three orthogonal axes and are reflected with reversed circular polarization by mirrors and $\lambda/4$ wave plates in the liquid helium bath. The three $\lambda/4$ wave plates are temperature-insensitive zero-order thin mica. He($^2\text{S}$) atoms are produced by a weak 3.03MHz rf discharge in the helium gas entrance tube. The cold discharge products (mostly helium ground state atoms, with $10^9$–$10^{10}$ metastable He($^2\text{S}$) atoms per cm$^3$) enter the M.O.T through an orifice (0.2mm diameter with thin and sharp edges), where the He($^2\text{S}$) atoms are trapped by the MOT and ground state helium atoms are rapidly cryopumped by zeolite pellets that cover most of the cell bottom. Only a "puff" of helium gas is admitted to the discharge tube to assure that the outermost surface adsorption sites of the zeolite molecular sieves are available for cryopumping, hence maximizing the pumping speed. (The ideal pumping speed is $\frac{1}{4} \alpha n v_m S_{\text{zeolite}}$, where $0.5<\alpha<1$ is the sticking coefficient for helium on the zeolite surface, $n$ is the gas density, $v_m(T)$ is the mean atomic speed, $S_{\text{zeolite}}$ is the effective pumping surface area.) At temperatures above about 4K, surface adsorbed helium migrates to sites inside the zeolite pellets, thus clearing the surface
to cryopump subsequent puffs of helium. However, at lower temperatures (~1.3K) where the M.O.T efficiency is greater, the surface sites are slow to clear, and the pumping speed decreases after two-or three helium puffs.\textsuperscript{[50]}

The laser used here is a Ti:Sapphire ring laser described in detail elsewhere \textsuperscript{[51]}. A version of this laser, CR-899, with special adaptations designed to increase the output at longer wavelength, is used in the present work and produces 300 mW of 1.083\textmu m light. Long term laser frequency stabilization is achieved by using a superlock technique developed at this laboratory \textsuperscript{[52]}. This technique is illustrated schematically in Figure 5.2. A small fraction of the Ti:Sapphire output is superimposed with the orthogonally-polarized output of a stabilized Helium-neon laser (Aerotech, Inc. Model 110-SF) and directed through a scanning confocal Fabry-Perot etalon (Burleigh Instruments Inc. Model CFT 100 with RC-45 controller). The etalon outputs two series of sharp transmission peaks, one associated with each wavelength. Ti:Sapphire laser frequency drift is controlled by maintaining a constant separation between a particular pair of neighboring peaks in the scan. This method is noteworthy both for its simplicity and because it can be readily applied to any actively-stabilized laser. Stabilization to within ± 1MHz for a period of many hours and highly-reproducible scanning of the laser frequency over intervals of up to ~1GHz is possible as shown in Figure 5.3.
Figure 5.1 Trap Apparatus
Figure 5.2 Laser Frequency Stabilization Scheme.

Figure 5.3 Ti: Sapphire Laser Frequency Drift Measurement
Figure 5.4 Doppler-free Spectroscopy

Doppler-free spectroscopy on an rf excited helium absorption cell is used to locate the laser frequency within 2MHz of the center of He($2^3S$) - He($2^3P_2$) transition, as illustrated in Figure 5.4. Here the stronger pumping beam and a weaker probe beam
overlap spatially in the He\((2^3S)\) discharge cell. When the laser frequency is in resonant with the center of the transition, both pump beam and probe beam see only the atoms with near-zero velocities, hence give a Doppler-free signal with line width \(\sim 2\text{MHz}\).

