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ROTATIONAL ENERGY TRANSFER IN
LOW TEMPERATURE MOLECULES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate School
of The Ohio State University

By
Christopher D. Ball. M.S.

*****

The Ohio State University
1998

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ABSTRACT

We have extended the study of rotational energy transfer in gas-phase molecules into low temperature (~4 K) environments by combining the techniques of time resolved, millimeter wave double resonance with the collisional cooling method. Inelastic collisions in the low temperature regime are dominated by the resonant formation of quasibound complexes, rather than "action at a distance" mechanisms typical of ambient collisions. Variable temperature pressure broadening results of H$_2$S and SO$_2$ are presented to illustrate the transition between these two temperature regimes. Diagnostic tests of the low temperature double resonance apparatus were performed using the CH$_3$F-He collision system between 1 and 20 K, and the role of the coherent absorption of the millimeter wave radiation was explored. A more complete series of time resolved experiments involving H$_2$S-He collisions between 1 and 40 K are described, and the relative contributions of inelastic and elastic collisions to low temperature pressure broadening data are explicitly demonstrated. Propensities for inelastic collisions involving hyperfine and A-doublet states are presented for NO-He collisions at 4.2 K. A series of diagnostic quantum scattering calculations were performed for the CO-He system in order to make generalizations regarding other collision systems for which intermolecular potentials have not been derived. Pressure broadening and inelastic cross sections for the H$_2$S-He system were also calculated by quantum scattering theory and are compared to the experimental values. The double resonance results presented in this work represent the first direct measurement of rotationally inelastic cross sections involving low temperature molecules in an equilibrium
environment, and this investigation is an important step toward a deeper understanding of low energy molecular collisions and the dynamics of molecules found in gaseous interstellar clouds.
In March of 1996, I visited the laboratory of Dr. Manfred Winnewisser and Dr. Brenda Winnewisser in Giessen, Germany, to work on a collaborative effort involving collisional cooling with their Bruker FTIR spectrometer. During this visit, Manfred and Brenda took me to the museum dedicated to the work of the famous Giessen chemist, Justus Liebig. There was a sign-in sheet to document the visitors to the museum, and one was supposed to write their name and occupation. I wrote my name and hesitated about my occupation, since I was a student and on any official forms, that is what I would normally write. Manfred said I should write "physicist". I wrote it, but I felt strangely uncomfortable about it, since I had trouble identifying myself as anything but a student.

Since then, my frame of mind has undergone significant changes, and I now feel that I am indeed a physicist. I have my research adviser, Dr. Frank De Lucia, to thank for this. Through his guidance, I have successfully made the transition from learning science to actually doing science. He is a gifted scientist, with deep insights, incredible enthusiasm, boundless optimism, and amazing technical talents. These traits have rubbed off on me, and all his students, I believe. I am lucky to have worked with such an important scientist, and a truly kind person, and I thank him for all he has done for me.

I also wish to thank Professor Eric Herbst, for many conversations about interstellar molecules, Professor Greg Lafyatis, for his insights into the Autler-Townes effect, and Professor Linn Van Woerkom, for helping me understand some of the details of coherent interactions. Many current and former members of our research group have also
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I have been involved with several fruitful collaborative projects during my tenure with Dr. De Lucia’s research group. I wish to thank Dr. Manfred Winnewisser, Dr. Brenda Winnewisser, Georg Mellau, Dr. Michael Lock, and again Dr. Markus Mengel for being gracious hosts for my two visits to Giessen. I also thank Dr. Arlan Mantz for the opportunity to design the low temperature apparatus for his experiments at Franklin and Marshall College, and later Connecticut College. In addition, Dr. Joe Dutta of North Carolina Central College and Dr. Paul Helminger of the University of South Alabama both deserve my gratitude for their work with me on pressure broadening studies.

The facilities here at the Ohio State Department of Physics are of the highest caliber, and many aspects of my work would not have been possible without the help of the staff in this department. First, I wish to thank John Whitcomb for all his help with a variety of administrative and personal issues. Bob Kindler, Larry Wilkes, and Rich Kindler did an excellent job with all the projects I brought to their low temperature shop, and Bob Merritt kept the liquid helium flowing whenever I needed it. John Spaulding and Randy Mulford of the main machine shop did outstanding work on the many jobs I submitted to them, and Tom Kelch was incredibly helpful in the graduate student shop. John Hoftiezer and Chris Gecik, of the electronics shop, also deserve my thanks for designing and repairing various electronics, and for helping me make some of the apparatus work better than the factory specifications.
I would be remiss without recognizing Dr. David Woon of the Molecular Research Institute, for calculating an H$_2$S-He potential energy surface for us. Dr. Bob Le Roy of the University of Waterloo, for many enlightening conversations about molecular collision theory, and Dr. Jeremy Hutson of the University of Durham, for his assistance with MOLSCAT problems. I also thank NASA for a Global Change Fellowship, the Ohio State University for a Presidential Fellowship, and the Ohio Supercomputer Center for time on the Cray T90. I especially thank Dr. Patrick Thaddeus of Harvard University for several enlightening conversations about possible future double resonance measurements and for providing a wonderful opportunity for me to expand my knowledge and capabilities in his laboratory as a post-doctoral researcher.

Finally, I wish to thank my family for the boundless love and support they have given me. My mother, Kay, and my father, Dave, have always believed in me, and I cannot thank them enough for everything they have done. I also thank my godfather and best friend, William Gill, for all his support, his interest in my work, and all the ways in which he has made a positive impact on my life. My wife, Kristen, deserves the most thanks of all. Graduate school has been a long and arduous ordeal, and I could not have made it without her love, patience, and understanding. I am the luckiest man alive to have met and married such a beautiful, intelligent, and caring woman. Her faith in me is unwavering, and making her proud of me means more than any of the accolades I have received from the academic community. I dedicate this work to her.

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CHAPTER I

INTRODUCTION

The interactions between gas-phase molecules and electromagnetic radiation, as utilized in spectroscopic experiments, have been thoroughly studied and are well understood. When tuned to a specific resonant frequency, electromagnetic radiation can induce a transition between internal (electronic, vibrational, or rotational) energy states of a molecule, and such transitions are governed by well-defined, typically dipole-allowed, selection rules. High resolution spectroscopic data for a given molecule enables the formulation of spectroscopic constants, which are then related to the structural properties of the molecule, such as bond lengths, bond angles, and dipole moments.

However, molecule-molecule interactions in gas-phase samples are more difficult to characterize given the possibility of inelastic collisions which can transfer population among the internal energy states. Rather than simple interactions involving the dipole (or higher order multipole) moments of a molecule, as in the case of interactions with radiation, collision dynamics are mediated by a complicated electrostatic intermolecular potential. While approximations can be employed for many collision regimes of interest to simplify the collision theory, the complexity of the collision problem is such that a generalized "spectroscopic" theory, based on only a few physical parameters, has been difficult to develop.

Over the past four decades, many experimental and theoretical efforts have been devoted to the study of rotational energy transfer (RET) with the hope that eventually, a
self-consistent, invertible theory can be developed which connects rotationally inelastic collision processes to a small number of parameters based on the intermolecular potential. Experiments involving molecular beams and jets, as well as spectroscopic investigations with equilibrium samples, have yielded a large body of data related to RET processes. However, we are still a long way from the goal of a general "spectroscopic" framework for understanding and predicting RET observables.¹ ²

There are many applications for the knowledge obtained from RET experiments. At a fundamental level, measured inelastic collision rates or cross sections can yield information about intermolecular potentials as well as provide much needed tests of collision theories. Inelastic rates are also necessary for a complete understanding of the processes behind collision-induced spectral line broadening, or pressure broadening.³ In atmospheric studies, accurate pressure broadening parameters and inelastic rates are required for the analysis of data from spectroscopic remote sensing measurements of trace gas molecules. These accurate parameters enable a precise determination of trace gas mixing ratios, which in turn leads to better models for atmospheric processes, particularly ozone chemistry.⁴ In the interstellar medium, where gas-phase molecules exist in vast clouds which typically are not in local thermodynamic equilibrium, accurately measured inelastic cross sections are required to determine molecular concentrations from data acquired by radio telescopes. Mapping the concentrations of interstellar molecules within these clouds leads to better models for star formation and interstellar masers.⁵ ⁶ Studies of RET also have technological importance, particularly in the diagnostics of molecular, far-infrared gas lasers.⁷

The vast majority of RET experiments to date involve molecular collisions at ambient temperatures. In the ambient regime, the dynamics of rotationally inelastic collisions can be very complicated, since there are many open channels through which rotational energy is transferred. Ambient collision theories, however, are in general fairly
simple since they are semiclassical in nature and involve averages over all the open collision channels. The dominant physics behind ambient collisions can be characterized as "action at a distance", and the details of the complete intermolecular potential, particularly the attractive potential well, typically are not crucial in this temperature regime.

At low temperatures, the situation is reversed. On the surface, it would seem that low temperature inelastic collisions are simpler to calculate because the number of energetically accessible collision channels becomes quite small. However, because of the low collision energies at low temperatures, the details of the complete intermolecular potential become important, particularly the attractive well. As the collision partners approach each other at low energy, the attractive well makes possible the resonant formation of a quasibound complex. The collision partners form a temporary bound system, orbit around each other a few times, and then separate. The formation of these quasibound complexes translates into resonances in low energy collision cross sections. The dynamics of low temperature collisions is therefore more complicated than at ambient temperatures, and a fully quantum mechanical treatment of the collision problem is required, which relies on a precise characterization of the potential energy surface (PES). Since the dominant physics behind low temperature collisions is the resonant formation of these quasibound complexes, the low temperature regime presents fundamentally different kinds of challenges in the investigation of RET processes than in the ambient regime.

For low temperature experiments, the collisional cooling methodology of Messer and De Lucia enables quasi-equilibrium spectroscopic studies of molecules at temperatures below which they ordinarily have sufficient vapor pressure. Previously, this research group had focused on low temperature pressure broadening measurements in the millimeter wave frequency range, which have yielded a plethora of interesting results concerning low temperature collisions. Since the development of the collisional cooling technique, it has long been our goal to perform time resolved millimeter wave double resonance
experiments with a collisional cooling system to measure inelastic cross sections. Thus the primary focus of the work presented in this dissertation is the development of such a low temperature double resonance system, and the results obtained in our experiments represent the first direct measurements of low temperature rotationally inelastic collision cross sections in an equilibrium environment.

In the next chapter, we will discuss background information applicable to the development of a low temperature double resonance system. Ambient and low temperature collision theories are introduced, relevant discoveries of previous ambient RET experiments are discussed, and the collisional cooling technique is described. In Chapter 3, we discuss the details of the experimental apparatus, concentrating on several important issues involving the millimeter wave and low temperature systems. In Chapter 4, we present the results of variable temperature pressure broadening experiments involving SO₂ and H₂S, which serve to illustrate some of the fundamental differences between collisions in the ambient and low temperature regimes. In Chapters 5 through 7, we present the results of low temperature, time resolved double resonance experiments. First, in Chapter 5, we discuss diagnostic tests of the apparatus, which used the CH₃F-He collision system between 1 and 20 K. Then, in Chapter 6, we discuss a complete set of measurements of H₂S-He collisions over a temperature range of 1 to 40 K. The experiments presented in Chapter 7 involve exploration of propensities for inelastic collisions among hyperfine and Δ-doublet states of NO in collision with He at 4.2 K. In Chapter 8, we present the results of quantum scattering theory calculations of pressure broadening and inelastic cross sections. First, diagnostic calculations of the CO-He system were performed to qualitatively predict resonance phenomena for systems for which no PES has been developed. Second, we calculated pressure broadening and inelastic cross sections of H₂S-He with a new PES and compared these results with the experimentally measured cross
sections. Finally, in Chapter 9, we offer some conclusions as well as discuss some future directions for this low temperature double resonance experiment.

References

CHAPTER 2

BACKGROUND

Before describing the investigation of low temperature inelastic collisions, which is the focus of this dissertation, it is necessary to introduce and summarize the large body of work from which this study naturally follows. First, the theory of inelastic collisions and pressure broadening is introduced, including a discussion of what has been learned from the theory as well as its fundamental limitations. Then, a variety of ambient temperature rotational energy transfer (RET) experiments, which form the experimental foundation of the current study, is presented. Finally, the collisional cooling technique, which enables very low temperature spectroscopy, is described, including a discussion of previous low temperature pressure broadening measurements.

2.1 Molecular Collision Theory

2.1.1 Semiclassical Anderson Theory

For rotationally inelastic collisions of most molecules at ambient temperatures, where

\[ \Delta E_{\text{net}} \ll kT. \tag{2.1} \]

the semiclassical theory of Anderson,\(^1\) modified by Tsao and Curnutte,\(^2\) qualitatively characterizes the probability of collision induced transitions. It has been shown that if Eq.
2.1 holds, virtually all ambient collisions induce rotational transitions. Thus, any collision strong enough to change the phase of the molecular rotation, and hence cause spectral broadening, is strong enough to change the rotational state of the molecule.

The theory employs two fundamental assumptions. First, the impact approximation is assumed, where only bimolecular collisions with duration much less than the average time between collisions are considered. This assumption holds for virtually any gaseous systems below 1 Torr. Second, the molecules are assumed to follow classical trajectories, which is justified if the de Broglie wavelength of a molecule is much smaller than the average interaction distance. In addition, for most long range collisions, there is negligible deflection of these classical paths, and thus we also assume straight line trajectories. What follows below is a brief presentation of the basic equations of Anderson theory, as presented by Townes and Schawlow, with a discussion of the physical consequences.

The probability, \( P \), of a collision induced transition for two rotational levels (labeled \( |1⟩ \) and \( |2⟩ \)) can be expressed as a Fourier integral

\[
P_{1→2} = \left| \frac{1}{R} \int_{-∞}^{∞} \langle |V(t)|^2 \rangle \exp(i\omega_{12}t) \, dt \right|^2 ,
\]

(2.2)

where \( \langle |V(t)|^2 \rangle \) is a matrix element of the interaction potential \( V(t) \) and \( \omega_{12} \) is the transition frequency. Anderson \(^1\) originally used a dipole-dipole interaction potential, and Tsao and Curnutte expanded the calculations to include higher order multipole interactions.\(^2\) In general, a simple expression for a multipolar potential,

\[
V(t) = \frac{C}{R^m(t)} ,
\]

(2.3)

can be employed, where \( C \) is a constant (inside of which is contained the angular dependence), \( m \) is the order of the multipolar interaction (\( m=3 \), dipole-dipole; \( m=5 \)).
quadrupole-quadrupole; etc.), and $R$ is the intermolecular separation as shown in Fig. 2.1. From this geometry, $R$ can be expressed in terms of the relative velocity, $v$, and the impact parameter, $b$, by

$$R^2 = b^2 + (vt)^2. \quad (2.4)$$

Plugging Eqs. 2.3 and 2.4 into Eq. 2.2, we get

$$P_{1\to 2} = \left| \frac{C}{\hbar} \int_{-\infty}^{\infty} \frac{\exp(i\omega_{12} t)}{b^2 + v^2 t^2} dt \right|^2. \quad (2.5)$$

Making the substitutions

$$x = \frac{vt}{b} \quad \text{and} \quad k = \frac{b}{v} \omega_{12}. \quad (2.6)$$

Eq. 2.5 becomes

$$P_{1\to 2} = \left| \frac{C}{\hbar b^{\omega_{12}} v} \int_{-\infty}^{\infty} \frac{\exp(i k x)}{(1 + x^2)^{\omega_{12}/2}} dx \right|^2. \quad (2.7)$$

The Fourier integral of Eq. 2.7 provides qualitative physical insight into the interaction process. The variable $k$ is the ratio of the collision duration ($b/v$) to the time required to change the rotational phase of the molecule ($1/\omega_{12}$). For different values of $k$, the integral yields different physical results. If $k$ is small ($k \ll 1$), the collision is very fast compared to the oscillations of the molecule, and $P_{1\to 2}$ is of maximal value and nearly constant for variations in $k$. It is this condition that corresponds to most molecules in ambient conditions, where collisions very efficiently induce rotational transitions. If $k$ is
Figure 2.1. Geometric picture of colliding molecules with straight line, classical trajectories in a relative coordinate system.
large \((k\gg 1)\) the collisions are much slower and the transition probability decreases rapidly with increasing \(k\).

Inelastic cross sections are calculated from the transition probability by

\[
\sigma = \int 2\pi h P(h) dh
\]

where \(P(h)\) is the transition probability (sometimes called an opacity function \(^4\)) given by Eq. 2.7 and expressed as a function of \(b\). Figure 2.2 shows the behavior of \(P(h)\) as a function of \(1/k^2\), which is proportional to temperature. At high temperatures \((1/k^2\) large\), \(P(h)\), and therefore the cross section, is nearly constant. As temperature \((or \ 1/k^2)\) decreases, collisions cannot induce rotational transitions as efficiently and \(P(h)\) decreases sharply.

Pressure broadening cross sections can be calculated using Anderson theory. Here we consider probabilities of collision-induced transitions to many possible final states. The opacity function, \(P(b)\), in Eq. 2.8 is redefined by

\[
P(b) = \frac{1}{2} \sum_{i,M} \left( \frac{P_{i,M\rightarrow \ell}}{2J_i + 1} + \frac{P_{i,M\rightarrow \ell}}{2J_{i} + 1} \right)
\]

where \(J_i\) and \(J_{i}\) are the rotational states involved in the broadened transition, \(M\) represents the magnetic quantum numbers, and \(\ell\) represents all possible final states of a collision induced transition. Equation 2.9, with Eq. 2.8, thus defines a pressure broadening cross section as the sum of all inelastic cross sections for processes which move population out of the levels involved in the radiative transition. Complete solutions to Anderson theory calculations of pressure broadening show that the broadening cross sections obey the following temperature dependence in the \(k\ll 1\) limit:
Figure 2.2. The functional behavior of $P(h)$ on $1/k^2$ (proportional to $T$) for a generalized dipole-dipole interaction ($m=3$).
where \( T_0 \) is some reference temperature, typically 300 K, and \( \sigma(T_0) \) is the cross section at that temperature. The exponent \( n \) generally takes on values between 0 and 0.5, where \( n = 0 \) is the hard sphere limit. Non-zero values of \( n \) arise from coupling the rotational energy states of the collision partner into the semiclassical theory. Pressure broadening measurements of Goyette et al. show that for HDO collisions with He atoms (which are nearly hard sphere-like in character), the exponent \( n \) is close to zero, while for HDO collisions with \( \text{N}_2 \), \( n = 0.27 \) below 170 K. Figure 2.3 shows these broadening cross sections as a function of temperature with a fit of Eq. 2.10 to the data.

Figure 2.3 also shows that the HDO-\( \text{N}_2 \) cross sections diverge from the power-law temperature dependence of Eq. 2.10 below 170 K, where the cross sections are smaller than predicted. Here we see the case where the parameter \( k \) from Eq. 2.7 is no longer smaller than one, causing the cross sections to begin to decline with decreasing temperature as in Fig. 2.2. This same behavior has also been observed in \( \text{H}_2\text{O} \) collision systems. In contrast, \( \text{HNO}_3-\text{N}_2 \) does not exhibit this deviation (at least down to 100 K). \( \text{HNO}_3 \) has smaller rotational constants than HDO or \( \text{H}_2\text{O} \), thus the energy levels are more closely spaced together and \( k \) remains small at lower temperatures.

2.1.2 Quantum Scattering Theory

While the Anderson theory treatment is adequate for ambient inelastic collisions and pressure broadening, the assumption of classical trajectories breaks down at low temperature (typically \( T < 100 \) K). As relative thermal velocities become small, the de Broglie wavelength of a molecule becomes comparable to the average impact distance. In

\[
\sigma(T) = \sigma(T_0) \left( \frac{T_0}{T} \right)^n
\]  

(2.10)
Figure 2.3. Pressure broadening cross sections of HDO-He and HDO-N$_2$ as a function of temperature, including fit of Eq. 2.10 (solid lines) to the experimental values above 170 K.
addition, low collision energies enable a molecule to probe deeper into the radial
dependence of the interaction potential such that the attractive well becomes important to the
collision dynamics. Simple, long-range characterizations of the potential is no longer valid
in this regime. Therefore, a fully quantum mechanical scattering theory, which employs
accurate PESs, is required. Such quantum treatments are physically valid at all collision
energies, yet are generally tractable at only the lowest energies.