5.2. Estimates and Preliminary Results

The equilibrium number of He \((2^3S)\) atoms that can be trapped and the background-gas limited trap lifetime can be estimated in terms of the MOT design parameters, and the He \((2^3S)\) injection and ground state helium removal rates. The Ti:Sapphire laser provides three incident laser beams each of diameter \(L = 2\text{cm}\) and intensity \(I \equiv 6 \text{ mW/cm}^2\). The superconducting coils can easily produce a magnetic field gradient of 10 - 20 gauss/cm at the cell center. If the laser is detuned toward the red by 20 MHz (20 gauss) from the He\((2^3S)\) - He \((2^3P_2)\) resonance, the effective one-dimensional trap depth (see proceeding section) is approximately \(T_c = 2 z_1 F/3k_B \equiv 1.5\text{K}\) for \(z \equiv 1\text{cm}\). However, for a three-dimensional trap most of the atoms enter from direction off the optical axes where the local magnetic field and wave vector of the laser beam are not parallel. Lindquist, et al.\(^{[47]}\) have shown that in this case the magnetic field has far less influence in slowing the atoms than in the on-axis case because \(\Delta m = +1, 0, -1\) transitions all allowed. In consequence, the maximum capture velocity, hence effective trap depth, are greatly diminished. They have developed a numerical model for the three-dimensional MOT, and it predicts a maximum capture velocity of \(v_c = 31 \text{ m/s}\) for He \((2^3S)\) in our trap, corresponding to an effective trap depth \(T_c = mv_c^2/2k_B\) of only 0.16K.\(^{[56]}\) We shall use these latter values in the calculations that follow.

The densities of ground state He\((1^1S)\) and metastable He\((2^3S)\) atoms in the discharge tube are estimated to be about \(n_0 \sim 6 \times 10^{15} \text{ cm}^{-3}\) and \(n_0^* \sim 6 \times 10^9 \text{ cm}^{-3}\) respectively. At an operating temperature of 1.25K, their mean velocity is \(v_m = 72 \text{ m/s}\).
The entrance rates of He (1S) and He (2S) atoms into the trap cell, through an orifice area \( A \equiv 3 \times 10^{-4} \text{ cm}^2 \) are respectively
\[
R_E = \frac{1}{4} n_0 \nu_m A
\]
and
\[
R_E^* = \frac{1}{4} \beta n_0^* \nu_m A
\]
where \( \beta \leq 1 \) allows for the possibility that some of the metastables hit the edges of the orifice and are deexcited. A fraction \( f \equiv 0.5 \) of the injected He (2S) atoms pass through the trapping volume of diameter \( \sim 2 \text{ cm} \), and those with velocity less than \( \nu_c \) are captured. The fraction with \( \nu \leq \nu_c = 31 \text{ m/s} \) is
\[
\gamma = \frac{I(\nu_c)}{I(\infty)} \text{ where } I(\nu) = \int_0^{\infty} v^2 e^{-mv^2/2kT} dv
\]
and \( \gamma \equiv 0.18 \) for this trap at 1.25K.

Thus the rate at which He (2S) atoms are trapped is
\[
R_T^* = f \gamma R_E^* = \frac{1}{4} f \gamma \beta n_0^* \nu_m A
\]

The background helium gas is pumped away at a rate
\[
R_L = \frac{1}{4} \alpha n \nu_m S_Z
\]
where \( n \) is the gas density in the trap cell, \( S_Z \equiv 40 \text{ cm}^2 \) is the effective surface area of the zeolite pellets and \( \alpha \equiv 0.5 \) is the sticky coefficient.

The He (2S) loss rate due to collisions with the background helium gas is
\[
R_L^* = n \sigma \nu_m N^*
\]
where \( N^* \) is the number of trapped He (2S) atoms and \( \sigma = 5 \times 10^{-15} \text{ e}^{-\text{Tc/T}} \) the estimated cross section for scattering out of the trap, \( \text{e}^{-\text{Tc/T}} \) being the fraction of collisions with sufficient energy to eject a He (2S) atom.

In steady state, \( R_E = R_L \) and \( R_T^* = R_L^* \), and these equations yield for \( n \) and \( N^* \)
\[
n = \frac{A n_0}{\alpha S_Z} \sim 9 \times 10^{10} \text{ atoms/cm}^3
\]
and
\[ N^* = \frac{\beta \gamma S_z}{4\sigma} \frac{n_0^*}{n} \approx 9 \times 10^7 \text{ atoms,} \]

assuming \( \beta = 0.5 \). The trap lifetime \( \tau \) due to scattering by the background gas is

\[ \tau = \frac{1}{n \sigma v_m} = 0.3 \text{ s} \]