The derivation of the quantum scattering problem presented below follows very
closely the treatment of Green and Thaddeus,\textsuperscript{11} who employ the close-coupling
approximation of Arthurs and Dalgarno.\textsuperscript{12} Without an approximation, the quantum
formalism yields infinite sums over all good quantum numbers. The close-coupling
approximation involves coupling the various angular momenta of the scattering partners
into a total angular momentum representation in space-fixed coordinates. The infinite sums
are then truncated to include only energetically accessible states (open channels).
Typically, some closed channels are also included because, during the collision, a molecule
can undergo a "virtual excitation" into an energetically inaccessible state.\textsuperscript{13} The close-
coupling method is considered an "exact" calculation, though it is only computationally
affordable at low collision energies and for the lowest lying rotational states. At higher
energies, the coupled states approximation of McGuire and Kouri, which decouples
internal angular momenta and orbital angular momenta and defines them in a rotating,
body-fixed coordinate system, can greatly reduce the number of equations without
significant loss of accuracy.\textsuperscript{14}

The Schrödinger equation for a two molecule system is:

\[
\left[ H_A(R_A) + H_B(R_B) + V(R_A, R_B, R) - \frac{1}{2\mu} \nabla^2_R - E \right] \Psi(R_A, R_B, R) = 0, \quad (2.11)
\]
where $H_A$ and $H_B$ are the internal Hamiltonians for each molecule in terms of their nuclear coordinates ($R_A$ and $R_B$), $V$ is the interaction potential, $R$ is the relative collision coordinate, and $\mu$ is the reduced mass of the collision system. The wave function can be expanded in terms of partial waves and eigenfunctions of the internal Hamiltonians:

$$\Psi(R_A, R_B, R) = \sum_{\eta m} \Psi_A^\eta(R_A) \Psi_B^\eta(R_B) Y_\eta^m(W) f_{\eta m}(R).$$  \hspace{2cm} (2.12)

When Eq. 2.12 is plugged into 2.11, we get:

$$\left[ \frac{1}{2\mu} \frac{d^2}{dR^2} - \frac{\ell(\ell + 1)}{2\mu R^2} + \left( E - E_\gamma \right) \right] f_\gamma(R) = \sum_\rho V_\gamma^\rho(R) f_\rho(R),$$ \hspace{2cm} (2.13)

where $\gamma$ and $\rho$ represent all quantum numbers, $\ell$ is the orbital angular momentum of the system, and $V_\gamma^\rho$ is a matrix element of the interaction potential in the basis defined by Eq. 2.12.

To obtain physically measurable quantities, the asymptotic ($R \to \infty$) behavior of the radial solutions to Eq. 2.13 is determined by

$$f_\gamma^\rho(R) = \delta_{\gamma\rho} \exp\left[ -i\left( k_\gamma R - \ell \frac{\pi}{2} \right) \right] \left( \frac{k_\gamma}{|k_\rho^*|} \right)^{1/2} S_{\gamma\rho} \exp\left[ i\left( k_\rho^* R - \ell' \frac{\pi}{2} \right) \right].$$ \hspace{2cm} (2.14)

where $\hbar k_\rho = \sqrt{2\mu(E - E_\rho)}$. $\gamma$ represents initial quantum numbers, $\rho$ represents final quantum numbers, and $S$ is the scattering matrix (or S-matrix). Inelastic cross sections are then calculated by

$$\sigma(j' \to j) = \frac{\pi}{(2j+1)k_\gamma^2} \sum_{\ell, \ell'} (2J+1) |\delta_{\eta J} \delta_{\ell', \ell} - S'(j'\ell', j\ell)|^2,$$ \hspace{2cm} (2.15)
where $J$ is the total angular momentum, and pressure broadening cross sections are calculated by

$$\sigma(j_a \rightarrow j_b) = \frac{\pi}{k_B^2} \sum_{l,l',m} (2J_a + 1)(2J_b + 1) \left\{ \begin{array}{ccc} j_a & n & j_b \\ J_a & l' & J_b \end{array} \right\} \left\{ \begin{array}{ccc} j_a & n & j_b \\ l & \ell & J_b \end{array} \right\} \times \left[ \delta_{l',l} - S^J(j_b, j_a) \right] \right\} (2.16)$$

where $j_a$ and $j_b$ are the lower and upper levels of the radiative transition, $n=1$ for dipole transitions and $n=2$ for Raman transitions, and the braces represent 6-j symbols.\(^{15}\)

In order to solve for cross sections using the close-coupling or coupled states approximations, efficient computer programs are required. The MOLSCAT program of Green and Hutson \(^{16}\) numerically solves the quantum scattering equations for pressure broadening and inelastic cross sections for a variety of collision systems (diatomic-atom, diatomic-diatomic, symmetric top-atom, asymmetric top-atom, etc.). The HIBRIDON package of Alexander et al.\(^{17}\) calculates inelastic cross sections only, but is able to handle calculations for open shell molecules. The outputs of both of these programs are cross sections as functions of collision energy. To compare with experimental, thermally averaged cross sections, the temperature dependence is computed by

$$\sigma(T) = \frac{1}{(kT)^2} \int E \exp(-E/kT) \sigma(E) \, dE. \quad (2.17)$$

Assuming the aforementioned approximations have been used properly, the most severe limitation of quantum scattering calculations is the accuracy of the interaction potential. While many reasonable PESs have been used to precisely determine bulk properties of gases,\(^{18}\) extremely accurate potentials are required for calculations of low energy inelastic or pressure broadening cross sections. These cross sections are very sensitive to the depth of the attractive well and to the anisotropy of the PES. Currently,
many *ab initio* PESs have been derived for only the simplest collision systems. Unfortunately, for molecules with more than three or four atoms, the *ab initio* methods become computationally prohibitive.

An illustrative example of the application of the quantum scattering formalism is the CO-He system. For nearly 15 years, the *ab initio* PES of Thomas *et al.* was the accepted standard for this system, yet it improperly defined the well depth and anisotropy of the true interaction. Subsequently, Chuaqui *et al.* developed a more accurate PES based on the infrared spectrum of the CO-He dimer. This PES was then superseded by the “XCFit” PES of Le Roy *et al.* which is currently considered the most accurate CO-He surface to date. Calculations of pressure broadening and inelastic cross sections by Beaky *et al.* using MOLSCAT are shown in Fig. 2.4. These calculations employ the close-coupling approximation for the entire range of energies presented in the graph.

The cross sections in Figure 2.4 exhibit two fundamental phenomena which are not predicted in the semiclassical Anderson theory. First, the cross sections have resonance structures at the lowest energies. These are due to the resonant formation of quasi-bound states of the collision partners. In essence, the two collision partners temporarily form a bound complex, the lifetime of which is determined from the width of the resonance. Specific details about resonance phenomena are discussed in Chapter 8. The physical implication of these resonances is that the dominant interactions at low collision energy are of close range, rather than the “action-at-a-distance” multipolar mechanisms in the ambient regime. Second, some resonances in the inelastic and pressure broadening cross sections coincide, explicitly demonstrating the role of inelastic collisions in low energy broadening. However, at 1.09 cm⁻¹ and 3.16 cm⁻¹, the pressure broadening cross sections have resonances not found in the inelastic cross sections. This illustrates the relative importance, and sometimes dominance, of elastic collisions in low energy broadening, which is not predicted in the semiclassical theory.
Figure 2.4. Calculated pressure broadening ($j_i=0\rightarrow j_i=1$ transition) and various $j\rightarrow j'$ inelastic cross sections of CO-He as a function of collision energy.
2.2 Ambient Rotational Energy Transfer Experiments

A variety of experimental techniques have been employed to observe the effects of rotationally inelastic collision processes at ambient temperatures. These techniques include, among others, molecular beam scattering, laser induced fluorescence, pressure broadening, and double resonance. While all of these techniques have distinct advantages and disadvantages, those spectroscopic techniques which use microwave or millimeter wave sources (i.e. pressure broadening and double resonance) are particularly advantageous for rotational studies because of favorable frequency resolution and signal intensity. Several of these techniques are presented below, both in the context of the historical development of rotational energy transfer (RET) experiments and of the present development of a low temperature millimeter wave double resonance system.

2.2.1 Steady State Microwave Double Resonance

The general idea behind double resonance experiments for the study of RET is the use of a strong radiation source (a pump) to create a non-Boltzmann population distribution in the rotational energy levels and a weaker source (a probe) to monitor changes in population due to rotationally inelastic collisions. In a typical steady state microwave experiment, the pump radiation is tuned to a particular rotational transition in the ground vibrational state, and the probe monitors the change in the peak absorption of other rotational transitions. Maximal probe signal intensity is realized when the pump is sufficiently powerful to saturate the transition to which it is coupled. The efficiency of saturation, \( \phi \), is given by

\[
\phi = \frac{(\mu_p E_p / \hbar)^2}{(\omega_p - \omega_{p_0})^2 + (1/\tau)^2 + (\mu_p E_p / \hbar)^2} \tag{2.18}
\]
where \( \mu_p \) is the pump transition dipole moment, \( E_p \) is the amplitude of the pump electric field, and \( \tau \) is a characteristic relaxation time for the pump transition.\(^{26} \) When tuned to resonance (\( \omega_p = \omega_{p_0} \)), the pump achieves efficient saturation (\( \phi = 1 \)) if

\[
\mu_p E_p / h \gg 1/\tau.
\] (2.19)

The absorption coefficient for the probe transition (designated \( L \rightarrow U \)) is given by

\[
\alpha(v_s) = \frac{8\pi^3 \nu_s (n_L - n_U) |\langle U | \mu_s | L \rangle|^2 S(v_s, v_{so})}{3\hbar c}
\] (2.20)

where \( \mu_s \) is the probe transition dipole moment, \( \nu_s \) is the probe frequency, \( S(v_s, v_{so}) \) is a normalized line shape function, and \( n_L - n_U \) is the population difference between the upper and lower states.\(^{27} \) The molecular absorption of the probe power is given by

\[
P_{\text{abs}} = P_0 (1 - \exp(-\alpha x))
\] (2.21)

where \( P_0 \) is the incident probe power and \( x \) is the absorption path length. For a weak probe, which does not saturate the transition, \( \alpha x \ll 1 \) and the approximation

\[
P_{\text{abs}} = P_0 \alpha x
\] (2.22)

generally holds. Substituting Eq. 2.20 into Eq. 2.22 yields

\[
P_{\text{abs}} \propto (n_L - n_U).
\] (2.23)
Since the measured probe signal is proportional to $P_{\text{obs}}$, the observed probe intensity is proportional to the population difference of the upper and lower rotational states. Therefore, if the population of the upper or lower state changes, there is a corresponding change in the probe signal intensity. When the rotational states of the pump transition are not connected radiatively to the probe states, any change in the probe signal when the pump is turned on is due only to rotationally inelastic collisions.

One of the earliest demonstrations of steady state microwave double resonance was by Cox et al. who used the technique to argue against the likelihood of dominant $\Delta J=0$, $\Delta M=\pm 1$ inelastic processes in Stark shifted rotational states of OCS. The first successful observation of RET by microwave double resonance was by Oka, who pumped the $\text{2}_{31} \leftrightarrow \text{2}_{12}$ transition and probed the $\text{3}_{30} \leftrightarrow \text{3}_{21}$, $\text{3}_{21} \leftrightarrow \text{3}_{12}$, and $\text{2}_{11} \leftrightarrow \text{2}_{02}$ transitions of ethylene oxide (\((\text{CH}_2)_2\text{O})\). Figure 2.5 shows the relevant \((\text{CH}_2)_2\text{O}\) rotational energy levels and the pump and probe transitions. When the pump was tuned to resonance, the intensity of the $\text{3}_{30} \leftrightarrow \text{3}_{31}$ decreased by 7% while the intensity of the $\text{3}_{21} \leftrightarrow \text{3}_{12}$ increased by 12%. The intensity of the $\text{2}_{11} \leftrightarrow \text{2}_{02}$ transition showed no observable change. These results implied that the populations of the $\text{3}_{30}$ and $\text{3}_{12}$ levels increased, and that the population of the $\text{3}_{21}$ level decreased, as shown in Fig. 2.5. The likely explanation is that the excess population prepared in the $\text{2}_{31}$ level by the pump collisionally transfers to the $\text{3}_{30}$ and $\text{3}_{12}$ levels, while population of the $\text{3}_{21}$ level transfers to the pump depleted $\text{2}_{12}$ level. Therefore, the collision induced transitions in \((\text{CH}_2)_2\text{O}\) seem to obey b-type dipole selection rules ($\Delta J=1$ and $eo\leftrightarrow oe$).

Subsequent experiments have revealed that RET is governed by "propensity rules". The term "propensity" is used, rather than "selection", because the transition for specific RET processes are not as rigorous as the various multipole allowed radiative "selection rules". Studies of a wide variety of collision partners show that multiple mechanisms contribute to RET, and that generally the transitions are characterized by
Figure 2.5. Relevant rotational energy levels and pump/probe transitions of (CH$_2$)$_2$O in the steady state experiment of Oka.$^{29}$ Population changes ($\delta n$) are shown, as well as the collision induced transitions (dashed arrows) proposed to explain the data.
dominant and weaker, rather than “allowed” or “forbidden”, processes. For example, the typical inelastic channels for collisions between polar molecules are found to be the same as dipole allowed transitions ($\Delta J=1$).\textsuperscript{30,32} Collisions between some polar and non-polar molecules (or atoms), however, exhibit tendencies for $\Delta J>1$ processes, which can be just as likely or more likely than $\Delta J=1$ processes.\textsuperscript{31,33}

2.2.2 Time Resolved Infrared-Microwave Double Resonance

While these early steady state double resonance experiments were crucial to the discovery and formulation of various propensity rules, they have two fundamental limitations. First, the technique does not allow for the quantitative measurement of state-to-state inelastic collision rates. Typically, the observed steady state probe signal depends on a sum over many different inelastic rates. Even if one considers measurements of pressure broadening parameters, which, at ambient temperatures, are equal to the sum of the inelastic rates out of the two levels involved in the transition (see Eq. 2.9 above), there are always fewer equations (probe signals) than there are unknowns (inelastic rates). Second, the intensities of the probe signals are weak ($\leq$ few percent) because, for microwave transitions at ambient temperatures, $h \nu_p \ll kT$, and therefore even when a microwave pump saturates the transition, it can only change the rotational population distribution by a very small amount. Both of these limitations are overcome by employing time resolved double resonance techniques with an infrared pump source.

By pulsing the pump radiation, the dimension of time is added to the double resonance technique. Probe relaxation rates can then be directly measured and associated with individual state-to-state rates, typically through the judicious use of a model. The time resolved technique has its origins in the modulated microwave double resonance technique of Woods, et al.\textsuperscript{35} and the theoretical development of Gordon.\textsuperscript{36,37} Assuming that
population changes depend linearly on the populations themselves, the population flow of a system can be described by the Master equation:

\[
\frac{dn_i}{dt} = \sum_j \left( k_{ij} n_j - k_{ji} n_i \right)
\]  \hspace{1cm} (2.24)

where \( n_i \) is the population of the \( i \)th rotational level and \( k_{ij} \) is the rate of \( i \rightarrow j \) inelastic collisions. In words, Eq. 2.24 says that the time change of the population of a rotational energy level is due to the net flow of population into (first term) and out of (second term) that level. The upward and downward rates are related by the principle of detailed balance, for which

\[
n_i^0 k_{ij} = n_j^0 k_{ji}
\]  \hspace{1cm} (2.25)

where \( n_i^0 \) is the equilibrium population of the \( i \)th rotational level. By employing several probe transitions, the time response of the probe signals, and thus the probe level populations, can yield quantitative measurements of the inelastic rates.

The probe signal intensity has been found to be dramatically increased when a strong infrared pump source is used rather than a microwave pump.\(^{38,39}\) As mentioned above, for a microwave pump, \( h\nu < kT \) at room temperature, and the upper and lower levels are nearly equally populated, which limits the magnitude of the possible change in the Boltzmann population distribution due to the pump. The rotational levels are generally of nearly equal population to start with, so even if the pump saturates the transition, the populations of the pump levels change only by a very small amount. For an infrared pump source, \( h\nu \gg kT \) at ambient temperatures, which enables the pump, if sufficiently powerful, to move a significant amount of population from a populated rotational level in the ground vibrational state into an empty rotational level in an excited vibrational state.
Figure 2.6 graphically shows an example of the relative energy scales of rotational and vibrational energy levels relative to $kT$ at 300 K. Because more population is transferred with infrared pumps, microwave probe transitions in either the ground or excited vibrational state exhibit greatly increased signal intensity. For example, Shimizu and Oka observed in a steady state infrared-microwave study of NH$_3$ that the probe signals were as much as 10 times larger than for an equivalent microwave double resonance study. The general increase in probe signal enables the measurement of probe transitions which might normally yield no signal in the microwave pumped experiments.

The techniques of time resolved and infrared-microwave double resonance have been combined in several ambient RET experiments. The experiments of Everitt and De Lucia are particularly noteworthy because the results of time resolved infrared-millimeter wave double resonance experiments were used to build a simple model of RET in CH$_3$F. Using a CO$_2$ laser to pump molecules from $J$=4, $K$=3 in the ground vibrational state to $J$=5, $K$=3 in the $v_1$ vibrational state, they measured a wide variety of millimeter wave probe time responses in the $v_1$ state. They observed that the $\Delta J=1$, $\Delta K=0$ process was dominant and the $\Delta J >1$, $\Delta K=0$ processes, while slower, were significant. In addition, $\Delta K=3n$ (where $n=1,2,...$) processes, which are allowed by the nuclear symmetry of CH$_3$F, were easily measurable, and $\Delta K\neq3n$ processes, which involve a vibrational swap, contributed to a lesser degree.

Upon understanding the qualitative features of the probe data, Everitt and De Lucia developed a hierarchical model, shown schematically in Figure 2.7, where only a small number of parameters could be used to fit all of their time resolved data. Specifically, the fast $\Delta J=1$, $\Delta K=0$ was assigned its own rate, while all other $\Delta J>1$, $\Delta K=0$ rates were modeled by a combination of the infinite order sudden and statistical power gap approximations, which require only two unknowns to fit all of the $\Delta J=1$, $\Delta K=0$ rates. The $\Delta K$ and any other vibrational rates were analyzed by placing states of different
Figure 2.6. Approximate representation of the rotational energy levels in the ground and $v_3$ excited vibrational states of CH$_3$F. A sample infrared pump is shown, where $h\nu_{v_3} >> kT$ at room temperature.
Figure 2.7. Schematic diagram of the CH$_4$F RET model of Everitt and De Lucia.$^{43}$ All accessible rotational and vibrational transitions are modeled by the use of thermal pools, except for those transitions within the same $K$ manifold as the pump transition.
nuclear spin symmetries and also vibrational states into thermal pools, where one additional constant is required for the addition of a thermal pool to the model. In all, by proper implementation of the model, any rates of CH,F inelastic collisions could be determined using only a handful of fitting parameters.

2.2.3 Transient Absorption of Coherent Radiation

Typically in the time resolved infrared-millimeter wave double resonance experiments discussed above, the pump rate would be linearly dependent on the pump level populations. If an infrared or a microwave pump is strong enough to saturate the transition, then the time dependent responses of the probe signal must be described by non-linear equations. A more general formalism of the transient absorption of coherent radiation is required, particularly for time resolved microwave experiments, in which high power sources can easily saturate transitions of interest. Such formalism follows directly from the development of the coherent interactions of atoms and electromagnetic fields and leads to the optical Bloch equations, which are analogous to the transient equations developed for nuclear magnetic resonance studies.

The observation of optical coherent transient effects in molecules has its roots in photo echo and optical nutation studies. Brittain, et al. extended the study of coherent effects in molecules to the microwave region, and a similar series of microwave investigations by Flygare and co-workers directly followed. The development of the optical Bloch equations applicable to these microwave transient studies are derived from a density matrix description of the interactions between matter and electromagnetic radiation. The derivation presented below follows closely the derivations of McGurk, et al. for a two level system.
The dipole interaction of a two level system (denoted \(a\) and \(b\)) with electromagnetic radiation is given by:

\[
H = H_0 - 2\mu E \cos(\omega t - k z) \tag{2.26}
\]

where \(H_0\) is the time independent two level Hamiltonian with eigenvalues \(E_a\) and \(E_b\). \(E\) is the electric field amplitude. \(\omega\) is the radiation frequency, and \(k = \omega c\). The radiation induces a bulk polarization in an ensemble of two level systems with dipole moment \(\mu\). The polarization of \(N\) dipoles is given by:

\[
P = N \text{Tr}(\mu \sigma) \tag{2.27}
\]

where \(\sigma\) is a density matrix. Transforming the density matrix into the interaction representation by

\[
\rho = \exp\left[\frac{iS}{\hbar} (t - z/c)\right] \sigma \exp\left[-\frac{iS}{\hbar} (t - z/c)\right] \tag{2.28}
\]

where \(S\) is a diagonal matrix with eigenvalues of \(E_a\) and \(E_a + \hbar \omega\). The polarization can be rewritten as

\[
P = N \text{Tr}\left(\mu \exp\left[-\frac{iS}{\hbar} (t - z/c)\right] \rho \exp\left[\frac{iS}{\hbar} (t - z/c)\right]\right). \tag{2.29}
\]

Explicitly expanding the trace in terms of \(|a\rangle\) and \(|b\rangle\) (in which only off-diagonal dipole matrix elements are non-zero) yields

29
\[ P = N(\langle b|\mu|a\rangle\langle a|\rho|b\rangle\exp[i(\omega x - kz)] + \langle a|\mu|b\rangle\langle b|\rho|a\rangle\exp[-i(\omega x - kz)]) \quad (2.30) \]

which can be rewritten as

\[ P = (P_r + iP_i)\exp[i(\omega x - kz)] + (P_r - iP_i)\exp[-i(\omega x - kz)]. \quad (2.31) \]

where \( P_r \) and \( P_i \) are the real and imaginary parts of the bulk polarization.

The time dependent absorption coefficient is defined as

\[ \alpha = -\frac{4\pi \omega}{c} \frac{P_i}{E}, \quad (2.32) \]

so it is necessary to solve for the time dependence of the imaginary part of the polarization in order to characterize the time dependence of the absorption coefficient. Employing the rotating wave approximation, the time dependence of \( \rho \) is given by the commutator relation

\[ i\hbar \frac{d\rho}{dt} = [H_0 - S - E\mu, \rho]. \quad (2.33) \]

The matrix elements of Eq. 2.33 are then

\[ i\hbar \langle a|\frac{d\rho}{dt}|b\rangle = E\langle a|\mu|b\rangle[\langle a|\rho|a\rangle - \langle b|\rho|b\rangle] - \hbar\Delta \omega \langle a|\rho|b\rangle \]

\[ i\hbar \langle a|\frac{d\rho}{dt}|a\rangle = -E\langle a|\mu|b\rangle\langle b|\rho|a\rangle + E\langle a|\rho|b\rangle\langle b|\mu|a\rangle \quad (2.34) \]

\[ i\hbar \langle b|\frac{d\rho}{dt}|b\rangle = -E\langle b|\mu|a\rangle\langle a|\rho|b\rangle + E\langle b|\rho|a\rangle\langle a|\mu|b\rangle \]

where \( \Delta \omega = \omega_0 - \omega \) and \( \omega_0 \) is the resonance frequency of the transition.
Applying the definitions

\[ P_r + iP_i = \langle b|\mu|a\rangle\langle a|\rho|b\rangle \]
\[ N_a = N\langle a|\rho|a\rangle \]
\[ N_b = N\langle b|\rho|b\rangle \]  \hspace{1cm} (2.35)

Eqs. 2.34 can be rewritten as

\[ \frac{dP_r}{dt} + \Delta \omega P_r = 0 \]
\[ \frac{dP_i}{dt} - \Delta \omega P_r + \kappa^2 E \left( \frac{\hbar \Delta N}{4} \right) = 0 \]  \hspace{1cm} (2.36)
\[ \frac{d}{dt} \left( \frac{\hbar \Delta N}{4} \right) - EP_r = 0 \]

where \( \kappa = 2\mu_{ul}/\hbar \) and \( \Delta N = N_a - N_b \). First order relaxation times are phenomenologically introduced into Eq. 2.36.

\[ \frac{dP_r}{dt} + \Delta \omega P_r + \frac{P_r}{T_2} = 0 \]
\[ \frac{dP_i}{dt} - \Delta \omega P_r + \kappa^2 E \left( \frac{\hbar \Delta N}{4} \right) + \frac{P_i}{T_2} = 0 \]  \hspace{1cm} (2.37)
\[ \frac{d}{dt} \left( \frac{\hbar \Delta N}{4} \right) - EP_r + \frac{\hbar}{4} \left( \frac{\Delta N - \Delta N_0}{T_i} \right) = 0 \]

where \( T_2 \) is the characteristic relaxation of the bulk polarization and \( T_i \) is the relaxation time of the population, which includes collision-induced transitions within the two level system as well as transitions out of the two level system. The polarization (real or imaginary) has an equilibrium value of zero, and the equilibrium value of the population difference is \( \Delta N_0 \). Equations 2.37 are the optical Bloch equations for molecular two level systems. Note that
the steady state solution for \( P \) in Eq. 2.37, when plugged into Eq. 2.32, yields the steady state absorption coefficient for a power broadened line.

Solutions for \( P \), from Eq. 2.37 can be obtained analytically for the special cases of \( T_2 = T_1 \) or \( \Delta \omega = 0 \). Otherwise, numerical solutions to these coupled differential equations are required. In any case, it is possible to solve for the time dependent absorption coefficient by using Eq. 2.32, and thus data from single source transient absorption experiments can be analyzed in terms of \( T_1 \), \( T_2 \), and the radiation electric field amplitude \( E \).

Figure 2.8 shows an example of an on-resonance (\( \Delta \omega = 0 \)) solution for \( P \), where we have chosen \( T_1 = T_2 \) (typical of many ambient experiments, as discussed below) and \( \kappa E \gg 1/T_2 \) (the saturation condition). For this example calculation, the coherent radiation is switched on at \( t = 0 \) and off at \( t = \tau \). After the radiation is switched on, the polarization increases immediately and then behaves as a decaying sinusoid until a steady state is reached. This sinusoidal behavior corresponds to the radiation source coherently driving population transitions between the two levels at the Rabi frequency \( \Omega = \kappa E \). The Rabi frequency oscillations are damped by the \( T_1 \) and \( T_2 \) constants, and \( P \) eventually reaches a steady state. For \( t > \tau \), Eqs. 2.37 are uncoupled and \( P \) decays to its initial equilibrium value \( (P_i = 0) \) at a rate of \( 1/T_1 \).

The parameters \( T_2 \) and \( T_1 \), can be independently measured in single microwave source experiments using the techniques of transient absorption, transient emission, or \( \pi \) and \( \pi/2 \) pulse sequences. Instead of switching the microwave power on and off, these experiments typically involve applying pulsed Stark fields which switch a rotational transition into and out of resonance with a microwave frequency. For most molecules at room temperature, it has been shown from these experiments that \( T_2 = T_1 \). The quantity \( 1/T_1 \) is the total depopulation rate of a two level system, and \( 1/T_2 \) is the pressure broadening halfwidth. Therefore, it is not surprising that \( T_2 = T_1 \) at ambient temperatures, because, again, the broadening halfwidth is equal to the sum of inelastic rates out of the
Figure 2.8. An example of the time dependent behavior of $P$, under the influence of a powerful radiation field $E$ switched on at $t=0$ and off at $t=\tau$. 
two levels in a transition (total depopulation), as predicted by Eq. 2.9. The equality of $T_e$ and $T_f$ for most ambient solutions is one of the important conclusions of these transient single source experiments.

2.3 The Collisional Cooling Technique

At ambient temperatures, the experiments described above can be performed in standard equilibrium absorption cells because most of the molecular gases of interest have sufficient vapor pressure. However, at low temperature (<100 K), most molecular species have insufficient vapor pressure for spectroscopic studies in an equilibrium cell. A technique such as free expansion in a jet can be employed for certain types of low temperature experiments (e.g. for observing short lived species or dimers), but the gas sample does not have a well-defined temperature or pressure, which is desirable for collision studies. However, the collisional cooling technique, developed by Messer and De Lucia, is well suited for spectroscopic investigations of collisions because a low temperature, quasi-equilibrium gas sample can be prepared in which temperature and pressure are well-defined and measurable. Liquid nitrogen cooled collisional cooling cells have been previously used for spectral simplification and pressure broadening. Liquid helium cooled cells have been used for spectral simplification, translational temperature characterization, laboratory maser studies, and ion and neutral species pressure broadening.

The general operation of a collisional cooling cell is shown schematically in Fig. 2.9. A copper cell is cryogenically cooled to temperatures below which a sample gas has significant vapor pressure, and the cell is filled with a non-condensable buffer gas. Sample gas molecules enter the cell through a thermally isolated injector tube which is heated to preclude freezing of the sample gas. The initially "hot" molecules collide with the buffer gas atoms or molecules and lose thermal energy. In approximately $10^3$ collisions (under
Figure 2.9. Schematic representation of the collisional cooling process. Sample gas molecules are denoted by black circles, and buffer gas molecules are denoted by open circles. A typical collisional path for a sample molecule is shown.
typical conditions), the sample molecules have "collisionally cooled" to the temperature of the buffer gas. The sample molecules then random walk through the cell, eventually making contact with, and condensing on, the cell walls. For typical cell geometries, a sample molecule will undergo approximately $10^4$ collisions before reaching either the cell walls or the radiation path, insuring that the sample has adequately thermalized before being spectroscopically probed. A constant flow of sample molecules is required to maintain a quasi-equilibrium sample in the cell. Low flow rates of sample molecules are used so that very dilute mixtures of sample and buffer gases ($1:10^4-10^5$) are maintained and the sample gas does not significantly heat the buffer gas.

The collisional cooling technique has been particularly applicable in studies of the temperature dependence of pressure broadening and line shift over a temperature range from 1 to 600 K. These measurements demonstrate the transition from the ambient "action at a distance" temperature regime to the low temperature regime characterized by the resonant formation of quasibound complexes. Figure 2.10 shows examples of experimental pressure broadening and line shift cross sections as a function of temperature for the CO-He collision system. The top graph shows broadening cross sections and the bottom graph shows line shift cross sections for the $J=1\leftarrow 0$ transition of CO. In the ambient regime ($T>100$ K), the broadening cross sections are relatively constant in temperature, as predicted by the semiclassical Anderson theory. Below 100 K, the broadening cross sections increase as the result of the onset of quasibound complex formation. The line shift cross sections are zero (to within experimental uncertainty) above 20 K, while below 20 K the cross sections increase and are positive. The rapid increase of these cross sections are also attributed to the formation of quasibound complexes.

Figure 2.10 also shows the best available theoretical predictions for the same cross sections. These cross sections were calculated by the MOLSCAT quantum scattering code using the CO-He PES of Le Roy et al., and the resultant energy dependent
Figure 2.10. Graphs of the $J=1\leftarrow 0$ pressure broadening cross section (top) and line shift cross section (bottom) vs temperature for the CO-He collision system. Experimental values are from Beaky et al.\textsuperscript{24} and the theoretical predictions are calculated from the PES by Le Roy et al.\textsuperscript{23}
cross sections were thermally averaged by use of Eq. 2.17 to attain the temperature dependence. The theory agrees well with the experimental cross sections at ambient temperatures, but at low temperatures ($T<30$ K) there are significant differences between the predicted and measured cross sections. While the qualitative tendencies are consistent, it is clear that either the theory or experiment (or both) yield slightly incorrect cross sections. In either case, these experimental results demonstrate that the collisional cooling and low temperature pressure broadening measurements are useful tools for verifying the validity of PESs and the quantum scattering theory itself.

2.4 Motivation for Low Temperature Double Resonance Experiments

The comparison in Fig. 2.10 of the experimentally measured and theoretically predicted CO-He pressure broadening and line shift cross sections illustrates that our understanding of low temperature collisions is still incomplete. While the experimental values could be incorrect, it is more likely that either the PES does not completely characterize the CO-He system, or that the low temperature formulation of pressure broadening cross sections is in error. Quantum scattering calculations are very sensitive to the details of the PES, and low temperature broadening is far more susceptible to elastic collisions than that at ambient temperatures. Experimental measurements of low temperature inelastic cross sections would provide a much needed independent check of both the quality of PESs and the validity of the underlying quantum scattering theory.

To measure low temperature inelastic cross sections, the techniques of time resolved double resonance and collisional cooling are combined. At low temperatures, only the lowest rotational states in the ground vibrational state are significantly populated. Therefore a millimeter wave pump is effective in radiatively transferring population because $h\nu \geq kT$ for $T=4$ K. The probe absorption signals are much stronger than those in ambient microwave double resonance experiments both because population differences are typically
large, and the rotational partition function is small at low temperatures (see Eq. 2.20). Time resolved techniques enable the direct measurement of inelastic collision rates, assuming proper use of the optical Bloch equations (Eq. 2.37) or the Master equation (Eq. 2.24) where relevant. These rates are converted to cross sections by

$$k_{jj'} = n\bar{v}\sigma_{jj'}$$

(2.38)

where $k_{jj'}$ is the rate of collision-induced $J \rightarrow J'$ transitions, $n$ is the number density of molecules, $\bar{v}$ is the average relative velocity, and $\sigma_{jj'}$ is the inelastic cross section.

A practical motivation for the measurement of low temperature inelastic cross sections is for the analysis of molecular rotational lines measured by radio telescopes. Large interstellar clouds exist at temperatures between 10 and 100 K. These clouds are generally not in local thermodynamic equilibrium because inelastic collisions can collisionally pump rotational population into excited states. Molecular densities within interstellar clouds are so small that collisions typically occur at a slower rate than the spontaneous emission rate such that radiative rates dominate and most molecules are observed in emission. Accurate experimentally determined inelastic rates are needed to more precisely determine the densities of molecules in the interstellar clouds. Some interstellar molecules, because of vibrational relaxation or collisional pumping, can achieve population inversion and thus interstellar masers are observed for some molecules. Also, some interstellar molecules (i.e. H$_2$CO) are observed in anomalous absorption against the cosmic background, because inelastic collisions through preferred channels yield population distributions lower than the 3 K microwave background. A detailed study of low temperature inelastic collision processes will enable better understanding of these interstellar processes.
References


CHAPTER 3

EXPERIMENTAL APPARATUS

In the following sections, the experimental apparatus for three distinct spectroscopic systems are described, and the results of the experiments are presented in the following chapters. For pressure broadening measurements between 77 and 600 K, we use a yttrium iron garnet (YIG) oscillator/travelling wave tube (TWT) based millimeter wave system with liquid nitrogen (LN$_2$) cooled and electrically heated cells. For pressure broadening and double resonance at lower temperatures, we use a klystron based millimeter wave system with a liquid helium (LHe) cooled collisional cooling cell. The pump for the double resonance experiments is a backward wave oscillator (BWO) synthesizer. Details of all the apparatus appear below. In some cases, existing systems which have been previously described in detail elsewhere are summarized, with attention paid to those parts which were modified for the present investigations.

3.1 Millimeter Wave Systems

3.1.1 Radiation Sources

The experiments presented in this dissertation used three different microwave/millimeter wave sources: a YIG oscillator with TWT, klystrons, and BWOs. Each source was frequency stabilized by a phase locked loop (PLL), and radiation was quasi-optically propagated through a spectroscopic cell and into a detector. The klystron and YIG systems employ crossed waveguide harmonic generators to achieve the desired
millimeter wave frequency. While these systems are operated in fundamentally the same manner, the details of their operation vary.

The klystron based millimeter wave system uses two different OKI klystrons, depending on the frequency range of interest. A klystron oscillates by first generating a beam of electrons, which are bunched by the oscillating electric fields inside the cavity. This bunched beam is reflected back into the cavity by a negatively charged electrode (reflector), adding more energy to the cavity. The microwave radiation generated in the cavity is coupled out by waveguide. We use an OKI 35V11 klystron tube to cover the 32-37 GHz range (200-400 mW of power) and an OKI 40V12 tube to cover 37-42 GHz (300-500 mW). Both tubes are mounted on a rectangular RG-96 (or WR-28) waveguide system. A Power Designs 1570 high voltage DC power supply (~1 mV of ripple) provides the necessary high voltage to the klystron (-1800 or -2300 V on the cathode, >-500 V on the reflector) and a Power Designs 6050C DC power supply provides 6.3 V (0.54 A) to the filament.

The output frequency of the klystron is stabilized by a PLL to within 100-1000 Hz as shown in Fig. 3.1. A small amount of klystron power is transferred by a 20 dB crossed waveguide coupler into a side waveguide arm and mixed with a stabilized reference frequency offset from the desired klystron frequency by 30 MHz. The beat note of the mixed frequencies is compared to the 30 MHz internal oscillator in a Micro-Now 211CS stabilizer. The stabilizer applies a correction voltage to the klystron reflector, which is proportional to the phase offset of the beat note and the internal oscillator. The Micro-Now stabilizer bandwidth is sufficient to overcome typical klystron temperature and power supply fluctuations and can keep up with a several MHz sweep of the klystron frequency at a 60 Hz rate.

The sequence for generating the stabilized reference frequency is shown schematically in Fig. 3.1. The output frequency ($f_{up}$) of a Hewlett Packard 3325A
Figure 3.1. Block diagram of the PLL which stabilizes the klystron output frequency.
synthesizer (0-20 MHz, 1 mHz resolution) is mixed with a 100 MHz standard based on the WWVB signal. The upper sideband (100+\(f_{\text{kip}}\) MHz) is selected by a high pass filter and amplified by a Boonton 130A RF amplifier. An integer multiple, \(m\), of the output frequency of the Boonton 130A serves as the reference of a Miteq PLC-019-023A-0-15P phase locked oscillator (1.9-2.3 GHz). An integer multiple, \(n\), of the Miteq oscillator frequency is the stabilized reference frequency, which is mixed with the klystron radiation on a Sylvania 1N26 crystal. The reference frequency is set by the frequency of the HP3325A, such that

\[
f_{\text{klystron}} = 30 + n(m(f_{\text{kip}} + 100))
\]  

(3.1)

where \(f_{\text{klystron}}\) is the desired klystron frequency (in MHz).

To generate the desired millimeter wave frequencies from the stabilized klystron, we employ a crossed waveguide harmonic generator (or multiplier),\(^1\)\(^2\) the output of which is all integer multiples of the klystron frequency. A detailed recipe for the preparation of these multipliers has been prepared by Pearson,\(^3\) so only a short summary is presented here. The multiplier housings were machined in the Main Machine Shop at the Ohio State University Department of Physics, and each has a rectangular input waveguide, which connects to the klystron system, and an output waveguide, which connects to a circular horn for Gaussian mode propagation of the resultant millimeter waves. The fundamental klystron radiation is matched onto a 0.002" diameter tungsten wire (or "cat whisker"), as shown in Fig. 3.2. The cat whisker forms a non-linear point contact diode with a silicon crystal in the smaller, output waveguide, and integer multiples of the fundamental klystron frequency are generated. The dimensions of the output waveguide are chosen such that only those frequencies above the waveguide cutoff are passed. The output power of the millimeter wave output decreases with increasing harmonic, and the power in the multiplied
Figure 3.2. The internal structure of a crossed waveguide harmonic generator.
frequencies depends on the quality of the point contact between cat whisker and Si crystal, the depth of the cat whisker and crystal holders into each waveguide, and the amount of forward or backward bias current applied to the diode.

Another millimeter wave system used in our experiments is based on a Microsource MS01015-257-01 solid state YIG oscillator, which produces frequencies in the 10-15 GHz range at ~100 mW power and is voltage tunable by a 0-10 VDC power supply. The output frequency of the YIG oscillator is stabilized in a similar manner as the klystron system described above, with minor differences, as shown in Fig. 3.3. The output frequency of an HP3325A is again mixed with a 100 MHz standard, and the lower side band is selected by a low pass filter. This frequency is then the reference for a 500-525 MHz Miteq PLO-.500-.525-A-O-15P phase locked oscillator, and an integer multiple of the output frequency is mixed with the YIG oscillator frequency on a 1N23 crystal mixer. A 30 MHz beat note is compared to the internal 30 MHz oscillator in a Micro-Now 211CS stabilizer, which applies a small correction voltage to the YIG oscillator to stabilize its output frequency.

To generate millimeter waves, the output frequency of the YIG oscillator is first multiplied by a Honeywell tripler and then fed, via rectangular waveguide, into a Hughes 1077H traveling wave tube amplifier (TWTA). This particular TWTA covers a frequency range of 30-40 GHz with output power of 1-4 W. Inside the TWTA, the tripled YIG oscillator frequency bunches an electron beam, which radiates amplified power as the beam traverses a helical waveguide structure. The output of the TWTA is then matched onto a crossed waveguide harmonic generator of the same type described above.

A third millimeter wave source used for our experiments is a Russian-made KVARZ millimeter wave synthesizer, which is based on a BWO tube. Inside the BWO, an electron beam is generated and passed over a "slow wave" structure. The beam is bunched by the periodic field that it sees, and millimeter wave gain occurs at a single frequency. The KVARZ synthesizer employs a PLL referenced to an internal 5 MHz crystal oscillator,
Figure 3.3. Block diagram of the PLL which stabilizes the YIG oscillator output frequency.
and millimeter wave radiation is coupled out into WR-6 rectangular waveguide. The synthesizer covers a frequency range of 118.1-178.4 GHz with typical frequency resolution of 100 Hz and output power between 3-10 mW.

3.1.2 Waveguide Switches

As mentioned in section 2.2.2 above, time resolved double resonance experiments require that the sample molecules undergo time dependent resonant absorption of the pump radiation. This time dependent pump absorption is realized in three possible ways. Either the rotational transition can be shifted into resonance with a fixed frequency pump, the pump frequency can be shifted into resonance with the transition, or the pump power can be turned on and off while tuned to resonance. In each case, the most important factor is that the time duration of the change is very short compared to the collision processes to be measured.

The three possibilities for introducing a time dependent pump absorption are discussed below. First, the resonance frequency of the rotational transition can be shifted into or out of coincidence with a fixed frequency pump source. This is generally accomplished via the Stark effect as described in section 2.2.3 for previous transient absorption experiments. Given the small geometries of our liquid helium cooled collisional cooling cell, and the difficulties associated with maintaining a low temperature cell, this method was deemed too inconvenient. Second, the frequency of the millimeter wave source can be modulated by a square wave or pulse into and out of coincidence with the rotational transition of the molecules. Very fast switching is possible with this method, but the bandwidths of the stabilizers in the PLLs cannot keep up with such sudden changes, and the millimeter wave frequencies would then oscillate for several microseconds until phase lock is again achieved. Third, the millimeter wave source can be locked to the molecular rotational transition frequency, and the power can be turned on and off by a
waveguide switch. This method has proved most convenient for our particular experimental systems.