However, for trapped He \((2^3S)\) densities above about \(4 \times 10^7 \text{ cm}^{-3}\), the dominant trap loss mechanism will not be scattering by background gas, but He \((2^3S) - \text{He} (2^3P)\) Penning reactions with rate coefficient \(= 10^{-7} \text{ cm}^3 \text{s}^{-1}\). Assuming the volume of the trapped atoms to be \(\approx 1 \text{ mm}^3\), the trap loss rate due to Penning reaction is then

\[ R_L^P = 10^{-7} (n^* / 2)^2 \]

where \(n^* = N^* / V_{\text{trap}}\) is the combined densities of He\((2^3S)\) and He \((2^3P)\) atoms in a trap of volume \(V_{\text{trap}}\), and we assume the densities of the two species to be approximately equal in the presence of the laser trapping radiation. Thus in the limit of high trapped atom densities we must equal the trapping rate \(R_T^*\) with \(R_L^P\) rather than with \(R_L\), and this yields \(n^* = (10^{-7} \beta \gamma \sigma \nu_m A n_0^*)^{1/2} = 10^8 \text{ atoms/cm}^3\) and \(N^* = 10^5 \) total atoms trapped in steady state. The trap lifetime in this limit is \(\tau^* = (10^{-7} n^* / 2)^{-1} = 0.2 \text{ sec}\)

Preliminary trapping experiments were undertaken with the trap parameters discussed above (laser intensity \(\approx 6 \text{ mW/cm}^2\) in each beam, magnetic field gradient \(\approx 10\) gauss/cm, detuning \(\approx -20 \text{ MHz}\)). In each of six experimental runs, fluorescent 1083nm radiation from small volumes (a few mm\(^3\)) of trapped atoms were observed at both 4.2K and 1.3K using a hand-held infrared viewer with a S - 1 photocathode and P - 20 phosphor screen (Find - R Scope, Edmund Scientific Co.). The viewer was calibrated using a Ti:Sapphire 1083nm laser beam of approximately the diameter of the observed trapped atom radiation. The laser intensity was attenuated by neutral density filters until the brightness seen through the viewer was approximately the same to the eye as seen in the trapping experiments. From this crude calibration, we estimate that about \(10^5\) atoms were trapped at 4.2 K and \(\sim 10^6\) at 1.3K. In future experiments a cooled and calibrated S - 1
photomultiplier will be used to measure trap lifetime and to determine the numbers of trapped atoms more precisely.

5.3. Future Improvements

The preliminary experiments have also suggested improvements in the apparatus that should reduce the trap loss due to collisions with background gas and enable the retention of a sizable number of He (2³S) atoms after puff-loading. A serious deficiency in the present trap design is that the discharge self-extinguishes when the density in the discharge tube falls below about 5x10¹⁵ atoms/cm³. After that most of the remaining gas in the tube continues to flow through the orifice, sustaining a background helium density and collision rate that eventually empties the trap. Evacuation of the gas through the long ~50cm, small diameter fill tube is far too slow to prevent the trap loss. However, as illustrated in Figure 5.5, if a suitably designed second cryopump were attached to the fill tube, the fraction of the gas puff that finds its way down to the discharge region would serve to load the trap, yet most of the gas would then be rapidly pumped away by the new cryopump after the trap is loaded. The two cryopumps together should rapidly reduce the background pressure to a near-perfect vacuum in which trap losses might be monitored over a period of hours or possibly days. The background gas density both during loading and after could be further reduced by reducing the orifice diameter.

The cold copper baffle illustrated in Figure 5.5 would assure that the short lived gas pulse is thermalized at the liquid helium bath temperature. The new pump-out tube shown in Figure 5.5 would greatly facilitate evacuation and cleaning of the chamber and zeolite after exposure to air. In the present design, pumping must be done through the 0.2 mm diameter orifice.

In other future experiments, the laser beams will be turned off after the MOT is loaded, thus eliminating losses due to He (2³S) - He (2³P) Penning reactions. Having
been cooled on the MOT to a temperature of about 1mK, these He (2^3S) atoms in the m = +1 state (approximately 1/3 of them if no net optical pumping effect) will be retained in the purely magnetic quadrupole trap of depth ~ 2.4 mK (B ~ 20 Gauss), where they would expand to a volume of order 1cm^3. The He (2^3S) radiative lifetime might be measured in this way, by periodically probing the cell with 1083 nm laser radiation.