A simple way to square wave amplitude modulate the output of the klystron system is by placing a PIN diode in the waveguide before the harmonic generator. When a TTL pulse is applied to the PIN diode, the diode becomes a short circuit across the waveguide and no microwaves pass through. The Alpha 979B01 PIN diode covers a frequency range of 33-50 GHz and has typical risetimes of approximately 100 ns, which is favorable for a klystron based pump source. This particular diode is simple to use, requiring only +5 V and -12 V DC voltages for proper bias.

Unfortunately, the PIN diode causes problems with the klystron frequency stabilization system. When the diode switches microwave power on or off, some power is reflected back into the klystron tube, which then destabilizes the frequency. The Micro-Now stabilizer has insufficient bandwidth to keep up with these fast frequency variations, and the klystron frequency temporarily jumps out of phase lock, requiring several microseconds to restabilize. Therefore, we could not use the PIN diode for a pump system, however it was very useful for detector bandwidth tests (described in section 3.2 below), which do not require the klystron to be phase locked. It is possible in the future to reduce the back reflection from the PIN diode into the klystron by employing waveguide isolators and/or additional attenuation.

At higher frequencies (~100 GHz), full band PIN diodes are extremely expensive, if available at all. However, less expensive, yet slower, ferrite modulators can work well for the KVARZ millimeter wave synthesizer. The PLL in the synthesizer has more bandwidth than the Micro-Now stabilizer, and the frequency deviations from back reflections into the BWO tube are more quickly counteracted. A ferrite modulator works by Faraday rotation of the linear polarization of the BWO output. The millimeter waves pass, via waveguide, into a ferrite core which is surrounded by a coil of wire for generating a
magnetic field. The output waveguide of the modulator is oriented 45° relative to the input waveguide, as shown in Fig. 3.4. When current flows through the coil in one direction, the magnetic field causes the millimeter wave polarization to rotate 45° into coincidence with the output waveguide, and maximum power is transmitted. If current flows in the opposite direction, the millimeter wave polarization is rotated out of coincidence with the output waveguide, and minimum power is transmitted.

We use a Millitech FBM-06 fullband ferrite modulator (110-170 GHz) in the output waveguide of the KVARZ synthesizer. The FBM-06 has factory specifications of 3 μs risetime and 31 dB on/off ratio. The modulator requires approximately ±0.25 A to switch on and off, and this current is generated by a push-pull circuit, shown schematically in Fig. 3.5, which was developed and constructed by the Electronics Shop at the Ohio State University Department of Physics. For the first diagnostic tests of the modulator, V₀ was generated by 5 V DC power supplies, as suggested by Millitech, and resistor values were chosen accordingly. It was quickly determined that the 3 μs risetime specification was incorrect (we measured 16 μs) due to a 66 μH induction in the coil, rather than the specified 15 μH. Since an \( RL \) circuit time response is determined by

\[
I(t) = \frac{V_0}{R_1} \exp\left(-\frac{R_1}{L} t\right)
\]  

(3.2)

where \( V_0 \) and \( R_1 \) are shown in Fig. 3.5 and \( L \) is the coil inductance, we could overcome the inductance limitation by increasing \( R_1 \) from 2 to 100 Ω and increasing \( V_0 \) from 5 to 50 V. The ferrite modulator risetime, following these modifications, was measured to be less than 1 μs. Accurate measurements could not be performed because of detection bandwidth limitations, however risetimes of less than 1 μs are sufficient for these low temperature double resonance studies.
Figure 3.4. Faraday rotation of the millimeter wave polarization inside the core of a ferrite modulator. Arrows represent linear polarization vectors.
Figure 3.5. Schematic diagram of the ferrite modulator driver circuit.
3.1.3 Quasi-Optical Propagation

Because waveguide dimensions for frequencies above 100 GHz are inconveniently small and have relatively high loss, the millimeter waves in our experiments are propagated quasi-optically through a spectroscopic cell and into a detector. Because of the large impedance mismatch between waveguide and free space, we use tapered, circular horns to couple millimeter waves into free space. Similar horns are used to collect the radiation from free space and direct it toward a detector element. These horns have 7° or 10° tapers, and the diverging radiation is collimated by TPX or teflon lenses for propagation through the cell.

For the pressure broadening studies presented in Chapter 4, the cell windows are large (4” diameter) compared to typical wavelengths, and diffraction of the millimeter waves is negligible. For the LHe cooled collisional cooling cell, the windows are necessarily small (0.5” diameter), and diffraction by the windows can be significant and must be minimized. Therefore, the windows of the outer isolation vacuum jacket are TPX lenses (19 cm focal length) which focus the millimeter wave beam to the center of the cell. Figure 3.6 shows an overview of the quasi-optical propagation through the liquid helium cooled system. Additionally, because stray reflections inside the copper collisional cooling cell can lead to asymmetric lineshapes in pressure broadening studies, the inside of the cell is lined with Eccosorb, a 0.25” thick microwave absorbing material.

In order to co-propagate the millimeter wave pump and probe radiation through the LHe cooled system, the highly linear polarization of each source is exploited. The KVARZ BWO synthesizer and the klystron system emit vertically polarized radiation. As shown in Fig. 3.7, the polarization of the BWO radiation is rotated 90° by a periscope. A simple wire grid polarizer, oriented like a beamsplitter, is then used to co-propagate the two beams, where the vertically polarized klystron radiation passes through the polarizer and the horizontally polarized BWO radiation reflects off of the polarizer.
Figure 3.6. Quasi-optical propagation of the frequency multiplied klystron radiation through the liquid helium cooled cell using horns and lenses.
Figure 3.7. Quasi-optical co-propagation of the klystron and BWO synthesizer radiation using a wire polarizer.
The wire grid polarizers were manufactured by Dr. Wei Guo at Ohio State University out of 0.003" diameter copper or stainless steel wire at a spacing of 0.018". The polarizer passes those components of the millimeter wave polarization which are perpendicular to the orientation of the wire grid, and it reflects components which are parallel to the grid. The ideal dependence of the transmitted power on the relative angle of the polarizer is given by

\[
\frac{P}{P_0} = \sin^2 \theta
\]

where \( P \) is the transmitted power, \( P_0 \) is the incident power, and \( \theta \) is the angle between the direction of the wires and the polarization vector of the radiation. The measured fractional transmitted power as a function of angle is shown in Fig.3.8. It is clear that the curve qualitatively agrees with Eq. 3.3, but that the extrema do not reach one or zero. The wires in the grids are not perfect conductors, and some power can be absorbed. Additionally, the wires in the grid can be inconsistently spaced, which leads to more transmitted power.

3.1.4 Millimeter Wave Filters

When performing a double resonance experiment, it is crucial to prevent as much of the pump radiation as possible from entering the detector and hindering measurements of the probe power. Often, the probe absorption signal is quite weak, and residual pump power on the detector can overwhelm this small signal. Several strategies can be employed to prevent pump radiation from entering the detector, including the use of tuned cavities, dichroic filters, or capacitive grids.\(^5\)\(^6\) The most convenient methods for these initial double resonance experiments was the use of dichroic filters and wire polarizers.
Figure 3.8. Measured fractional transmitted power vs polarizer angle relative to the linear polarization direction of the millimeter wave radiation.
For cases when the pump frequency is greater than or equal to the probe frequency, the majority of the pump power can be reflected away from the detector by wire grid polarizers similar to those used to co-propagate the pump and probe beams. Unfortunately, as shown in Fig. 3.8, the wire grid polarizers always allow some of the pump power (a few percent) to pass through. This is due both to small horizontal polarization components in the radiation as well as imperfections in the polarizers. For the H₂S experiments presented in Chapter 6, when pumping and probing at the same frequency, the residual pump power incident on the detector was not a problem both because the pump was 95% attenuated and because the probe signals were very large. However, in the NO experiments of Chapter 7, a class of experiments could not be performed because the residual pump signal was much larger than the probe signals.

For cases when the pump frequency is less than the probe frequency, the pump power can be very efficiently prevented from entering the detector by use of dichroic filters. A millimeter wave dichroic filter is a metal plate with many tiny, circular holes, which act as small waveguides. The pump radiation is reflected from the dichroic if the frequency is below the circular waveguide cutoff frequency, given by

\[ f_c = \frac{\lambda_{mn}c}{2\pi r} \]  

(3.4)

where \( \lambda_{mn} \) is the \( n^{th} \) zero of the first derivative of the \( J_n(x) \) Bessel function and \( r \) is the waveguide radius. For the dominant \( TE_{11} \) mode, \( \lambda_{mn} = 1.841 \), and \( f_c \) (in GHz) is then given by

\[ f_c = \frac{87.84}{r} \]  

(3.5)

where \( r \) is in millimeters. The attenuation coefficient, \( \alpha \), is defined by
\[ \alpha = \frac{2\pi}{c} \sqrt{f_i^2 - f_s^2} \]  

(3.6)

where \( f \) is the frequency of the pump. To determine the attenuation of pump power in dB, we first employ

\[ \frac{P}{P_0} = e^{-\alpha x} \]  

(3.7)

where \( P \) is the transmitted power, \( P_0 \) is the incident power, and \( x \) is the thickness of the dichroic filter, and then

\[ \text{Attenuation(dB)} = -10(\log_{10} e)\alpha x. \]  

(3.8)

A series of six aluminum dichroic filters, shown schematically in Fig. 3.9, were constructed by the Main Machine Shop at the Ohio State University Department of Physics. The filters are 0.25" thick, and the holes are drilled 0.0005" apart in a 5/8" to 1" square pattern (the number of holes ranges from 200 to 500). Table 3.1 shows the hole diameters and predicted cutoff frequencies (from Eq. 3.5) for the six filters, and Fig. 3.10 shows the predicted attenuation vs frequency curves of each filter, as well as measured attenuation curves for three of the filters.

3.2 Millimeter Wave Detection and Signal Processing

The millimeter wave sources described above emit average output power on the order of 1-10,000 \( \mu W \), thus very sensitive detectors with low thermal noise are required. In addition, the time resolved measurements presented below require \( \sim 1 \text{ MHz} \) of bandwidth. Therefore, LHe cooled hot electron bolometers, which have sensitivity of
clearance holes for 4-40 bolts on a 2.12" diameter

small, drilled holes in a square pattern

Figure 3.9. Schematic drawing of a dichroic filter constructed for this study. The small holes are not drawn to scale.
Table 3.1. Predicted cutoff frequencies, as a function of hole diameter, for the six dichroic filters constructed for this study.
Figure 3.10. Predicted attenuation vs frequency curves (solid lines) for the six dichroic filters constructed for this study. Measured values for the filters with 126, 161, and 176 GHz cutoff frequencies are also shown (dashed lines).
~5 kV/W, thermal noise of ~0.5 pW/√Hz, and bandwidth of ~1 MHz were selected for these experiments. The detector element is an indium antimonide (InSb) chip from QMC Instruments, with electrical leads connected by indium solder. For the pressure broadening measurements of Chapter 4, the detector element is submerged in LHe inside a double glass dewar system. For all other measurements, the detector is mounted on a copper plate, which serves as the bottom of a metal LHe dewar, manufactured by Infrared Laboratories.

Millimeter wave radiation incident on the InSb chip increases the mobility of the free electrons, thereby changing the resistance of the chip. Approximately 30 μA of bias current is applied to the InSb chip, and thus changes in the incident millimeter wave power are measured as a change in voltage across the detector element.

Since the time resolved double resonance experiments require as much bandwidth as possible, care must be taken in reducing the RC time constant in the detector leads. At 4.2 K, the InSb chip has a resistance of approximately 8 kΩ, therefore capacitance in the leads on the order of 100 pF can reduce bandwidth below the desired 1 MHz. Typically, the leads are heat sunk to the 4.2 K copper plate inside the metal dewar to prevent thermal conduction from 300 K to the InSb chip. Unfortunately, such heat sinking schemes add a great deal of capacitance to the circuit. We reconnected the leads directly to the detector without heat sinking to reduce capacitance, and we found that detector sensitivity and noise were not adversely affected. We measure approximately 20 pF of capacitance, which yields an RC time constant of ~0.2 μs, quite sufficient for a detector element with 1 MHz bandwidth.

Detector signals can be as small as 0.5 μV, and the output impedance is ~8 kΩ. Therefore, a low-noise preamplifier is used both to amplify the weak signals and to drive 50 Ω coaxial cables. For the pressure broadening measurements in Chapter 4, an EG&G Ortec 5004 preamplifier with a voltage gain of 1000 and 1 MHz bandwidth was used. For the measurements in Chapters 5 and 6, we used a QMC ULN 95 preamplifier with a
selectable gain of 100 or 1000 and bandwidth of 1 MHz. For the measurements in Chapter 7, we modified a QMC ULN 30 preamplifier by adding a unity gain operational amplifier at the input stage to prevent the internal capacitance of the preamplifier circuit from further degrading the bandwidth. We achieved ~3 MHz bandwidth with the modified ULN 30, and the measured amplification vs frequency curve for this preamplifier, before and after the modification, is shown in Fig. 3.11. Additional amplification for the Ortec 5004 was provided by an EG&G PARC 113 roll off amplifier, and additional amplification for the QMC preamps was provided by a Stanford Research Systems SR560 roll off amplifier. For pressure broadening studies, the high frequency roll off was set to 10 or 30 kHz, and for double resonance, the maximum 1 MHz setting was used.

The amplified detector signals are read into an Apple Macintosh desktop computer in several ways. First, for all pressure broadening measurements, we used a National Instruments NB-MIO-16 multifunction I/O board (12-bit resolution, 100 kS/s) to digitize the lineshapes. For the time resolved double resonance experiments of Chapters 5 and 6, we used a National Instruments NB-A2000 high speed analog board (12-bit resolution, 1 MS/s) to digitize the probe signal. For both acquisition boards, signal averaging was performed in the controlling software, either a FORTRAN routine by Dr. William Ebenstein (Chapter 4) or virtual instruments in the LabVIEW programming environment (all others). For the double resonance measurements in Chapter 7, we used a combination of modules in a CAMAC rack for data acquisition. A Transiac 2001S transient recorder (8-bit resolution, up to 100 MS/s) digitized the probe signal and a Transiac 4100 averaging memory performed the signal averaging. The data was then transferred to the computer over the General Purpose Interface Bus (GPIB) by a Le Croy 8901 GPIB interface. Operation of the CAMAC rack was controlled by LabVIEW virtual instruments, and commands were transmitted across GPIB.
Figure 3.11. Measured amplification vs frequency curves (60 dB gain setting) for the QMC ULN 30 preamplifier before (open circles) and after (solid squares) modification of the input stage.
3.3 Spectroscopic Cells

In the pressure broadening studies of Chapter 4, a traditional equilibrium cell was used for temperatures at which the sample gas (H₂S or SO₂) has sufficient vapor pressure for spectroscopic measurements. The cell, shown in Fig. 3.12, is a 2 foot long, 2” diameter quartz tube with fused quartz windows inside a 4 foot long copper jacket. The whole assembly is wrapped in fiberglass insulation for thermal isolation. The copper jacket, and thus the cell, can be heated by resistive heating tape using a Variac variable AC transformer. Copper tubing (3/8” outer diameter) is coiled around the jacket, and LN₂ can be flowed through this tubing to cool the cell down to ~100 K. An Omega CN2001 temperature controller maintains the cell temperature by opening a solenoid valve on a LN₂ dewar when the cell temperature rises above a programmable set point. Temperatures are measured by two chromel-alumel thermocouples (one at the end of the copper jacket and one at the middle) which are soldered to small copper blocks held tightly to the copper jacket by hose clamps. A Fluke 77 multimeter reads the thermocouple voltages to within 0.1 mV, which gives a typical temperature resolution of 3-5 K. The cell pressure is measured by an MKS capacitance manometer, and the cell pressure is varied by introducing gas through a computer controlled solenoid valve.

For the same pressure broadening studies, a new LN₂-cooled collisional cooling cell was constructed for measurements at temperatures below which the sample molecules have measurable vapor pressure. Originally, the cell was designed to fit into a sample compartment of a Bruker IFS 120 HR Fourier transform infrared spectrometer, thus a similarly sized rectangular isolation vacuum chamber, shown in Fig. 3.13, was constructed for this system. Five 1/2” thick stainless steel plates were welded together as a box, and two 4” diameter teflon windows were installed along the millimeter wave beam path. An o-ring groove was milled into the top of the vacuum chamber, on which sits a 3/8” thick stainless steel top plate.
Figure 3.12. The equilibrium cell used for pressure broadening measurements.
The collisional cooling cell, shown in Fig. 3.14, is a 9.5" long section of 4.125"
outer diameter copper water pipe, which is suspended 5" below the stainless steel top plate
by a 1.5" stainless steel injector tube inlet and a 1" stainless steel buffer gas and pump out
line. At each end of the copper pipe, 0.005" thick mylar windows are held in place by
brass flanges, and a vacuum seal is achieved by crushed indium wire. Sections of 3/8"
outer diameter copper tubing are soldered along the sides of the cell and out through the top
plate to conduct LN$_2$ for cooling. Two chromel-alumel thermocouples (one toward one end
of the cell and one at the center) are mounted for monitoring the cell temperature, which is
again maintained by an Omega CN2001 temperature controller. Buffer gas is introduced
into the cell by a computer controlled solenoid valve, and the cell pressure is measured by
an MKS capacitance manometer.

The injector tube for this collisional cooling system is shown in Fig. 3.15. A 15"
length of 1" outer diameter stainless steel tubing forms a vacuum jacket for a heated 1/8"
diameter aluminum injector line. The length of this aluminum tube is wrapped with two
sections of teflon coated copper wire, which can independently heat sections of the injector
tube. A smaller 0.032" outer diameter stainless steel tube is connected to the outlet of the
aluminum tube by Stycast 2850 epoxy. Electrical current is flowed through the walls of the
stainless steel tube for additional heating, and the tube is bent back toward the aluminum
tube for the current return. A small hole is nicked into the side of the stainless steel tubing
near the bend, and this is where the sample molecules enter the cell. The bent stainless
steel tubing protrudes through a 0.005" thick mylar sheet, and a vacuum seal is achieved by
use of Armstrong A12 epoxy. The mylar is also sealed to outer stainless steel vacuum
jacket by the A12 epoxy, which serves to thermally isolate the outer jacket from the warm
injector tube. Three chromel-alumel thermocouples monitor the injector temperature at
different positions, as shown in Fig. 3.15. All thermocouple and heater wires pass
through the top of the injector assembly through 1/8" outer diameter stainless steel tubes.
Figure 3.13. The isolation vacuum chamber for the liquid nitrogen cooled collisional cooling system.
Figure 3.14. The liquid nitrogen cooled collisional cooling cell.
Figure 3.15. Injector assembly for the liquid nitrogen cooled collisional cooling cell.
and these electrical feedthroughs are vacuum sealed by Hardman gap-filling epoxy. The
injector tube is inserted into the cell through the 1.5” outer diameter stainless steel port and
vacuum sealed above the top plate by a 1” Cajon Ultra-Torr fitting.

For the experiments presented in Chapters 5-7, a LHe cooled collisional cooling cell
was used. The details of this system are discussed elsewhere\(^7\), and since the current
studies required no modifications, only the main points are summarized. This system was
initially designed for low temperature pressure broadening measurements by Dr. J. Jerome
Holton\(^8\) and was significantly modified by Dr. Matthew Beaky.\(^7\) The collisional cooling
cell is mounted inside a 40 cm diameter anodized aluminum isolation vacuum jacket, shown
in Fig. 3.16. Also inside the vacuum jacket is a 5 L LN\(_2\) reservoir and a 6.5 L LHe
reservoir, each of which is thermally connected to a heat shield which surrounds the cell.
These heat shields reduce the radiative heating of the cell by room temperature blackbody
radiation. All vacuum environments in this system are evacuated by combinations of
diffusion and mechanical pumps.

The temperature of the cell is controlled by filling a small (200 mL) reservoir, called
the pot, with LHe. The cell and pot system is shown in Fig. 3.17 and is constructed from
a single piece of oxygen free high conductivity copper. Two fill lines connect the 6.5 L
LHe reservoir to the pot, either a quick fill line for rapid cool down or a continuous fill line
which leaks small amounts of LHe into the pot. To attain temperatures below 4.2 K, the
LHe in the pot can be pumped on by a Stokes pump, and the lowest temperature this
system has reached is 1.19 K. For temperatures above 4.2 K, a feedback loop is employed
in which either cold He vapor or simple thermal conduction cool the cell and a resistive
heater warms it. A Spectra Physics SP5720 cryogenic stabilizer controls the feedback
loop. The temperature of the cell/pot assembly is measured by a Lake Shore 820 cryogenic
thermometer, which performs 4-lead resistance measurements of two germanium resistors
located inside the pot.
Buffer Gas Line  
Pot Pumping Line  

LN\textsubscript{2} Reservoir  
LHe Reservoir  
Vacuum Jacket  
Continuous LHe Fill Line  
Sample Gas Injector  
4K and 77K Heat Shields  

Figure 3.16. Composite sketch of the liquid helium cooled collisional cooling system.
Figure 3.17. Close up of the collisional cooling cell and liquid helium pot.
Figure 3.18. Injector assembly for the liquid helium cooled collisional cooling cell.
The collisional cooling cell has an interior diameter of 2.75" and depth of 1.75". and has two 0.010" thick, 1/2" diameter mylar windows sealed to the cell by crushed indium wire. The heated injector assembly is shown in Fig. 3.18. Unlike the injector mentioned above, this injector is mounted directly to the surface of the cell, and is thermally isolated from the cell by 0.010" thick mylar. The mylar is epoxied to the injector tube by Armstrong A12, and an indium gasket is used to seal the mylar to the cell. The tip of the injector is 1/32" outer diameter copper-nickel needle tubing, and the heater wire and a single iron-constantan thermocouple are attached to a larger, conical copper piece. A computer controlled General Valve Series 9 solenoid valve is mounted on this copper piece to control the flow of sample gas into the cell. The valve was placed close to the injector tip to reduce the effects of buffer gas flow out through the injector during the experiment.

References
CHAPTER 4

VARIABLE TEMPERATURE PRESSURE BROADENING OF SO$_2$ AND H$_2$S

4.1 Introduction

4.1.1 Motivation

In Chapter 2, we introduced the relevance of the pressure broadening of rotational transitions to both the semiclassical theory of ambient collisions and the quantum theory of low temperature collisions. The temperature dependence of pressure broadening is one way to investigate the characterization of intermolecular potentials as well as the underlying fundamental collision theory. Unfortunately, the availability of experimental temperature dependent broadening parameters is generally lacking, and those measurements which have been reported typically cover only a small range of temperatures. Previous experiments by this research group have involved the measurement of pressure broadening parameters between 1 and 600 K, and the measurements of SO$_2$ and H$_2$S pressure broadening presented in this chapter are a continuation of this effort.

Besides the connection to fundamental collision theory, it is also important to measure pressure broadening parameters for a wide range of molecules and transitions to compare to other experimental efforts. The accuracy of many pressure broadening measurements was recently called into question in a paper by Gamache et al., which presented a survey of measured pressure broadening parameters of H$_2$O. They found that broadening parameters varied by as much as 10-15% between different laboratories, and they cited underestimation of experimental uncertainty as the cause. Pressure broadening...
measurements are quite complicated and difficult relative to standard energy level spectroscopy, requiring accurate pressure and temperature measurements and accurate characterization of instrumental sources of broadening. The significant instrumental linewidths and spectral overlap typical of infrared experiments is the main source of the variations presented by Gamache et al. In a later paper, Goyette et al.\textsuperscript{13} reported broadening parameter variations within 5\% for millimeter wave measurements of HNO\textsubscript{3} from two different laboratories using two different methods. The narrow-banded nature of millimeter wave sources translates to negligible instrumental linewidth, and narrower Doppler widths reduces the likelihood of spectral overlap. In any case, it is important to continue to compile precise broadening parameters to test the overall accuracy of pressure broadening methods.

In addition to these fundamental scientific issues, pressure broadening parameters are also necessary in the analysis of spectroscopic data from atmospheric remote sensing experiments, particularly satellite measurements. Accurate broadening parameters (<5 \% error) yield accurate mixing ratios of trace atmospheric constituents.\textsuperscript{14} SO\textsubscript{2} and H\textsubscript{2}S both play an important role in the chemistry of the Earth's atmosphere. These sulfur-based molecules are typically introduced into the atmosphere by the refinement and use of fossil fuels, as well as by natural sources such as volcanoes. Specifically, in 1991, the Microwave Limb Sounder (MLS) aboard the Upper Atmosphere Research Satellite measured a significant increase in the amount of SO\textsubscript{2} in the stratosphere following the eruption of Mt. Pinatubo.\textsuperscript{15} Early calculations of the mixing ratios of SO\textsubscript{2} from the MLS data relied only on a measured room temperature broadening parameter for a different transition of SO\textsubscript{2} than the one observed, broadened only by N\textsubscript{2}.\textsuperscript{16} Since our LN\textsubscript{2} cooled and electrically heated cells easily cover the atmospheric temperature range, we are able to measure both the N\textsubscript{2} and O\textsubscript{2} broadening parameters over a wide range of temperatures for the same transition of SO\textsubscript{2} observed by the MLS after the Mt. Pinatubo eruption. In
general, our measured temperature dependent broadening parameters are important for filling databases relied upon by remote sensing investigators.\textsuperscript{17}

4.1.2 Experimental Procedures

The YIG oscillator based millimeter wave spectrometer described in section 3.1 was used for the pressure broadening measurements between 90 and 600 K presented below. The system was operated in a "true lineshape" mode, where the millimeter wave frequency was swept rapidly through a rotational line. The detection bandwidth was sufficient to preserve all Fourier components of the lineshape. Baseline undulations, caused by reflections within the quasi-optical path, were also preserved by the detection bandwidth. These baseline effects were minimized by adjusting the millimeter wave optics for measurements using the equilibrium cell described in section 3.3. In collisional cooling measurements, the sample molecules freeze on the cell walls in \sim 10 \text{ ms}, and this rapid freezing permits a subtraction procedure which eliminates unwanted baseline effects. The flow of sample molecules is modulated at \sim 1 \text{ Hz}, and alternate sets of sweeps taken with sample present and absent were subtracted. Figure 4.1 shows examples of lineshapes acquired with and without the baseline subtraction technique.

A Voigt profile, which is the convolution of a Gaussian (Doppler broadened) lineshape and a Lorentzian (pressure broadened) lineshape, was fit to each digitized lineshape. This convolution takes the form of

\begin{equation}
V(v) = L(v) \otimes G(v) = \frac{\sqrt{\ln 2} \Delta v_L}{\pi^{1/2} \Delta v_D} \int_{-\infty}^{\infty} \exp \left[ -\ln 2 \left( \frac{\zeta - v_0}{\Delta v_D} \right) \right] \frac{\zeta}{(v - v_0 - \zeta)^2 + (\Delta v_L)^2} d\zeta \tag{4.1}
\end{equation}

where \Delta v_D is the Gaussian Doppler width, \Delta v_L is the Lorentzian pressure broadening width, and \nu_0 is the rotational transition frequency. Exploiting the convolution theorem and
Figure 4.1. Typical lineshapes for the $18_{3,15} \leftarrow 18_{2,16}$ transition of SO$_2$ for equilibrium (top graph) and for collisional cooling (bottom graph) measurements, where the baseline has been subtracted in the bottom graph.
Fast Fourier Transform methods, the Voigt profile can be quickly fit to experimental lineshape data by a desktop computer. Any baselines were fit by a combination of linear and quadratic functions.

With the LN$_2$ cooled collisional cooling cell and the equilibrium cell, broadening parameters can be measured between 90 and 600 K. At each temperature, 25 to 40 lineshapes were recorded over a pressure range from 10 to 150 mTorr for the collisional cooling cell and 10 to 500 mTorr for the equilibrium cell. The broadening gases used for these studies were H$_2$, He, N$_2$, and O$_2$. For equilibrium measurements, the cell was filled with less than 1 mTorr of sample so that self broadening components were reduced. Figure 4.2 shows a typical plot of pressure broadening halfwidths vs collision gas pressure, which exhibits a characteristic linear behavior given by

$$\Delta \nu_L = \gamma p,$$  \hspace{1cm} (4.2)

where the slope $\gamma$ is defined as the pressure broadening parameter, usually expressed in units of MHz/Torr, and $p$ is the pressure of the broadening gas. The pressure broadening cross section, $\sigma$, can be calculated from $\gamma$ by

$$\gamma = \frac{n\bar{v}\sigma}{2\pi}.$$  \hspace{1cm} (4.3)

where $n$ is the density of the broadening gas and $\bar{v}$ is the average relative velocity.

Employing the ideal gas law

$$p = nkT$$  \hspace{1cm} (4.4)

and the definition of $\bar{v}$,
Figure 4.2. Lorentzian halfwidths (solid circles) vs pressure for the $2_{2,0} \leftrightarrow 2_{1,1}$ transition of H$_2$S in collision with N$_2$ at 295 K. Also shown is the linear fit of the data (solid line).
\[ \bar{v} = \frac{8kT}{\pi \mu}. \]  

(4.5)

the cross section can be expressed as

\[ \sigma = 0.447 \sqrt{\mu T \gamma}. \]  

(4.6)

where \( \sigma \) is in \( \text{Å}^2 \) and \( \mu \) is in atomic mass units. Whether broadening parameters or cross sections is used in the literature depends strongly on which research community is interested in the results. Since the broadening data over the 90 to 600 K temperature range is of interest to the atmospheric remote sensing community, we present results in terms of broadening parameters.

The sources of error for the broadening parameters presented below are dominated by systematic effects. Statistical error can be lower than 2\% for much of the data, however we believe it necessary to conservatively estimate total systematic errors at 5\%. A potential major source of error involves the measurement of the cell pressure. When the temperature of the cell is different than the temperature at the manometer, thermal transpiration effects can become significant. Using a formula of Takaishi and Sensui, we found for the worst cases that the transpiration correction for typical cell pressures and temperatures is less than 3\%, and that broadening parameters are changed by less than 1\%. Therefore, for faster data reduction, we ignored transpiration effects for these broadening measurements.
4.2 Pressure Broadening of SO$_2$

Sulfur dioxide is a near prolate asymmetric rotor with rotational constants $A=60.778.79$, $B=10.318.10$, and $C=8799.96$ MHz.$^{19}$ Figure 4.3 shows the geometric structure of SO$_2$, which has a bond angle of 119.536° and bond lengths of 1.4321 Å.$^{20}$ Owing mostly to a dipole moment of 1.59 D and a favorable rotational partition function,$^{19}$ absorption coefficients for the two transitions studied ($^{18}_{1,15}$→$^{18}_{2,16}$ and $^{13}_{1,13}$→$^{12}_{0,12}$) are sufficiently strong for spectroscopic measurements over the 90 to 500 K temperature range. Above 500 K, absorptions are weak, and test data acquired at these high temperatures were unreliable. Gaseous SO$_2$ has enough vapor pressure for equilibrium measurements down to 165 K. Below 135 K, the collisional cooling technique is used. For the temperature gap between 135 and 165 K, neither the equilibrium or collisional cooling environments yield dependable results because of a build up of weak residual equilibrium lines which vary greatly in strength during the course of the measurements.

The SO$_2$ foreign gas (H$_2$, He, N$_2$, and O$_2$) broadening parameters, $\gamma$, for the two transitions are listed in Tables 4.1 and 4.2. Figures 4.4 and 4.5 display plots of these data vs temperature on a log-log scale. For both transitions, H$_2$ caused the largest broadening parameters, followed by N$_2$, O$_2$, and He. This is not surprising, given that H$_2$ molecules have relatively larger thermal velocities and larger quadrupole moments than the other broadening gas molecules.

Another salient feature of Figs 4.4 and 4.5 is that the temperature dependence of all the broadening parameters obey the power-law relation

$$\gamma(T) = \gamma(T_0) \left(\frac{T_0}{T}\right)^\alpha, \quad (4.7)$$

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Figure 4.3. Sketch of the geometric structure of SO₂.
Table 4.1. Measured pressure broadening parameters at various temperatures for the $18_{3,1S} \leftrightarrow 18_{2,1O}$ transition of SO₂. Absolute uncertainty is estimated at ±5%.

<table>
<thead>
<tr>
<th>Temperature (Kelvin)</th>
<th>$\gamma$ (MHz/Torr) He</th>
<th>$\gamma$ (MHz/Torr) H₂</th>
<th>$\gamma$ (MHz/Torr) O₂</th>
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Figure 4.4. Measured $N_2$ (solid circles), $O_2$ (open circles), $He$ (solid squares), and $H_2$ (open squares) broadening parameters of the $18_{3,15} \leftarrow 18_{2,16}$ transition of SO$_2$ plotted as a function of temperature on a log-log scale. Solid lines are the result of a least-squares fit to Eq. 4.7.
<table>
<thead>
<tr>
<th>Temperature (Kelvin)</th>
<th>$\gamma$ (MHz/Torr) He</th>
<th>$\gamma$ (MHz/Torr) H$_2$</th>
<th>$\gamma$ (MHz/Torr) O$_2$</th>
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Table 4.2. Measured pressure broadening parameters at various temperatures for the $13_{1,13} \leftrightarrow 12_{0,12}$ transition of SO$_2$. Absolute uncertainty is estimated at ±5%.
Figure 4.5. Measured \( \text{N}_2 \) (solid circles), \( \text{O}_2 \) (open circles), \( \text{He} \) (solid squares), and \( \text{H}_2 \) (open squares) broadening parameters of the \( 13_{1,1,5} \leftarrow 12_{0,1,2} \) transition of \( \text{SO}_2 \) plotted as a function of temperature on a log-log scale. Solid lines are the result of a least-squares fit to Eq. 4.7.
where $\gamma(T_o)$ is the broadening parameter at some reference temperature $T_o$ (chosen to be 300 K) and $n$ is the temperature exponent. Note that the power-law takes on the same form as for broadening cross sections in Eq. 2.10. Each set of measured broadening parameters for a given transition and broadening gas is fit to Eq. 4.7, and the fitted values of $\gamma(T_o)$ and $n$, with statistical uncertainties, are listed in Table 4.3. The values of $n$ for H$_2$, N$_2$, and O$_2$ are roughly similar, while the values of He are smaller. This is indicative both of the longer range dipole-quadrupole interactions of the diatomic molecules with SO$_2$ and of the involvement of internal rotational degrees of freedom of the diatomics.

As we show in Chapter 2 above, previous variable temperature broadening studies of H$_2$O and HD0 show that the broadening parameters obey Eq. 4.7 except at temperatures below 150 K. At these lower temperatures, the broadening parameters take on smaller values than predicted by Eq. 4.7, as shown in Fig. 2.3. Figures 4.4 and 4.5, however, show that SO$_2$ broadening parameters can be adequately described by the power-law over the whole range of temperatures investigated. The SO$_2$ molecule has larger moments of inertia, and thus more closely spaced rotational energy levels than H$_2$O and HD0. According to the Anderson theory integral in Eq. 2.7, there should be temperatures below which the Fourier components of the collision are no longer effective at broadening the spectral line. For SO$_2$, the parameter $k$ in Eq. 2.7 remains small over the 90 to 500 K temperature range because of the more closely spaced energy levels. Therefore, the broadening efficiency for SO$_2$ does not fall off above 90 K as it does for the lighter H$_2$O and HD0 molecules. Similar results have been reported in the broadening of HNO$_3$.

To our knowledge, the only other variable temperature pressure broadening measurements of SO$_3$ were recently reported by Sumpf et al. Using diode laser measurements in the infrared, they measured broadening parameters in the $v_1$ and $v_3$ bands of SO$_2$ in collision with He and air over a temperature range from 250 to 360 K. Though the restricted temperature range employed in their measurements yields large statistical
Table 4.3. Least-squares fit results for $\gamma(T_o)$ and $n$ for both transitions of SO, and all broadening gases. Uncertainties are one standard deviation taken from the fit.
errors in the values of $n$. Their averaged results of $n=0.73\pm0.20$ for $\text{SO}_2$-He and $n=0.83\pm0.24$ for $\text{SO}_2$-air are consistent with our results in Table 4.3. Air broadening parameters are calculated from our $\text{O}_2$ and $\text{N}_2$ parameters by the relation

$$\gamma(\text{air}) = 0.8\gamma(\text{N}_2) + 0.2\gamma(\text{O}_2).$$

(4.8)

With only the broadening parameters of the two transitions presented here and the data for two other transitions ($4_{1,2} \leftrightarrow 3_{1,3}$ and $26_{4,22} \leftrightarrow 26_{1,33}$) measured earlier, it is difficult to characterize the rotational state behavior of $\gamma(T_\alpha)$ and $n$. We can, however, compare our values of $\gamma(T_\alpha)$ with the rotational state dependence of other room temperature experimental results and calculations. Figure 4.6 shows the $\text{N}_2$ broadening parameters of our work, plotted as a function of $J$ (lower rotational state) superimposed on both the broadening parameters calculated by Tejwani and those measured experimentally by Wolf and Mäder. Our results are consistent with those of the previous studies, and state variations in our data are presumably due to possible $K$ state dependence. In addition, there is a trend of larger broadening parameters at the smaller values of $J$, with the broadening parameters decreasing by approximately 20% over the range of $J$. Figure 4.7 shows a similar plot for $\text{O}_2$ broadening which has seemingly less state dependence than $\text{N}_2$ broadening. Note that the calculations of Tejwani are somewhat larger than the experimental values for $\text{N}_2$ broadening and are significantly smaller for $\text{O}_2$ broadening. It is well known that because $\text{O}_2$ has no electric dipole moment and a relatively small quadrupole moment, calculations of pressure broadening parameters based solely on the dipole-quadrupole interaction, like those of Tejwani, typically underestimate the parameters. Figure 4.8 shows a comparison of the calculated air broadening parameters of this work with the experimental results of Kuhnemann et al. and Sumpf et al. Because modest differences which result from different $K$ states can be expected, Fig. 4.8 shows
Figure 4.6. Comparison of room temperature N$_2$ broadening parameters as a function of $J$. Experimental data comes from this work (solid squares)$^{22}$ and Wolf and Mäder (open squares).$^{23}$ Theoretical values were calculated by Tejwani (plus signs).$^{24}$
Figure 4.7. Comparison of room temperature O$_2$ broadening parameters as a function of $J$. Experimental data comes from this work (solid squares)$^{22}$ and Wolf and Mäder (open squares)$^{23}$ Theoretical values were calculated by Tejwani (plus signs).$^{24}$
Figure 4.8. Comparison of room temperature air broadening parameters as a function of $J$. Data comes from this work (solid squares),\textsuperscript{22} Sumpf \textit{et al.} (plus signs),\textsuperscript{1} and Kuhnemann \textit{et al.} (open squares).\textsuperscript{25}
Figure 4.9. Comparison of room temperature He broadening parameters as a function of $J$. Data comes from this work (solid squares)\textsuperscript{22} and from Sumpf \textit{et al.} (plus signs and open squares).\textsuperscript{1, 27}
Figure 4.10. Comparison of room temperature H$_2$ broadening parameters as a function of $J$. Data comes from this work (solid squares)$^{22}$ and from Sumpf et al. (open squares).$^{1}$
general agreement between the experiments. The HITRAN database lists a general air broadening parameter of 3.34 MHz/Torr, which is also consistent with the low J results of this work. Figure 4.9 shows the He broadening parameters of this work compared with experimental results of Sumpf. et al. The discrepancies at low J in this plot are unusually large and merit further investigation. Figure 4.10 shows the H₂ broadening parameters of this work compared, again, with those of Sumpf, et al. Agreement between these data are satisfactory, though our data points are somewhat small compared to those of Sumpf, et al.

4.3 Pressure Broadening of H₂S

4.3.1 Ambient Temperature

Hydrogen sulfide is a near oblate asymmetric rotor with rotational constants $A=316,304$, $B=276,512$, and $C=147,536$ MHz. Figure 4.11 shows the geometric structure of H₂S, which has a bond angle of 93.3° and bond lengths of 1.3455 Å. Owing to a dipole moment of 1.02 D, a favorable rotational partition function, and the fact that the two transitions investigated ($\ell_{1,0} \leftarrow \ell_{0,1}$ and $\ell_{2,0} \leftarrow \ell_{2,1}$) are low lying in rotational energy, the absorption coefficients for each transition are sufficiently strong over the 100 to 600 K range for spectroscopic measurements. Gaseous H₂S has adequate vapor pressure over this temperature range to enable equilibrium measurements, with 100 K being a lower limit for available vapor pressure.

The H₂S foreign gas (H₂, He, N₂, and O₂) broadening parameters, $\gamma$, for the two transitions are listed in Tables 4.4 and 4.5. Data for the H₂ and He broadening of the $\ell_{1,0} \leftarrow \ell_{0,1}$ transition were measured by this group several years before this study, and those results are also included here for completeness. It should also be noted that no broadening parameters for O₂ are reported above 520 K. At these temperatures, spectral
Figure 4.11. Sketch of the geometric structure of H₂S.
<table>
<thead>
<tr>
<th>Temperature (Kelvin)</th>
<th>$\gamma$(MHz/Torr) He</th>
<th>$\gamma$(MHz/Torr) $\text{H}_2$</th>
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Table 4.4. Measured pressure broadening parameters at various temperatures for the $\ell_{1,0} \leftarrow \ell_{0,1}$ transition of $\text{H}_2\text{S}$. Absolute uncertainty is estimated at ±5%.
Figure 4.12. Measured \( \text{N}_2 \) (solid circles), \( \text{O}_2 \) (open circles), \( \text{He} \) (solid squares), and \( \text{H}_2 \) (open squares) broadening parameters of the \( 1_{1,0}\rightarrow 1_{0,1} \) transition of \( \text{H}_2\text{S} \) plotted as a function of temperature on a log-log scale. Solid lines are the result of a least-squares fit to Eq. 4.7.
<table>
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<tr>
<th>Temperature (Kelvin)</th>
<th>$\gamma$(MHz/Torr) He</th>
<th>$\gamma$(MHz/Torr) $\text{H}_2$</th>
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Table 4.5. Measured pressure broadening parameters at various temperatures for the $2_{2,0}\leftrightarrow 2_{1,1}$ transition of H$_2$S. Absolute uncertainty is estimated at ±5%.
Figure 4.13. Measured N\textsubscript{2} (solid circles), O\textsubscript{2} (open circles), He (solid squares), and H\textsubscript{2} (open squares) broadening parameters of the $2_{2,0} \rightarrow 2_{1,1}$ transition of H\textsubscript{2}S plotted as a function of temperature on a log-log scale. Solid lines are the result of a least-squares fit to Eq. 4.7.
lines would disappear, presumably due to the oxidation of H$_2$S at sufficiently high temperatures. This phenomenon was not observed for the other broadening gases.