5.4. Discussion and Conclusions

The decay processes of the atoms in the trap are summarized as follows:

\[
\text{He}(2^3S) + \text{He}(+ KE) \rightarrow \text{He}(2^3S) (+ KE) + \text{He} \quad \text{decay rate: } \alpha_{4n} n^* \quad \text{(5-1)}
\]
Figure 5.5 proposed Improved Trap Design
\[ \text{He}^+(2^3S) + \text{He}^+(2^3S) \rightarrow \text{He}^+ + \text{He}(1^1S) + e^- \quad \text{decay rate: } \alpha_{2a} p_s p_s n^* n^* \quad (5-2a) \]
\[ \text{He}(2^3S) + \text{He}(2^3P) \rightarrow \text{He}^+ + \text{He}(1^1S) + e^- \quad \text{decay rate: } \alpha_{2b} p_d p_p n^* n^* \quad (5-2b) \]
\[ \text{He}(2^3P) + \text{He}(2^3P) \rightarrow \text{He}^+ + \text{He}(1^1S) + e^- \quad \text{decay rate: } \alpha_{2c} p_p p_p n^* n^* \quad (5-2c) \]
\[ \text{He}(2^3S_{m=1}) \rightarrow \text{He}(2^3S_{m=0, -1}); \quad \text{Majorana transitions near trap center,} \]
\[ \text{decay rate: } \alpha_3 n^* \quad (5-3) \]
\[ \text{He}(2^3S) \rightarrow \text{He}(1^1S) + 19.8 \text{eV} \quad \text{decay rate: } \alpha_4 n^* \quad (5-4) \]

where \( n \) is the density of background helium, \( n^* \) is the density of trapped atoms, and \( p_s \) and \( p_p \) are the percentages of trapped atoms in the S and P states respectively. Therefore the equation governing the decay is:

\[
\frac{d n^*}{d t} = - (\alpha_{2a} p_s p_s + \alpha_{2b} p_d p_p + \alpha_{2c} p_p p_p) n^* n^* - (\alpha_1 n + \alpha_3 + \alpha_4) n^*
\]

It is important to distinguish between two fundamentally different kinds of collisions at low temperatures. The first type of collisions occurs in the absence of the light field. These collisions are described by the normal well developed wavefunction methods of scattering theory using a conservative Hamiltonian, and exhibit the familiar Wigner threshold law (quantum effects associated with the long de Broglie wavelength as \( T \rightarrow 0 \), \cite{53}). The second kind are collisions in the presence of a light field. If the light frequency is sufficiently near to the cooling transition resonance, the "preparation" of the atoms for the collision can not be isolated from the collision itself\cite{54}, because of the very long time and distance scales of the collision. Such collisions should be treated by quantum mechanical methods which explicitly treat the dissipation due to excited state spontaneous emission during the "collision". It is this dissipative aspect of ultra-cold collisions in a light field that gives ultra-cold collisions of laser cooled atoms novel and distinctive features which are not yet very well understood.

In our trap, the achievable lifetimes due to collisions with background helium, \((\alpha_1 n)^{-1}\), might be of the order of days after those improvements suggested above. Therefore this term can be neglected, an advantage of a trap operating at liquid helium
Therefore this term can be neglected, an advantage of a trap operating at liquid helium temperatures. The rates of He(2$^3$S) and He(2$^3$P) Penning reactions (5 - 2b) could then be determined simply by measuring the time evolution of the trapped atoms while the laser is on.

The loss rate due to the Majorana transitions can be determined by measuring the time evolution of the trapped atoms after the cooling laser is turned off. If high enough density of trapped atoms can be achieved in the magnetic trap, measurements should also yield the loss rate of processes (5 - 2a). If one can not get a high enough density of spin polarized He(2$^3$S) atoms in the magnetic trap, a modification of the magnet (with non zero field at center) would be needed to measure the spin-polarized He(2$^3$S) - He(2$^3$S) Penning reaction rate. With this modification, the losses due to Majorana transitions can be eliminated (with strong enough field), and the He(2$^3$S) radiative decay rate might be obtained.