Figures 4.12 and 4.13 display plots of these data vs temperature on a log-log scale. As in the case of SO$_2$, collisions of H$_2$S with H$_2$, N$_2$, and O$_2$ yield larger broadening parameters than collisions with He. However, in this case, N$_2$ collisions cause the largest broadening parameters, as opposed to H$_2$ for SO$_2$ broadening.

As in the case of SO$_2$ data, the temperature dependent broadening parameters are fit to the power-law of Eq. 4.7, and $\gamma(T_0)$ and $n$ are listed for both transitions and each broadening gas in Table 4.6. The H$_2$, N$_2$, and O$_2$ broadening parameters all obey Eq. 4.7 over the entire temperature range, while the He parameters do not. Below 300 K, the He broadening parameters are smaller than those predicted by Eq. 4.7, and thus the fit was performed only between 300 and 600 K. The H$_2$S-He broadening parameters deviate from the power-law, unlike the SO$_2$-He broadening parameters, because the rotational energy levels are much sparser than those in SO$_2$. We expect that the $k$ parameter of Eq. 2.7 becomes larger than one for H$_2$S-He around 300 K, and therefore broadening efficiency is diminished, much like the H$_2$O and HDO broadening discussed above.$^{3-5}$ We believe that this deviation does not occur for the other broadening gases because of the role of their internal rotational states in the collisions.

To the best of our knowledge, the only other variable temperature pressure broadening studies of H$_2$S were for H$_2$ and He collisions between 1 and 600 K, reported by this group.$^6,7$ Room temperature air and He broadening parameters have been measured in the infrared by Waschull et al.$^{28}$ and Sumpf et al.$^{29,30}$ Figure 4.14 compares the air broadening parameters of this work (calculated by Eq. 4.8) with the infrared measurements as a function of $J$, and Fig. 4.15 compares the He broadening parameters. While the infrared measurements exhibit a great deal of scatter, it is clear that
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Table 4.6. Least-squares fit results for $\gamma(T_0)$ and $n$ for both transitions of H₂S and all broadening gases. Uncertainties are one standard deviation taken from the fit.
Figure 4.14. Comparison of room temperature air broadening parameters as a function of $J$. Data comes from this work (solid squares), Waschull et al. (open squares for $v_2$ band),$^{28}$ and Sumpf et al. (open circles for $v_1$, open triangles for $v_3$).$^{29}$
Figure 4.15. Comparison of room temperature He broadening parameters as a function of $J$. Data comes from this work (solid squares), Waschull et al. (open squares for $v_2$ band),$^{28}$ and Sumpf et al. (open circles for $v_1$, open triangles for $v_3$).$^{30}$
our room temperature parameters are consistent with these other investigations. To our knowledge, no previous theoretical calculations of \( \text{H}_2\text{S} \) broadening have been performed.

### 4.3.2 Low Temperature

During the low temperature double resonance experiment of \( \text{H}_2\text{S}-\text{He} \) presented in Chapter 6, we remeasured the previously reported low temperature \( \text{H}_2\text{S}-\text{He} \) pressure broadening cross sections for the \( 1_{1,0} \leftarrow 1_{0,1} \) transition.\(^6\)\(^7\) The accuracy of the previous measurements have been questioned because recent refinements in the LHe cooled cells have yielded discrepancies between new and old data.\(^10\)\(^11\) We used the LHe cooled collisional cooling cell and the klystron based spectrometer discussed above in Chapter 3. The new measurements cover a temperature range of 1.3 to 30 K, and at each temperature the pressure broadening halfwidth was measured over a typical pressure range of 1 to 10 mTorr. At these low temperatures and pressures, transpiration effects become significant, and the transpiration corrections of Takaishi and Sensui were employed for all data.\(^18\) Pressure-induced line shift cross sections were also measured, since at low temperature the shift cross sections can become large due to the onset of resonance phenomena. At ambient temperatures, line shifts are typically smaller than the frequency resolution of our spectrometers.

Figure 4.16 shows all measured pressure broadening and pressure shift cross sections for the \( 1_{1,0} \leftarrow 1_{0,1} \) transition of \( \text{H}_2\text{S} \) in collision with He. Table 4.7 lists the newly measured broadening and shift cross sections only. Above 6 K, the newly measured broadening cross sections are consistent with those previously reported by Flatin \textit{et al.}\(^7\) However, below 6 K, the new cross sections are larger than those of the previous study by as much as 25\%. The new cross sections are also larger than the older cross sections of Willey \textit{et al.} by as much as 50\%.\(^6\) These discrepancies are due mostly to advancements in the low temperature system as well as increased millimeter wave power throughput in the
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure Broadening Cross Sections (Å²)</th>
<th>Pressure Shift Cross Sections (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.36</td>
<td>13.69</td>
<td>-0.53</td>
</tr>
<tr>
<td>1.48</td>
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</tr>
<tr>
<td>31.0</td>
<td>12.18</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

Table 4.7. Low temperature pressure broadening and shift cross sections for the $\text{l}_{1,0} \leftrightarrow \text{l}_{0,1}$ transition of $\text{H}_2\text{S}$ in collision with He. Absolute uncertainty is estimated at ±5%.
Figure 4.16. Pressure broadening and shift cross sections of the $1_{1.0} \leftrightarrow 1_{0.1}$ transition of H$_2$S in collision with He from several different experiments by this group. Cross sections below the zero line are pressure shift cross sections. Represented in this graph are data from the current work (solid circles), ambient (solid squares), Flatin et al.\textsuperscript{7} (open circles), and Willey et al.\textsuperscript{6} (open triangles).
collisional cooling cell. With more millimeter wave power, fewer H$_2$S molecules are needed in the cell for good signal-to-noise ratios, thus allowing decreased H$_2$S flow rates. Reduced flow rates translates into better likelihood that the H$_2$S molecules are efficiently cooling by collisions with He atoms. Also, the addition of an Eccosorb lining along the cell walls (as discussed in Section 3.1.3) eliminates asymmetric lineshapes, which can also yield incorrect broadening parameters.

The new low temperature broadening cross sections clearly show the explicit effects of low energy resonances due to the formation of quasibound H$_2$S-He complexes. Between 20 and 3 K, the broadening cross sections increase, rather than continue toward zero. This effect can only be attributed to resonance phenomena, since we expect cross sections to tend to zero in the absence of these low energy resonances. The older broadening cross section measurements did not indicate this behavior at all. More details of the low temperature broadening cross sections are discussed below in Chapter 8, where we have performed calculations using the MOLSCAT computer code and a new H$_2$S-He PES.

References


CHAPTER 5

LOW TEMPERATURE DOUBLE RESONANCE OF CH₃F

5.1 Introduction

The time resolved double resonance experiments presented in this and subsequent chapters represent the first attempts to measure inelastic collision processes at low temperatures in an equilibrium environment. Therefore, the first series of experiments were diagnostic in nature, requiring the selection of a good test molecule. We chose methyl fluoride (CH₃F) for a variety of reasons. First, room temperature double resonance studies had been previously completed, giving us a good preliminary understanding of what to expect for inelastic collisions involving CH₃F. Also, low temperature pressure broadening cross sections had been previously measured, providing a good basis of comparison for low temperature inelastic cross sections. Most importantly, at low temperatures, CH₃F has very strong low-J absorption coefficients, and there are several transitions that are easily accessible by the KVARZ BWO synthesizer and the klystron based spectrometer. Unfortunately, no PES exists for CH₃F-He collisions, making theory calculations impossible. Also, CH₃F has not been observed in the interstellar medium, and as previously mentioned, one of the primary motivations for the low temperature double resonance experiment is to measure inelastic cross sections of interstellar molecules. Nevertheless, CH₃F was more than adequate for proper diagnostic tests of this new experiment.
Figure 5.1. Geometric structure of CH$_3$F.
The CH$_3$F molecule is shown schematically in Fig. 5.1. It is a prolate symmetric rotor with spectral constants $B=25,536.12$ MHz and $A=154,000$ MHz. The hydrogen atoms are bound to the carbon atoms with three-fold $C_3$ symmetry, with typical bond lengths of 1.39 Å (C-F) and 1.11 Å (C-H) and H-C-H bond angle of 110°. Figure 5.2 shows the relevant low $J$ rotational energy levels of CH$_3$F, divided into $K$ stacks. Each $K$ stack has a distinct nuclear symmetry due to the nuclear spin of each H atom, and these symmetries are designated either $A$ for $K=3n$ ($n=0,1,2,...$) or $E$ for $K\neq 3n$. Purely rotationally inelastic collisions are forbidden between the $A$ and $E$ states because the electrostatic interaction cannot induce a change in nuclear spin states.

Figure 5.2 also shows the relevant pump and probe transitions for the diagnostic experiments. The KVARZ synthesizer could be tuned to the line center of any of the $J=3\leftarrow 2$ transitions ($K=0,1,or 2$) near 153.2 GHz, though we chose to use only $K=0$ and 1 for these tests because the $J=3\leftarrow 2, K=2$ transition becomes increasingly weak at the lowest temperatures. The ferrite modulator amplitude modulated the pump power with typically a 10 kHz square wave. The 50 μs period when the pump power is turned off by the ferrite modulator was generally sufficient for collisional relaxation back to equilibrium. The klystron system was then tuned to the line center of any of the $J=4\leftarrow 3$ transitions ($K=0,1,or 2$) near 204.2 GHz. A dichroic filter with hole diameter of 0.0394” (176 GHz cutoff frequency) was used to filter the pump power at the detector. The 1 MHz bandwidth of the detection system and 1 MS/s sampling rate of the National Instruments NB-A2000 data acquisition board were sufficient, with the exception of higher pressures ($>10$ mTorr). At these higher pressures, both the constraints of bandwidth and sampling rate precluded accurate time resolved measurements. Therefore, typical He gas pressures in the LHe cooled collisional cooling cell were 1 to 8 mTorr. The cell temperatures for this study ranged from 1.4 to 16.5 K, and typical backing pressures for the CH$_3$F gas at the injector
Figure 5.2. Relevant low $J$ rotational energy levels of CH$_3$F with pump and probe transitions designated.
were 0.5 to 5 Torr. To further increase the signal-to-noise ratio, we signal averaged the time resolved data for 0.1 to 1 second (1,000 to 10,000 sweeps).

5.2 Preliminary Data

Our original hypothesis for the behavior of the time resolved probe signals was that the probe signal would exponentially decay back to equilibrium when the pump was turned off by the ferrite modulator at time $\tau$. This exponential decay would be related to the inelastic collision rates which restore the Boltzmann population distribution disrupted by the pump radiation. Because the first tests would be performed at a cell temperature of 4.2 K, we could assume that, given the $\sim 6.8 \text{ cm}^{-1}$ energy level separation between $J=3$ and $J=4$, the dominant inelastic process after $t=\tau$ would be $J=3 \rightarrow 2$. Thus, the probe signal would be fit to a simple exponential function,

$$a + b \exp(-kt).$$  \hspace{1cm} (5.1)

for $t>\tau$, where $k$ is the $J=3 \rightarrow 2$ decay rate. In reality, $k$ has contributions from other inelastic processes, but to a good approximation, the $J=3 \rightarrow 2$ rate is dominant. A more complete analysis would involve probing other transitions and developing a self-consistent model based on the Master equation (Eq. 2.24), like in the room temperature CH$_3$F double resonance experiments discussed in section 2.2.2 above.

However, the first time resolved data revealed that the situation would not be quite so simple. Figure 5.3 shows a typical time resolved probe trace for the CH$_3$F-He collision system at 4.2 K. The pump switches on at $t=0$ and off at $t=50 \mu$s. In the first few microseconds, there is an expected increase in the probe absorption signal, because the $J=3$ level is gaining excess population due to the absorption of pump radiation. After this initial rise, there is an unexpected sharp decrease in probe signal for a few microseconds, and
Figure 5.3. Typical time resolved probe absorption signal for the CH₃F-He collision system at 4.2 K (solid squares) with a fit to Eq. 5.1 (solid line).
then the probe signal reaches a steady state value (within the noise). At 50 µs, when the pump has been switched off, there is an unexpected increase in probe absorption signal for a few microseconds, after which the probe decays exponentially to the original t=0 equilibrium value. Attempts to fit this decaying signal to Eq. 5.1 yielded inconsistent results depending on the initial starting time for the fit. Figure 5.3 also shows an attempt at fitting the decaying tail to Eq. 5.1. It became clear at this point that the data would not be properly fit without the inclusion of coherent absorption effects, as discussed in section 2.2.3.

The explanation for the unexpected behavior of the time resolved probe absorption signal is that the pump is sufficiently strong to induce the Autler-Townes phenomenon, which is an AC Stark effect due to rapidly oscillating electromagnetic fields. Ignoring degeneracy, when the pump radiation is sufficiently powerful to saturate the pump transition, the AC Stark effect splits the pump energy levels by \( \Delta E \), where

\[
\Delta E = h\Omega \tag{5.2}
\]

and \( \Omega \) is the Rabi frequency. The Autler-Townes effect can be derived either by the use of the optical Bloch equations (Eqs. 2.37)\(^8\) or by a dressed-states approach.\(^9\)\(^,\)\(^10\) Figure 5.4 shows the Autler-Townes splitting for a generalized, non-degenerate three level system. The splitting of the pump levels causes the steady state probe lineshape to broaden in the case of weaker, yet saturating pump power (\( \Omega=k \)). Very strong pump power (\( \Omega>>k \)) will lead to the case where two distinct lines are resolved by sweeping the probe radiation. For our measurements, the Rabi frequency was on the order of the inelastic collision rates (\( \Omega=k \)), so that a broadening of the line is observed, as shown in the top graph in Fig. 5.5. However, if the pump frequency is detuned off of line center by several hundred kHz, then
Figure 5.4. Autler-Townes splitting of a generalized three level pump/probe system.
Figure 5.5. Probe lineshapes for pump on line center (top graph) and 300 kHz off line center (bottom graph).
sweeping the probe frequency reveals a doublet-like structure, as shown in the lower graph of Fig. 5.5.

In order to apply the Autler-Townes effect to our time resolved data, we must consider the relationship between probe absorption coefficient at line center and the overall integrated absorption coefficient, \( \alpha \), where

\[
\alpha = \int \alpha(v) dv. \tag{5.3}
\]

If we activate a pump which moves population into the lower probe level without saturating the transition, then the line center absorption coefficient and the integrated absorption coefficient will both increase, reflecting the population change, and the linewidth will remain constant. If the pump saturates the transition, moving more population into the lower probe level, then the integrated absorption coefficient will increase proportional to the increased population transfer, and the lineshape will be broadened by saturation effects. Therefore, the line center absorption coefficient can be smaller than that in the non-saturating case to account for the additional saturation broadening.

In the context of our data, which involves only the absorption coefficient at line center, we expect a smaller steady state absorption coefficient with a saturating pump than with a non-saturating pump. This is why the probe signal initially rises then falls when the pump is first turned on, as shown in Fig. 5.3. The decrease in signal reflects the formation of the Autler-Townes doublet structure in the presence of a saturating pump. When the pump is switched off, the probe signal rises, as the Autler-Townes doublet collapses. Population decay is slower than the collapse of the doublet, meaning the width of the probe lineshape decreases and the height of the line increases to maintain a relatively constant integrated absorption coefficient in the first few microseconds after the pump is switched off.
Figure 5.6. Time progression of the probe lineshape (solid lines) superimposed on the equilibrium pump off lineshape (dashed lines), with each probe line center point associated with data points of the time resolved probe absorption signal (lower trace).
The progression of the probe lineshape after the pump is switched off, and the evolution of the absorption coefficient at line center, is modeled pictorially in Fig. 5.6. The steady state, "pump off" lineshape is superimposed on each lineshape for contrast. At 50 μs, when the pump is switched off, the probe lineshape is broader than the "pump off" lineshape due to pump saturation. Between 50 and 55 μs, the probe lineshape becomes progressively narrower and taller as the Autler-Townes doublet collapses. At 55 μs, the probe lineshape has roughly the same width as the "pump off" lineshape. At times later than 55 μs, the probe signal decreases in height as excess population is removed from the lower probe level by inelastic collisions until approximately 67 μs, where the "pump off" equilibrium has again been achieved.

5.3 Integrated Lineshape Method

While the influence of the Autler-Townes effect on our time resolved data was physically interesting, it was not the purpose of this experiment to explore coherent effects, but rather to measure rotational energy transfer processes. One way to circumvent these coherent effects would be to simply attenuate the pump power until the Autler-Townes effect became negligible. While this would become the method of choice for the experiments presented in the next two chapters, we chose to explore the possibility of another method of extracting inelastic rates.

As mentioned in the previous section, the integrated probe absorption coefficient is proportional to the population difference of the probe rotational levels. For the \( J=4 \rightarrow 3, K=0 \) probe transition,

\[
\int \alpha(v) dv \propto (n_1 - n_4)
\] (5.4)
where \( n_j \) and \( n_s \) are the probe level populations. If we can determine the integrated lineshape as a function of time, then we have determined the time dependence of the probe level populations. The strategy then is to record time resolved probe absorption data at a variety of frequencies within the probe lineshape, and then perform a numerical integration by summing these time resolved data. The continuous integral of Eq. 5.4 is then replaced by a discrete sum.

\[
\int \alpha(v,t) dv = \sum \alpha(v,t) \Delta v \propto (n_j(t) - n_s(t)) \tag{5.5}
\]

where \( \Delta v \) is the separation between frequencies along the probe lineshape. Thus, by artificially integrating the time dependent probe lineshape, we can experimentally measure the time dependence of \( n_j \) and \( n_s \).

Figure 5.7 shows schematically how we implemented Eq. 5.5 into our data acquisition process. The steady state lineshapes represent the cases when the pump is on (the broader lineshape) and off (the narrower lineshape). The vertical lines represent the nine different probe frequencies we employed to artificially integrate the lineshape. In essence, we are determining the time dependence of the area between the "pump on" and "pump off" lineshapes, which represents the excess population in the probe levels. The choice of probe frequencies depended on the He gas pressure in the cell, since the probe lineshape becomes broader or narrower by pressure broadening. In general, we used nine different probe frequencies separated typically by 50 kHz. For each probe frequency, we maintained the same cell pressure and temperature. Figure 5.8 shows an example of the nine time dependent probe signals for a He pressure of 1 mTorr and cell temperature of 4.2 K.

Following the data acquisition, the nine probe signals were summed using the trapezoid rule.
Figure 5.7. Plot of typical “pump on” (broader line) and “pump off” (narrower line) steady state probe absorption lineshapes. The vertical lines represent the frequencies selected for nine different time resolved measurements, which are summed together to determine the integrated absorption coefficient.
Figure 5.8. Nine different time resolved probe absorption signals at frequencies relative to the probe line center (He pressure = 1 mTorr, cell temperature = 4.2 K).
\[ \sum \alpha(v_i,t) \Delta v = \Delta v \left( \frac{1}{2} \alpha(v_i,t) + \alpha(v_i,t) + \ldots + \alpha(v_i,t) + \frac{1}{2} \alpha(v_i,t) \right) \]  

(5.6)

to determine the integrated absorption coefficient, and therefore the time dependence of the probe levels. A typical composite time resolved trace, acquired by summing the probe absorption signals in Fig. 5.8 by Eq. 5.6, is shown in Fig. 5.9. This composite trace shows the behavior we initially expected for this double resonance experiment. When the pump is turned on at \( t=0 \), there is an immediate increase in the probe absorption since the population of the \( J=3 \) level is increased by the absorption of pump radiation. The system reaches a steady state after the first few microseconds. When the pump is turned off at \( t=50 \mu s \), the probe signal decreases as population relaxes back to thermal equilibrium. The decaying probe signal after \( t=50 \mu s \) was then fit to the exponential function of Eq. 5.1, and the fit results were consistent regardless of the chosen starting point for the fit.

Using this integrated lineshape method of data acquisition, we measured decay rates, \( k \), as a function of He gas pressure at several low temperatures. Figure 5.10 shows the pressure dependence of \( k \) (in kHz) along with the result of a linear fit. Statistical error bars are included both for \( k \) and for the cell pressure, which reflect pressure drifts during the acquisition time. At higher cell pressures, it has been shown that back diffusion through the injector tube is likely, and thus the pressure error bars increase with increasing pressure. There is also a non-zero intercept, which is due mostly to the coarseness of the frequency grid (\( \Delta \nu \)) chosen for the numerical integration of the absorption coefficient. Subsequent tests showed that a finer frequency grid reduced the intercept without significantly changing the slope. From the slope, the cross section is calculated by
Figure 5.9. Time dependence of the probe integrated absorption coefficient, as determined by numerical integration of the nine time resolved signals in Fig. 5.8.
Figure 5.10. Pressure dependence of the "pump off" decay rate $k$, with statistical error bars and linear fit result (solid line) included.
\[ \sigma = 0.447 \sqrt{\mu T \gamma} \]  

(5.7)

where \( \mu \) is the reduced mass of the collision system in amu, \( T \) is the cell temperature in K, and \( \gamma \) is the slope in MHz/Torr. Note that Eq. 5.7 is equivalent to Eq. 4.6, which is used to calculate pressure broadening cross sections.

5.4 Discussion

Figure 5.11 shows the temperature dependence of CH\(_3\)F-He inelastic collision cross sections, calculated from decay rates acquired by the integrated lineshape method. Also plotted in Fig. 5.11 are the \( J=4 \leftrightarrow 3 \) pressure broadening cross sections and inelastic cross sections determined from our preliminary data, discussed in section 5.2 above. Table 5.1 lists these same cross sections. It is clear from Fig. 5.11 that the preliminary data yield smaller cross sections than those of the integrated lineshape method at the lowest temperatures. However, at 16.5 K, the cross sections obtained by the two methods are equivalent because the Autler-Townes effect becomes negligible at higher temperatures, mainly because the Doppler effect introduces additional dephasing rates which minimize coherent effects.

To properly discuss the inelastic cross sections obtained by the integrated lineshape method, we must first define these cross sections. As mentioned above, our expectation is that the exponential decay in Fig. 5.9 is due mostly \( J=3 \leftrightarrow 2 \) inelastic collisions. While at the lowest temperatures (\( T<4.2 \) K) this may be a good approximation, it is not sufficiently general to cover data over a wide range of temperatures. Particularly, at 16.5 K, the \( J=4 \leftrightarrow 3 \) and \( J=5 \leftrightarrow 4 \) inelastic processes are energetically allowed, and their rates are
Figure 5.11. Measured pressure broadening (solid circles) and inelastic cross sections (open squares) of CH₃F-He at low temperatures. Also plotted are inelastic cross sections determined from the preliminary data (open triangles), for which coherent effects have not been considered.
Table 5.1. Pressure broadening and inelastic cross sections of CH₃F-He as a function of temperature.
included in the overall decay rate, \( k \). Without a more general experimental treatment, and the development of a rotational energy transfer model, we cannot extract individual state-to-state rates from just one pump/probe combination. Since the eventual focus of our research is not the inelastic processes of CH\(_2\)F, we simply define the decay rate \( k \) as a total depopulation rate, or \( 1/T \), in the vernacular of the transient absorption experiments discussed in section 2.2.3.

Perhaps the most interesting aspect of Fig. 5.11 is that the depopulation cross sections are significantly smaller than the pressure broadening cross sections. At ambient temperatures, we expect these cross sections to be equal because in general \( T_1 = T_2 \). The fact that the cross sections are not equivalent at low temperatures is evidence that the pressure broadening cross sections have large contributions due to elastic processes. Quantum scattering calculations of the CO-He system show that low energy pressure broadening cross sections have significant elastic components, as shown in Fig. 2.4 above, and there is no reason to expect that the CH\(_2\)F-He system should behave differently. Therefore, the fact that the measured depopulation and pressure broadening cross sections of Fig. 5.11 are not equal is the first experimental evidence of elastic effects in low temperature pressure broadening.

In conclusion, this set of diagnostic tests of the low temperature double resonance system have been useful both for understanding the operation of the apparatus and for understanding the physical processes inherent to the data. We have learned that coherent effects cannot be ignored in these low temperature time resolved studies, and we have developed a simple model to circumvent coherent effects. We have also demonstrated experimentally for the first time the role of elastic collisions in low temperature pressure broadening. With these accomplishments, we were able to move on to more relevant collision systems, such as those for which a PES could be developed or those which are important in the interstellar medium.
References


6.1 Introduction

For our first set of intensive low temperature double resonance measurements, we chose to use the H$_2$S molecule.\textsuperscript{1} At low temperatures (<27 K), the $l_{0,1}$ and $l_{1,0}$ rotational energy levels are effectively an isolated two-level system. Figure 6.1 shows these and other low $J$ rotational levels of H$_2$S. Like H$_2$, because of the H-atom nuclear spin symmetries, H$_2$S has para and ortho species, which are designated by $J_{\epsilon,\epsilon}$ or $J_{\epsilon,\eta}$ for para and $J_{\epsilon,\eta}$ or $J_{\epsilon,\zeta}$ for ortho. Rotational energy transfer between ortho and para levels is not allowed, since the molecular interaction is electrostatic and cannot change nuclear spin. The $l_{0,1}$ and $l_{1,0}$ levels are part of the ortho species, so the closest rotational level to them is the 2$_{1,2}$ level, which is 19 cm$^{-1}$ higher in energy than $l_{1,0}$. Therefore, by pumping and probing the $l_{1,0} \rightarrow l_{0,1}$ transition at 168.762 GHz, low temperature inelastic rates involving only these two levels can be extracted. These pump/probe transitions are also shown in Fig. 6.1.

Aside from the simplicity of the experiment, low temperature H$_2$S-He collisions are important for two reasons. First, H$_2$S has been observed in the interstellar medium by radio astronomers,\textsuperscript{2} and it has been important in the development of chemical formation models for molecules in interstellar clouds.\textsuperscript{3} Second, H$_2$S-He is sufficiently simple that quantum scattering calculations using MOLSCAT can be done. When these experiments began, no H$_2$S-He PES had appeared in the literature. However, several H$_2$O-He PESs...
Figure 6.1. Low $J$ rotational energy levels of $\text{H}_2\text{S}$ with pump and probe transitions employed in this experiment. Numbers listed below each rotational level are their energies in cm$^{-1}$. 
had been published.\textsuperscript{1-6} and since H\textsubscript{2}S and H\textsubscript{2}O are of similar geometry, we were confident that an H\textsubscript{2}S-He PES could be developed. Very recently, an H\textsubscript{2}S-He PES was computed by Dr. David Woon of the Molecular Research Institute, and quantum scattering calculations using this PES with MOLSCAT are presented in Chapter 8.

With the LHe cooled collisional cooling cell described in Chapter 3, we have measured inelastic collision cross sections of H\textsubscript{2}S-He over a temperature range from 1 to 40 K. The 40 K upper limit is imposed by signal strength considerations. As temperature increases, the population difference between the $l_{0,1}$ and $l_{1,0}$ levels becomes smaller. Fewer molecules then can undergo transitions between the $l_{0,1}$ and $l_{1,0}$ states under the influence of the pump, and the time dependent probe absorption signal becomes very small. Typical He gas pressures in the collisional cooling cell ranged from 1 to 15 mTorr, which is larger than the pressure range in the CH\textsubscript{3}F study discussed in the previous chapter. The H\textsubscript{2}S-He inelastic rates are significantly slower than those for CH\textsubscript{3}F-He, allowing us to perform measurements at higher pressures. Typical backing pressures of H\textsubscript{2}S in the injector line were between 0.4 and 5 Torr.

In the CH\textsubscript{3}F-He measurements, we successfully demonstrated that coherent effects in the time resolved data could be circumvented by use of an integrated lineshape model. However, this method requires much more time than simply measuring time resolved probe signals at line center. Therefore, for subsequent double resonance experiments, we chose to attenuate pump power to minimize coherent effects. We used a wire grid polarizer to attenuate the pump power by simply changing the angle between the wire grid and the pump polarization, giving us variable attenuation as shown in Fig. 3.8 above. Typically, the polarizer was oriented such that the pump was attenuated by $\sim 90\%$. The pump power was square wave amplitude modulated by the ferrite modulator at a 6 kHz rate. The slower inelastic rates of H\textsubscript{2}S-He required more time than CH\textsubscript{3}F-He to relax to equilibrium after the pump was switched off. Both the pump and probe systems were tuned to the line center of
the $l_{1,0} \leftarrow l_{0,1}$ transition, though this experiment could actually have been performed with the pump source only. If the pump were switched off partially, then the "pump off" power could measure the time dependence of the relaxation of the probe level populations back to equilibrium. This method was technically feasible for us to try, but in the interest of time, it was faster for us to use two sources and do the experiment rather than wait for the necessary modifications to the ferrite modulator driver circuit.

Because the pump and probe sources were tuned to the same transition, we used a wire grid polarizer to filter as much pump power as possible out of the detector. Despite attenuating the pump power, residual pump radiation would enter the detector and distort the probe absorption signal. Fortunately, the probe signals were generally quite large, and the residual pump signal could be subtracted away by a baseline subtraction routine similar to that employed in the pressure broadening studies of Chapter 4. In this particular routine, the injector valve was opened to permit $\text{H}_2\text{S}$ into the cell with pump and probe tuned to line center. After approximately 1,000 to 10,0000 sweeps, the probe was detuned away from the line center by several MHz, and more sweeps were taken. The pump signal was then eliminated by subtracting the two averaged signals. The injector valve was left open so that any pump transient absorption signals would also be subtracted, though these signals were generally much smaller than the noise.

### 6.2 Optical Bloch Model

Figure 6.2 shows an example of the time dependent probe absorption following the baseline subtraction routine. This time resolved trace shows an initial decrease in probe signal when the pump is turned on at $t=0$, contrary to the $\text{CH}_3\text{F}$ data which showed an initial increase. This is because the pump radiation moves rotational population from the $l_{0,1}$ level into the $l_{1,0}$ level, decreasing the absorption coefficient for the transition. Between $t=0$ and $t=83.3 \mu$s, the time resolved data are very noisy, while after $t=83.3 \mu$s,
Figure 6.2. A typical time resolved probe absorption signal for the $1_{0,0} \leftrightarrow 1_{0,1}$ transition of H$_2$S, acquired with a cell temperature of 2.58 K and He gas pressure of 2.00 mTorr. Included in the graph is a fit of the data to Eq. 6.5 (solid line).
when the pump is off, the noise decreases substantially. The excess noise when the pump is on is due to heterodyne mixing of the probe and residual pump radiation on the detector chip. This mixing amplifies all signals, including the noise. While it is possible to fit the whole time resolved trace to an appropriate model, this excess noise made it inconvenient to do so. Like in the CH₃F experiment, we chose to fit only the decay of the probe signal following the time at which the pump radiation was switched off.

Since the pump power was attenuated to minimize coherent effects, the exponential decay function of Eq. 5.1 could be fit to the data to determine an inelastic decay rate, k. However, at low pressures, where inelastic rates are slow, it was possible that coherent effects could be strong enough to still be a factor in our data. Therefore, to investigate the reliability of an exponential fit, we developed a more complete model based on the optical Bloch equations, which includes both coherent and inelastic effects.

The optical Bloch equations, introduced in Section 2.2.3 above, are presented in Eqs. 2.37. For our experiment, we needed to solve these equations for $P_\text{r}$, the imaginary part of the bulk polarization, which is related to the absorption coefficient in Eq. 2.32. Since both pump and probe were tuned to line center, we set $\Delta \omega = 0$ in Eqs. 2.37, which decouples the differential equations for the real and imaginary parts of the polarization. We are then left with

$$\frac{dP_\text{r}}{dt} + \kappa^2 E \left( \frac{\hbar \Delta N}{4} \right) + \frac{P_\text{r}}{T_\text{r}} = 0$$

$$\frac{d}{dt} \left( \frac{\hbar \Delta N}{4} \right) - EP_\text{r} + \frac{\hbar}{4} \left( \frac{\Delta N - \Delta N_0}{T_\text{i}} \right) = 0$$

(6.1)

where $\Delta N$ is the population difference for the two-level system and $\kappa E$ is the Rabi frequency. Using Laplace Transform techniques, these two coupled differential equations can be solved analytically. We impose the initial condition that $\kappa E = \kappa E_{\text{pump}}$ for $t<0$ and
that $\kappa E = \kappa E_{\text{probe}}$ after $t=0$. This assumes that the pump radiation is more powerful than the probe radiation, and that the pump switches off at $t=0$. The analytical expression for $P_i$ becomes

$$P_i(t) = P_i(0) + [P_i(0) - P_i(\infty)] \exp(-t/T) \cos \Omega t$$

$$+ \left[ \frac{1}{2} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) P_i(0) - \frac{\hbar}{4} \Delta N(0) \kappa^2 E - \frac{1}{T} P_i(\infty) \right] \frac{\exp(-t/T) \sin \Omega t}{\Omega}$$

(6.2)

where $P_i(0)$ is the initial polarization, $P_i(\infty)$ is the equilibrium polarization, $\Delta N(0)$ is the initial population difference.

$$\frac{1}{T} = \frac{1}{2} \left( \frac{1}{T_1} + \frac{1}{T_2} \right)$$

(6.3)

and

$$\Omega^2 = (\kappa E)^2 - \frac{1}{4} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^2$$

(6.4)

For the purposes of fitting the time resolved data, Eq. 6.2 can be simplified to

$$P_i(t) = a + b \exp(-t/T) \left( \cos \Omega t + \frac{1}{T \Omega} \sin \Omega t \right)$$

(6.5)

where $a$ and $b$ are time independent fit constants related to the relative magnitudes of $P_i(0)$, $P_i(\infty)$, and $\Delta N(0)$. Standard non-linear least squares fitting routines were then used to determine $a$, $b$, and $T$. The value of $T_2$ was assigned from pressure broadening measurements, which are discussed in Section 4.3.2 above. Equation 6.4 defines $\Omega$, which can be imaginary if $\kappa E$ is small and $T_2 < T_1$, thus the sin and cos functions in Eq. 6.5 become sinh and cosh functions. For the low temperature data, the hyperbolic functions...
generally were required because the probe Rabi frequency was close to zero and $T_2 \neq T_1$ at all temperatures. In general, the fitted results for $T_1$ were insensitive to $\kappa E$ in the limit that $\kappa E \ll 1 / T_1$.

In virtually every case, the fitted value of $k$ using the exponential decay model was equal to $1/T_1$, determined by the fit using the optical Bloch model, to within typical statistical uncertainties. Therefore, our attenuation of the pump radiation power was sufficient to eliminate coherent effects in our data for all conditions. While the exponential fit was shown to be sufficient, we analyzed all of the data with the optical Bloch model because of its simplicity and generality.

The key result from the fit for each time resolved probe absorption is the value of $T_1$. While technically defined as a total depopulation rate, $T_1$ can be easily decomposed into individual state-to-state rates for an isolated two-level system. Consider a two-level system, designated as levels 0 and 1, with populations $n_0$ and $n_1$. In the absence of coherent interactions (i.e. a long time after the pump has been turned off), Eqs. 6.1 yields

$$\frac{d\Delta N}{dt} = -\frac{1}{T_1}(\Delta N - \Delta N_0)$$

(6.6)

where $\Delta N = n_0 - n_1$ and $\Delta N_0$ is the equilibrium value of $\Delta N$. From the Master equation (Eq. 2.24),

$$\frac{dn_0}{dt} = -k_{01}n_0 + k_{10}n_1$$
$$\frac{dn_1}{dt} = -k_{10}n_1 + k_{01}n_0 = -\frac{dn_0}{dt}$$

(6.7)
where $k_{o1}$ and $k_{i0}$ are the individual upward and downward state-to-state rates. Employing number conservation ($n_o + n_i = n$ = constant) and detailed balance (Eq. 2.25), Eqs. 6.6 and 6.7 can be combined to reveal

$$\frac{1}{T_i} = k_{o1} + k_{i0}. \quad (6.8)$$

Therefore, for an isolated two-level system, the depopulation rate is simply the sum of the upward and downward inelastic rates. For the $l_{0.1}$ and $l_{1.0}$ rotational levels of $\text{H}_2\text{S}$. Eq. 6.8 holds at temperatures below 9 K. Above 9 K, other inelastic processes become significant, as shown in the $\text{H}_2\text{S}$-$\text{He}$ quantum scattering calculations in Chapter 8.

6.3 Pressure Dependence

The fitted values of $1/(2\pi T_i)$, which is in units of Hz, have a linear dependence on the He buffer gas pressure in the collisional cooling cell. Figure 6.3 shows an example of this linear dependence, including $1\sigma$ error bars representing the statistical uncertainty in the determination of $T_i$. At higher pressures, these error bars are significantly larger than those at low pressure. As the inelastic rate becomes faster, there are fewer digitized points along the exponential decay of the probe signal after the pump is turned off, and in general the probe signal is weaker at higher pressures. These two effects yield larger statistical uncertainty in the optical Bloch model fits. In general, though, the linear pressure dependence of the $T_i$ rates were quite satisfying, and the slope of $1/(2\pi T_i)$ vs pressure was used to calculate cross sections by Eq. 5.7.

Similar plots of $1/(2\pi T_i)$ vs pressure were generated at cell temperatures ranging from 1 to 40 K. At the lowest temperatures ($< 10$ K), the zero pressure intercept was effectively zero to within experimental uncertainty. However, at temperatures greater than
Figure 6.3. Plot of $1/T_1$ decay rate vs He gas pressure for H$_2$S-He at 2.58 K, including a linear fit to the data (solid line). Error bars represent 1σ uncertainties in the fitted values of $T_1$. 
10 K, we noticed that the zero pressure intercept became larger with increasing temperature. This intercept can be caused by a variety of factors, including improper zeroing of the pressure gauge, additional Doppler dephasing from incomplete collisional cooling, and transit time effects. The zeroing of the pressure gauge, while important, is not the cause of the this systematic effect because we would have noticed non-zero intercepts at all temperatures. The notion of additional Doppler contributions is also excluded because collisional cooling is actually more efficient at higher temperatures, and there is less likelihood of incomplete collisional cooling. This leaves transit time effects as the probable cause for the non-zero intercepts.

When the pump radiation creates a non-Boltzmann rotational population in the low temperature sample gas, the principle means by which rotational equilibrium is restored is through inelastic collisions. However, during the measurement of the time dependent probe absorption signal, rotationally excited molecules can also exit the probe radiation path and molecules in thermal equilibrium can enter the radiation path. Therefore, transit time effects must be considered as an additional mechanism for restoring rotational equilibrium following the disruption of pump absorption. This transit time mechanism has basically the same formalism as thermalizing wall collision rates, which can cause additional broadening of spectral lines in spectroscopic cells of sufficiently small dimensions.9

In the absence of inelastic collisions, the transit rate, $k_\tau$, is implemented into the optical Bloch equations by

$$
\frac{d\Delta N}{dt} = -k_\tau(\Delta N - \Delta N_0)
$$

which states that excess population ($\Delta N - \Delta N_0$) decays away at the transit rate. Including $T_i$ and radiative absorption, the equation for $\Delta N$ in the optical Bloch equations then becomes
Therefore, an effective \( \frac{1}{T_i} \) can be determined which is actually the sum of \( \frac{1}{T_i} \) and the transit rate.

At the lowest pressures, where the mean free path of \( \text{H}_2\text{S-He} \) collisions is on the order of the cell window radius (0.5 cm), a rotationally excited \( \text{H}_2\text{S} \) molecule can exit the probe beam path without undergoing any collisions. This ballistic transit rate is then defined as

\[
k_i^{\text{ball}} = \frac{v}{R}
\]  

(6.11)

where \( R \) is the window radius and \( v \) is the thermal velocity of the \( \text{H}_2\text{S} \) molecule of mass \( m \).

\[
v = \sqrt{\frac{8kT}{\pi m}}.
\]  

(6.12)

Therefore, with this ballistic rate, we expect larger transit rates at higher temperatures.

For completeness, we must consider transit rates for all cell pressures, not just the smallest pressures. At pressures where the mean free path is smaller than the cell radius, and the \( \text{H}_2\text{S} \) molecules undergo several collisions before exiting the probe radiation path, the transit rate is equal to a net diffusion rate, given by

\[
k_i^{\text{diff}} = \frac{1}{N_i \tau}
\]  

(6.13)

where \( \tau \) is the average time between collisions and \( N_i \) is the average number of collisions in a random walk process. The average time between collisions is given by
\[ \tau = \frac{\lambda}{v_{rel}} \]  

(6.14)

where \( \lambda \) is the mean free path and \( v_{rel} \) is the relative thermal velocity of H_2S-He (Eq. 4.5). The mean free path is defined by

\[ \lambda = \frac{1}{\sqrt{2}n\sigma} \]  

(6.15)

where \( \sigma \) is a kinetic collision cross section and \( n \) is the number density of molecules given by the ideal gas law (Eq. 4.4). The average number of collisions is determined by

\[ N_i = \left( \frac{R}{\lambda} \right)^2 \]  

(6.16)

Combining Eqs. 6.13-6.16 yields a diffusion rate of

\[ k_{\text{diff}} = \frac{1}{\rho \sigma R^2} \sqrt{\frac{4(kT)^3}{\pi\mu}} \]  

(6.17)

where \( \rho \) is the He gas pressure and \( \mu \) is the reduced mass of H_2S-He.