Due to the large cross section (~ 10$^{-7}$cm$^2$)$^{[24]}$ for He(2$^3$S) - He(2$^3$P) Penning ionization, the Bose-Einstein condensation of spin polarized He(2$^3$S) atoms is probably very difficult to achieve. The other interesting experiments that one might consider are single trapped He(2$^3$S) atom experiments; however due to the poor quantum efficiency of the PMT (< 0.1%) at this wavelength and the large trapping volume, this may prove to be very difficult.

In conclusion, a magneto-optical trap for He(2$^3$S) atoms has been built and demonstrated in liquid helium. Further improvements of this trap, and measurements of the trap lifetime should yield valuable information about resonantly-enhanced $^4$He(2$^3$S)-$^4$He(2$^3$P) Penning reactions, spin polarized $^4$He(2$^3$S) - $^4$He(2$^3$S) collisions in the ultra-cold quantum collision regime, and possibly the $^4$He(2$^3$S) natural lifetime.
References


Appendix I

Kinetic Model for He(23S) - He(23P) Transition Line Shape
and Radiation-Coupled He(23S) and He(23P) States

A. He(23S) - He(23P) Transition Line Shape

As discussed in Chapter 2, the proper line shape function \( g(\omega, \omega_0) \) is not Gaussian but rather a Voigt function \( g_v(\omega, \omega_0) \).

The convolution integral is:

\[
\tilde{g}_v(\omega, \omega_0) = \int_{-\infty}^{\infty} \tilde{g}_L(\omega, \Omega_i) g_G(\Omega_i, \omega_0) \, d\Omega_i
\]

where \( \tilde{g}_L(\omega, \Omega_i) = \frac{1}{\pi} \frac{1}{(\Omega_i - \omega) + i \left( \frac{1}{T_2} \right)} \) with line width \( \Delta \omega_L = \frac{2}{T_2} \)

and \( \frac{1}{T_2} = A + \sigma_p v N \), where \( \sigma_p \) is p-state mixing cross-section.

\[
g_G(\Omega_i, \omega_0) = \frac{0.939}{\Delta \omega_G} \exp\left[ -4(\ln2) \left( \frac{\Omega_i - \omega_0}{\Delta \omega_G^2} \right)^2 \right] \text{ with } \Delta \omega_G = \frac{2 \omega_0}{c} \left[ \frac{2kT \ln2}{M} \right]^{1/2}
\]

The imaginary part of \( g_v(\omega, \omega_0) \) governs absorption, i.e.

\[
g_v(\omega, \omega_0) = \text{Im}\left\{ \tilde{g}_v(\omega, \omega_0) \right\}
\]

To get in a form where integral tables can be used, we need to introduce a change of variable.

Let \( \sqrt[4]{\ln2} \left( \frac{\Omega_i - \omega_0}{\Delta \omega_G} \right) = -t \Rightarrow (\Omega_i - \omega_0) = -0.6 \Delta \omega_G \), and \( d\Omega_i = -0.6 \Delta \omega_G \, dt \)

So \( \tilde{g}_L(\omega, \Omega_i) g_G(\Omega_i, \omega_0) \, d\Omega_i = \frac{0.939}{\pi \Delta \omega_G} \frac{e^{-t^2}}{t - \rho} \)

where \( \rho = 1.665 \frac{(\omega_0 - \omega)}{\Delta \omega_G} + i \left( 0.833 \frac{\Delta \omega_L}{\Delta \omega_G} \right) \)
\[ \begin{align*} 
\therefore \quad \tilde{g}_v(\omega, \omega_0) &= \int_{-\infty}^{\infty} \tilde{g}_1(\omega, \Omega_i) g_c(\Omega_i, \omega_0) \, d\Omega_i = \frac{0.939}{\Delta \omega_G} (1) \int_{-\infty}^{\infty} \frac{e^{-t^2}}{\rho - t} \\
\text{set} \quad Z(\rho) &= \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2} \, dt}{\rho - t} \\
\Rightarrow \quad \tilde{g}_v(\omega, \omega_0) &= \frac{0.939}{\Delta \omega_G} \cdot i \cdot Z(\rho) \\
Z(\rho) \text{ is a tabulated function.}^{[55]} \text{ The real part of } Z(\rho) \text{ is responsible for absorption.} 
\end{align*} \]

B. Kinetic Model

Starting with equation (3-1) and (3-2) from page 24,

\[ \begin{align*} 
\frac{dS}{dt} &= - \left( \frac{g_p}{g_s} + \frac{\Theta_s}{\Lambda^2} + k_s N^2 \right) S + (R+A) P \\
\frac{dP}{dt} &= \frac{g_p}{g_s} - \left( \frac{\Theta_p}{\Lambda^2} + k_p N^2 + R + A \right) P 
\end{align*} \]

We select a solution of form \( S, P \sim e^{-\alpha t} \), where the time constant \( \alpha^{-1} \) govern \( S(t) \) and \( P(t) \). The secular determinant

\[ \begin{vmatrix} 
\alpha - \left( \frac{g_p}{g_s} + \frac{\Theta_s}{\Lambda^2} + k_s N^2 \right) & R + A \\
\frac{g_p}{g_s} & \alpha - \left( \frac{R + A + \frac{\Theta_p}{\Lambda^2} + k_p N^2}{\Lambda^2} \right) 
\end{vmatrix} = 0 \]

\[ \Rightarrow \quad \alpha^2 - \left[ R \left( 1 + \frac{g_s}{g_p} \right) + A + \frac{\Theta_s + \Theta_p}{\Lambda^2} + (k_s + k_p) N^2 \right] \alpha \]

\[ \quad + \left\{ \frac{1}{\Lambda^2} \left[ (R + A) \Theta_s + R \frac{g_p}{g_s} \Theta_p + \frac{\Theta_p \Theta_s}{\Lambda^2} \right] + N^2 \left[ \Theta_s k_p + \Theta_p k_s \right] \right\} = 0 \]
\[
N^2 \left[ (R + A)k_s + \frac{g_p}{g_s} k_p + k_s k_p N^2 \right] = 0
\]

\([A + R(1 + g_p/g_s)]\) is $\gg$ all other terms for all laser intensities, therefore

\[
\alpha_+ \equiv A + R \left(1 + \frac{g_p}{g_s}\right)
\]

\[
\alpha_- \equiv \frac{(A+R)(k_s N^2 + \Theta_s^0/\Lambda^2 N) + R(g_p/g_s)(k_p N^2 + \Theta_p^0/\Lambda^2 N)}{A+R(1+g_p/g_s)}
\]
Appendix II

Theory of Temperature Dependence of the He(2$^3$P) Conversion Coefficient

Based on a Model Which Pictures Ternary Collisions as Two Binary Collisions

The number of "sticky" collisions per second per unit volume between $n_p$ helium atoms/cm$^3$ in the 2$^3$P$_2$ state and $n_0$ atoms/cm$^3$ in the ground state, with impact parameter between $b$ and $b + db$ ($b \leq b_0$) is

$$Z_1 = d\sigma \nu n_p n_0 = 2\pi b \nu n_p n_0$$

The collision duration is

$$t(b) = 2\pi \int_0^{b_0} \frac{dr}{r} = 2\sqrt{\frac{\mu}{2}} \int_0^{b_0} \frac{dr}{\sqrt{E_k - \frac{J^2}{2\mu r^2} + \frac{\xi}{r^6}}}$$

where $J^2 = 2E_kb^2$, $\mu$ is reduced mass.

The number of collision pairs per unit volume in steady state is $Z_1 t(b)$, and the number of collisions per second per unit volume between $n_0$ ground state atoms and $Z_1 t(b)$ collision pairs is $\sigma_2(\nu) n_0 Z_1 t$ where $\sigma_2(\nu)$ is the collision cross section. Therefore the three-body reaction rate is, integrating over impact parameters from 0 to $b_0$,

$$R(\nu) = n_0^2 \int_0^{b_0} (2\pi b \nu db) t(\nu) \sigma_2(\nu)\nu$$

$$= 2\pi \sigma_2(\nu) n_0^2 \nu^2 \int_0^{b_0} bt \nu db$$

$$= 4\pi \sigma_2(\nu) n_0^2 \nu^2 \sqrt{\frac{\mu}{2}} \int_0^{b_0} \frac{db}{\sqrt{E_k - \frac{J^2}{2\mu r^2} + \frac{\xi}{r^6}}}$$
\[ = 4\pi \sigma_2(v) n_0^2 v^2 \sqrt{\frac{\mu}{2}} \int_0^{b_0} \frac{1}{2} \frac{db^2}{\sqrt{E_k - \frac{r^2}{2\mu r^2} + \frac{\xi}{r^6}}} \]

Set \( y = \frac{E_k b^2}{r^2} \), \( dy = \frac{E_k}{r^2} \, db^2 \).

\[ \therefore R(v) = 4\pi \sigma_2(v) n_0^2 v^2 \sqrt{\frac{\mu}{2}} \int_0^{b_0} \frac{r^2}{2E_k} \int_0^{E_k b_0^2} \frac{dy}{\sqrt{E_k - y + \frac{\xi}{r^6}}} \]

\[ R(v) = 4\pi \sigma_2(v) n_0^2 v^2 \sqrt{\frac{\mu}{2}} \frac{1}{E_k} \int_0^{b_0} r^2 d\theta \int_0^{E_k b_0^2} \frac{dy}{\sqrt{E_k + \frac{\xi}{r^6}}} \]

\[ = 4\pi \sigma_2(v) n_0^2 v^2 \sqrt{\frac{\mu}{2}} \frac{1}{E_k} \int_0^{b_0} \frac{r^2}{E_k} \left[ \sqrt{E_k + \frac{\xi}{r^6}} - \sqrt{E_k + \frac{\xi}{r^6} - \frac{E_k b_0^2}{r^2}} \right] \, dr \]

\[ = 4\pi \sigma_2(v) n_0^2 v^2 \sqrt{\frac{\mu}{2}} \frac{1}{E_k} \int_0^{b_0} \frac{r^2 E_k b_0^2}{r^2} \sqrt{E_k + \frac{\xi}{r^6} + \sqrt{E_k + \frac{\xi}{r^6} - \frac{E_k b_0^2}{r^2}}} \, dr \]

\[ = 4\pi \sigma_2(v) n_0^2 v^2 \sqrt{\frac{\mu}{2}} \frac{b_0^2}{b_0} \int_0^{b_0} \frac{dr}{\sqrt{E_k + \frac{\xi}{r^6} + \sqrt{E_k + \frac{\xi}{r^6} - \frac{E_k b_0^2}{r^2}}}} \]

\[ = 4\sigma_1(v) \sigma_2(v) n_0^2 v^2 \sqrt{\frac{\mu}{2}} \int_0^{b_0} \frac{dr}{\sqrt{E_k + \frac{\xi}{r^6} + \sqrt{E_k + \frac{\xi}{r^6} - \frac{E_k b_0^2}{r^2}}}} \]

Set: \( x = \frac{r}{b_0} \), \( dx = b_0 \, dx \).
\[ R(v) = 4\sigma_1(v)\sigma_2(v)\eta_0^2\nu^2\sqrt{\frac{\mu}{2}} \int_0^1 \frac{b_0 \, dx}{\sqrt{E_k + \frac{c}{x^6b_0^6}} + \sqrt{E_k + \frac{c}{x^6b_0^6} - \frac{E_k}{x^2}}} \]

Since \( \frac{c}{b_0^6} = \frac{4E_k}{27} \) (see Chapter 2),

\[ \therefore R(v) = 4\sigma_1(v)\sigma_2(v)\eta_0^2\nu^2\sqrt{\frac{2E_k}{\mu}} \int_0^1 \frac{dx}{\sqrt{1 + \frac{4}{27}x^6} + \sqrt{1 + \frac{4}{27}x^6 - \frac{1}{x^2}}} \]

\[ \therefore R(v) = 4\sigma_1(v)\sigma_2(v)\eta_0^2\nu^2\left(\frac{b_0}{\nu}\right)B \]

where \( B = \int_0^1 \frac{dx}{\sqrt{1 + \frac{4}{27}x^6} + \sqrt{1 + \frac{4}{27}x^6 - \frac{1}{x^2}}} \)

\[ = \int_0^1 f(x) \, dx \quad \text{is a numerical factor.} \]

\( \sigma_1, \sigma_2 \) are two-body collision cross sections. As shown in Chapter 2:

\[ \sigma_1, \sigma_2 \sim \frac{1}{T^{1/3}}, \quad b_0 \sim \frac{1}{T^{1/6}}, \quad \nu \sim T^{1/2} \]

\[ \therefore R(v) = B \sigma_1 \sigma_2 \eta_0^2 \nu b_0 \sim \frac{1}{T^{2/3}} \times T^{1/2} \times \frac{1}{T^{1/3}} \sim \frac{1}{T^{1/3}} \]

We can also write \( R(v) = \eta_0^2 \sigma_1 \nu \bar{\tau} \nu \sigma_2 \), where \( \bar{\tau} \) is average two-body collision time for all collision parameters. Comparing this with above formula, we get

\[ \bar{\tau} = Bb_0/\nu \sim \frac{1}{T^{2/3}} \]

In summary, treating the ternary collision as two binary collisions in rapid succession predicts a \( T^{-1/3} \) dependence of the rate coefficient, whereas the experiment yields a \( T^{-1} \) dependence. It is easy to show that the \( T^{-1/3} \) dependence predicted by this
collision model is unaltered by introduction of the Maxwellian distribution of velocities. If we consider

$$R(v_1, v_2) = n_0^2 \sigma_1(v_1) v_1 \tilde{u}(v_1) \sigma_2(v_2) v_2$$

with velocity distribution $f(v, T)$, we have:

$$R(T) = \int_0^\infty \int_0^\infty R(v_1, v_2) f_1(v_1, T) f_2(v_2, T) \, dv_1 \, dv_2$$

$$= \int_0^\infty \int_0^\infty n_0^2 \sigma_1(v_1) v_1 \tilde{u}(v_1) f_1(v_1, T) \, dv_1 \int_0^\infty \sigma_2(v_2) v_2 f_2(v_2, T) \, dv_2$$

$$= n_0^2 \int_0^\infty \left[ \frac{8}{\pi \mu_1^3 (kT)^3} \right] \frac{1}{E_k} \sigma_1(E_1) e^{-E_1/kT} \tilde{u}(E_1) \, dE_1$$

$$\times \int_0^\infty \left[ \frac{8}{\pi \mu_2^3 (kT)^3} \right] \frac{1}{E_k} \sigma_2(E_2) e^{-E_2/kT} \, dE_2$$

where: $\mu_1 = \frac{m}{2}$, $\mu_2 = \frac{2m}{2m + m} = \frac{2}{3} m$

$$\therefore \quad R(T) = \frac{n_0^2}{\sqrt{\mu_1 \mu_2}} \left[ \frac{8}{\pi (kT)^3} \right] \int_0^\infty E_1 \sigma_1(E_1) \tilde{u}(E_1) e^{-E_1/kT} \, dE_1$$

$$\times \int_0^\infty E_2 \sigma_2(E_2) e^{-E_2/kT} \, dE_2$$

$$\sigma_1(E_1) \sim \frac{1}{E_1^{1/3}}, \quad \tilde{u}(E_1) \sim \frac{1}{E_1^{2/3}}, \quad \sigma_2(E_2) \sim \frac{1}{E_2^{1/3}}$$

therefore:

$$R(T) \sim \frac{n_0^2}{\sqrt{\mu_1 \mu_2}} \left[ \frac{8}{\pi (kT)^3} \right] e^{-E_1/kT} \int_0^\infty E_2^{2/3} e^{-E_2/kT} \, dE_2$$

$$= \frac{n_0^2}{\sqrt{\mu_1 \mu_2}} \left[ \frac{8}{\pi (kT)^3} \right] (kT)^{5/3} A_1 A_2$$
\[ \sim \frac{1}{T^{1/3}} \]

where: \[ A_1 = \int_0^\infty e^{-y} \, dy, \quad A_2 = \int_0^\infty y^{2/3} e^{-y} \, dy \]