The net transit rate for any cell pressure is given by

\[ \left( \frac{1}{k_i} \right)^2 = \left( \frac{1}{k_i^{\text{ball}}} \right)^2 + \left( \frac{1}{k_i^{\text{diff}}} \right)^2 \]  

(6.18)

which depends both on temperature and pressure. Figure 6.4 shows calculated values of the transit rate from Eq. 6.18 as a function of pressure at several different temperatures, using the kinetic cross section \( \sigma \) for H_2S-He from Hirschfelder, et al. At the lowest temperatures, the transit rate contributes a negligible amount to the overall probe signal.
Figure 6.4. Transit rates calculated with Eq. 6.18 plotted as a function of He pressure for \( \text{H}_2\text{S}-\text{He} \) collisions at 1.35 K (solid circles), 4.2 K (open squares), 16.9 K (solid squares), and 45 K (open circles). Window radius in these calculations is 0.5 cm.
Figure 6.5. Measured (solid circles) and calculated (solid line) zero pressure intercepts (ballistic rates) for H$_2$S-He inelastic decay rates.
decay rate over the range of pressures relevant to the experiment. At higher temperatures (T>10 K), the transit time rate contributes significantly to the overall pressure dependent probe signal decay rate. Therefore, the transit rate is modeled in all of the data, and transit rate information is removed from the overall probe decay to extract $1/T_r$.

With this transit time analysis, we found that the zero pressure ballistic rate, which increases with increasing temperature, is responsible for the non-zero intercepts in our plots of probe signal decay rate vs pressure. To check the validity of the transit time model, we plot measured predicted intercepts vs temperature in Fig. 6.5. While there is significant statistical scatter in the measured intercepts, it is clear from Fig. 6.5 that the zero pressure transit rate qualitatively predicts the temperature dependent intercepts.

6.4 Results and Discussion

As mentioned above, cross sections are calculated from the slopes of the plots of $1/(2\pi T_r)$ vs He pressure at a variety of temperatures between 1 and 40 K. Though not precisely a state-to-state inelastic cross sections, for the sake of labeling we will designate them as depopulation cross sections, since they are a measure of the depopulation rates which return the probe levels to equilibrium following the disruption of the pump. The depopulation cross sections are plotted as a function of temperature in Fig. 6.6, and they are listed in Table 6.1. While typical statistical errors for these cross sections are less than 10%, we feel that assigning general 10% error bars, which are also shown in Fig. 6.6, are conservatively reflective of systematic errors.

The cross sections shown in Fig. 6.6 tend toward zero with decreasing temperature. This result implies that individual state-to-state cross sections should tend to zero as well. Energetically, any inelastic process which transfers rotational population downward in energy is allowed at any relative collision energy. Below 9 K, these
Figure 6.6. Measured depopulation cross sections of \( \text{H}_2\text{S-He} \) for the \( J=1_{10}\leftarrow 1_{01} \) transition plotted as a function of temperature. The 10\% error bars are conservative estimates of the systematic errors associated with the measurements.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Depopulation Cross Sections (Å²)</th>
</tr>
</thead>
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<tr>
<td>1.36</td>
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</tr>
<tr>
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<td>13.22</td>
</tr>
<tr>
<td>35.3</td>
<td>11.93</td>
</tr>
</tbody>
</table>

Table 6.1. Measured temperature dependent depopulation cross sections of H₂S-He for the \( J=1_{10} \leftarrow 1_{01} \) transition.
depopulation cross sections are dominated by the \( l_{1,0} \rightarrow l_{0,l} \) inelastic cross section, and even though this process is energetically allowed at the lowest temperatures, its cross section goes to zero with decreasing temperature. More comments on these matters are reserved for Chapter 8, where the experimental results are compared to theoretical calculations.

One issue of concern for these data points had to do with the relative linear polarizations of the pump and probe radiation. As described in Chapter 3 above, the pump and probe are co-propagated with the help of a wire grid polarizer, which admits the pump and probe radiation into the cell at relative polarizations of 90°. If we define an axis of quantization, \( z \), along the polarization of the pump, then pump absorption obeys the selection rule \( \Delta J = 1, \Delta M = 0 \), where \( M \) is the projection of \( J \) along the \( z \)-axis. The probe, polarized 90° relative to the pump, induces absorption which obeys the selection rule \( \Delta J = 1, \Delta M = \pm 1 \). The degeneracy was not included in the model because it overly complicates the analysis. Therefore, to test the relative effects of \( M \)-changing or preserving collisions, we devised a scheme to co-propagate the pump and probe with the same polarization.

The method of using parallel pump/probe polarization relies on two factors. First, we attenuate the pump radiation by a wire grid polarizer (≈90%). Second, the wire grid polarizers are not ideal. We believe that some polarization components parallel to the wire grids can pass through the grids rather than reflect. Therefore, to co-propagate the pump and probe beams with parallel polarization, we used a configuration of two wire grid polarizers as shown in Fig. 6.7. The first polarizer reflects the pump beam toward the cell with overall horizontal polarization. However, we assume that some vertical polarization components survive. The second polarizer reflects away the horizontally polarized pump radiation such that, to a good approximation, the pump radiation entering the cell is vertically polarized, like the probe radiation. Placing a third polarizer before the detector did not significantly diminish the pump power on the detector, giving us confidence that the pump radiation in the cell was indeed vertically polarized. Excess pump power on the
Figure 6.7. Schematic diagram of the positioning of two wire grid polarizers for co-propagation of the pump and probe radiation with parallel linear polarization.
detector was successfully subtracted away using the baseline subtraction routine described above.

Time resolved probe absorption signals were measured as a function of He pressure at three temperatures (2, 4.2, and 24 K). The calculated cross sections from these time resolved measurements were, to within the 10% systematic uncertainty, equal to the cross sections measured for perpendicular polarizations. Since we measured the same results, the relative polarizations are not an issue either because the $\Delta M = 0$ and $\Delta M = \pm 1$ are equal or because the relative polarizations are most prominent in coherent effects, which are very small in this study. Further investigation would be required to properly account for either of these two possibilities.

Perhaps the most interesting consequence of these measured depopulation cross sections is their relationship to pressure broadening cross sections. In Section 4.3.2, we present the measured low temperature pressure broadening cross sections of the $J=1_{1,0} \leftrightarrow 1_{0,1}$ transition of H$_2$S in collision with He. Both the pressure broadening and depopulation cross sections are plotted on a logarithmic temperature scale in Fig. 6.8. We observe that the depopulation cross sections are equal to the broadening cross sections above 30 K and are significantly smaller at lower temperatures.

As discussed in Section 2.2.3 above, previous room temperature transient absorption experiments showed that typically $T_s = T_e$. Since $1/(2\pi T_s)$ is equal to the pressure broadening halfwidth, then at room temperature the depopulation and pressure broadening cross sections should be equal. However, Hoke et al.\textsuperscript{11} show that for an ideal two-level system in the absence of elastic collisions, the depopulation cross section should be twice the pressure broadening cross section. This is due to the fact that collisions which deplete one level necessarily populate the other. By this reasoning, we would expect that at temperatures below 9 K, our measured depopulation cross sections should be larger than
Figure 6.8. Measured pressure broadening (open squares) and depopulation cross sections (solid circles) of H₂S-He for the \( J=1_{0,0} \leftrightarrow 1_{0,1} \) transition plotted on a logarithmic temperature scale.
the broadening cross sections by a factor of 2. What we observe is that the broadening cross sections are as much as a factor of 3 larger than the depopulation cross sections.

Since we are confident in the two-level approximation at low temperatures, the aforementioned deviation can only be explained by the presence of elastic processes in low temperature pressure broadening. While this is not a surprising result, based on previous low energy quantum scattering calculations of the CO-He system described in Section 2.1.2 above, it is the first experimental verification, to our knowledge, of the existence of elastic components in pressure broadening cross sections of rotational transitions. It seems probable that a low energy resonance (or resonances) is responsible for the “hump” in the broadening cross sections between 1 and 10 K. Since a similar “hump” is not observed in the depopulation cross section, we can further guess that the low energy resonance structure must be due to elastic collisions only. These issues are discussed in more detail in Section 8.2 below.

References


CHAPTER 7

LOW TEMPERATURE DOUBLE RESONANCE OF NO

7.1 Introduction

Nitric oxide (NO) is ubiquitous in many fields of study for its importance in atmospheric, interstellar, combustion, and biological processes. While investigations of NO have generated many scientific papers, only the work of Alexander and co-workers \(^1\) and Smith and co-workers \(^2\)–\(^6\) have dealt significantly with low energy and low temperature NO-He inelastic collisions. In addition, Willey et al. have measured low temperature NO-He pressure broadening cross sections (1.8–4.2 K) using a collisional cooling cell and a millimeter wave source.\(^7\)\(^8\) NO is a radical in a \(^3\)\(\Pi\) electronic ground state, and as will be shown below, rotational energy transfer in NO is much more complicated than in typical \(^1\)\(\Sigma\) species because its rotational energy levels of NO are split into \(\Lambda\)-doublets, which are further split into resolvable hyperfine levels.\(^9\) With the high frequency resolution of our millimeter wave sources, a low temperature double resonance experiment allows us to study inelastic collisions involving these hyperfine and \(\Lambda\)-doublet states.

7.1.1 Electronic and Rotational Energy Levels

NO has one unpaired electron which occupies a doubly degenerate \(\pi\) orbital. The projection (\(\Lambda\)) of total orbital angular momentum (\(L\)) about the internuclear axis is a good quantum number, and \(|\Lambda|=1\) determines the electronic state designation \(\Pi\) for NO. The total electronic spin (\(S\)) for NO is 1/2, and from \((2S+1)=2\), the electronic state designation is
modified to \(^{3}\Pi\). The electronic spin-orbit coupling orients the total spin angular momentum about the internuclear axis such that \(S\) precesses about this axis similarly to \(L\). The projection of \(S\) along the internuclear axis (\(\Sigma\)) is also a good quantum number. The resultant total electronic angular momentum (\(\Omega\)) is defined as

\[
\Omega = \Lambda + \Sigma. \tag{7.1}
\]

For NO, \(|\Omega|\) has values of 1/2 and 3/2, which define the two fine structure states \(^{3}\Pi_{1/2}\) and \(^{3}\Pi_{3/2}\). Figure 7.1 shows the geometry of the NO molecule (bond length=1.151 Å)\(^9\) as well as the coupling of the various angular momenta.

NO exhibits good Hund’s case (a) coupling in its lowest rotational states, which are the focus of our experiment.\(^9\) Therefore, \(L, S,\) and \(R\) (the end-over-end rotation of the molecule) couple to form total angular momentum \(J\), a good quantum number for small values of \(J\). Stronger coupling of \(L\) and \(S\), such that \(L\) is weakly coupled to the internuclear axis, leads to Hund’s case (c), while extremely weak spin-orbit coupling (for which \(\Sigma\) is not well defined) leads to Hund’s case (b). NO undergoes a transition from case (a) to case (b) as \(J\) increases above the lowest few levels.\(^10\)

Because \(R\) is quantized with integer values \(R=0,1,2,\ldots\) total angular momentum \(J\) takes on odd-half-integer values of \(J=1/2, 3/2, 5/2, \ldots\) for \(|\Omega|=1/2\) and \(J=3/2, 5/2, 7/2, \ldots\) for \(|\Omega|=3/2\). The fine structure splitting is determined by a spin-orbit term in the molecular Hamiltonian

\[
H_{so} = AL \cdot S. \tag{7.2}
\]

For molecules with outer electron configuration (\(\pi\))\(^1\) (e.g. NO), \(A>0\), while for outer electron configuration (\(\pi\))\(^3\) (e.g. OH), \(A<0.\)\(^11\) The fine structure constant, \(A\), for NO is
Figure 7.1. The geometric structure of NO with relevant angular momentum couplings.
approximately 120 cm$^{-1}$. Figure 7.2 displays the rotational energy levels of the two fine structure states of NO.

A total Hamiltonian, which incorporates spin-orbit and end-over-end rotation, is

$$H = A \mathbf{L} \cdot \mathbf{S} + B \mathbf{R}^2.$$ \hspace{1cm} (7.3)

If $\mathbf{R}$ is rewritten as $J \cdot L - S$, then the Hamiltonian can be rewritten explicitly in terms of components of $L$, $S$, and $J$, following the treatment of Carrington \(^{11}\) as:

$$H = A \Lambda \Sigma + B \left\{ J(J+1) + S(S+1) - 2 \Omega \Sigma - \Lambda^2 \right\}$$

$$- 2B(J,J_z + J,S_z) + (A + 2B)(L_z,S_z + L,S_z)$$

$$- 2B(J,J_0 + J,L_0) + B(L_z^2 + L_z^2) \hspace{1cm} (7.4)$$

Those terms which are first order in $L_z$ or $J_z$ couple electronic states differing in $\Lambda$ by ±1, thus lifting the two-fold $|\Lambda|=1$ degeneracy. This effect is known as $\Lambda$-doubling. While $\Lambda$-doublet splittings are largest for the lightest molecules, high resolution spectrometers are required to resolve these doublets. For NO at $J=1/2$, the $\Lambda$-doublet splitting is approximately 0.01 cm$^{-1}$.\(^{12}\)

The parity of the $\Lambda$-doublet levels are labeled in several ways in the literature. To be consistent with the theoretical work of Alexander,\(^{3}\) we employ the following scheme. Each $J$ energy level of a $^3\Pi$ molecule is doubly degenerate and contains two inversion symmetries. The $\Lambda$-doubling removes the degeneracy, and the upper and lower levels of the doublet have opposite parity. These parities are labeled $e$ and $f$ in the following manner. For a given value of total angular momentum $J$ and electron spin $S$, levels with parity $+(-1)^{J-S}$ are labeled $e$ levels, and levels with parity $-(-1)^{J-S}$ are labeled $f$ levels. The left side of Figure 7.3 shows the $\Lambda$-doublet structure and symmetries of the $J=1/2$ to $J=5/2$ levels of the $^3\Pi_{1/2}$ fine structure state. The selection rules for allowed electric dipole
Figure 7.2. Energy levels of total angular momentum $J$ for the two fine structure levels of NO ($E<180$ cm$^{-1}$).
transitions, in terms of \( e \) and \( f \) labels, between the \( \Lambda \)-doublet levels are\(^{13}\):

\[
\Delta J = 0, \ e \leftrightarrow f \\
\Delta J = \pm 1, \ e \leftrightarrow e, \ f \leftrightarrow f
\]

The NO \( \Lambda \)-doublet levels are further split into hyperfine levels by the coupling of the nuclear magnetic moment of the nitrogen atom to the moment of the \( J \) vector. Figure 7.4 shows the hyperfine vector coupling geometrically. An additional term is added to the Hamiltonian:

\[
H_{hf} = \pm CI \cdot J
\]

where \( C \) is a coupling constant, \( I \) is the nuclear spin of the N-atom \((I=1)\), the + sign is for the upper \( \Lambda \)-doublet level and the - sign is for the lower \( \Lambda \)-doublet level.\(^9\) We then define

\[
F = I + J
\]

and, since \( I=1 \), the split \( \Lambda \)-doublet levels are designated by \( F=J+1, J, \) and \( J-1 \), as shown in Fig. 7.3. Note that the \( \Lambda \)-doublet levels in \( J =1/2 \) are split only into \( F=1/2 \) and \( F=3/2 \). The order of increasing energy of the \( F \) states is reversed in the upper and lower \( \Lambda \)-doublet levels due the \( \pm \) in Eq. 7.6. The unequal spacing of the hyperfine splitting in the upper and lower states is due to an additional electron spin-nuclear spin interaction component (for molecules with \( S=0 \), the hyperfine splittings are equal). The electric dipole selection rules of Eq. 7.5 are modified to include

\[
\Delta F = 0, \ \pm 1
\]
Figure 7.3. A-doublet and hyperfine levels of $J=1/2$ to $J=5/2$ of the $^2\Pi_{1/2}$ fine structure state of NO. The $\Lambda$-doublet and hyperfine splittings are not drawn to scale. Allowed electric dipole radiative transitions are also displayed.
Figure 7.4. The coupling of nuclear spin ($I$) with total angular momentum ($J$) to produce the hyperfine quantum number ($F$).
where typically the \( \Delta F = \Delta J \) processes yield the strongest radiative transition moments. All the dipole allowed transitions are shown in Figure 7.3.

### 7.1.2 Previous NO-He Theory and Experiment

The approach of a structureless collision partner such as He lifts the cylindrical degeneracy of a \( \Pi \) electronic state such that the wave function is antisymmetric (\( A'' \)) or symmetric (\( A' \)) with respect to reflection in the triatomic plane.\(^1\) These symmetries depend on the orientation of the \( \pi \) electron relative to the triatomic plane.\(^2\) As a result, two potential energy surfaces, one each of \( A' \) and \( A'' \) symmetry, are required to properly calculate the dynamics of the NO-He system. Early calculations of inelastic collision cross sections of NO-He were performed by Corey and Alexander \(^1\) using an electron gas potential surface.\(^14\) Various approximation schemes were employed in the calculations, but infinite order sudden approximations provided reliable calculations of thermal NO-He processes. A more detailed, \textit{ab initio} PES was developed by Yang and Alexander \(^3\) from which inelastic cross sections have been calculated and propensity rules have been investigated by coupled states and close coupling methods.\(^4\)

For the purposes of solving the quantum scattering of NO-He, the two PESs of \( A' \) and \( A'' \) symmetry are combined into \( V_{\text{sum}} \) and \( V_{\text{diff}} \) where

\[
V_{\text{sum}} = \frac{1}{2} \left[ V_{A''}(R,\theta) + V_{A'}(R,\theta) \right]
\]

and

\[
V_{\text{diff}} = \frac{1}{2} \left[ V_{A''}(R,\theta) - V_{A'}(R,\theta) \right].
\]

\( V_{\text{sum}} \) and \( V_{\text{diff}} \) are expressed as expansions of radial functions by
\[ V_{\text{cum}} = \sum_{\lambda \neq 0} V_{\lambda,0}(R)P_{\lambda}(\cos \theta) \quad 7.11 \]

and

\[ V_{\text{def}} = \sum_{\lambda = 2}^{\infty} V_{\lambda,2}(R)d_{\lambda,0}^d(\theta) \quad 7.12 \]

where \( P_{\lambda}(\cos \theta) \) is a Legendre polynomial, \( d_{\lambda,0}^d(\theta) \) is a reduced rotation matrix element, and \( V_{\lambda,0} \) and \( V_{\lambda,2} \) are the leading order radial terms for each expansion. Yang and Alexander show, from calculations using the HIBRIDON 4 package,\(^1\) that the \( V_{\text{cum}} \) and \( V_{\text{def}} \) potentials mediate spin-orbit conserving and spin-orbit changing collisions, respectively.

NO is nearly homonuclear in character, and thus the symmetric even-\( \lambda \) terms dominate the expansions of the PESs in Eqs. 7.11 and 7.12. A consequence of the dominance of these even-\( \lambda \) terms is that inelastic collisions for which \( \Delta J \) is even are preferred over odd \( \Delta J \) processes. In addition, overall parity should be conserved during the collision. Therefore, inelastic collisions mediated by even-\( \lambda \) terms are either \( \Delta J=\text{even} \) with \( e/f \) being conserved or \( \Delta J=\text{odd} \) with \( e/f \) changing. Because the odd-\( \lambda \) terms are non-zero, the processes where \( \Delta J=\text{even} \) and \( e/f \) changes or \( \Delta J=\text{odd} \) and \( e/f \) is conserved are possible, but not as likely as those processes associated with the even-\( \lambda \) terms. In their theoretical calculations, Yang and Alexander calculate that these propensities for NO-He collisions indeed hold true, particularly at higher energies (\( E>500 \text{ cm}^{-1} \)).

Experimentally, low temperature inelastic cross sections of NO-He have been measured down to 7 K by Smith and co-workers.\(^4\) To achieve such low temperatures, dilute mixtures of NO and He were cooled by expansion through a Laval nozzle, such that the temperature and gas concentrations were well defined quantities.\(^16\)\(^17\) To measure inelastic cross sections, they employed infrared-ultraviolet double resonance techniques.
where a specific $J$ state in $v=3, \Omega=1/2$ was populated by the infrared pump, and the population transfer was monitored by ultraviolet laser induced fluorescence. Both total depopulation rates and state-to-state rates were measured. While they did not resolve the $\Lambda$-doublet or hyperfine transitions with this technique, they verified the $\Delta J=\text{even}$ propensity rule predicted by theory. They also observed that the $\Delta J=\text{even}$ propensity appears to be less strict at low temperatures (15 and 7 K) because there is increasingly less collision energy to induce transitions for which $\Delta J>1$.

7.2 Double Resonance Measurements

7.2.1 Experimental Procedures

Our millimeter wave spectrometers are capable of very high frequency resolution, and, with our low temperature double resonance system, we can investigate inelastic collisions between various low $J$ hyperfine and $\Lambda$-doublet states. NO has a rotational constant of 51,084 MHz, and, as shown in Fig. 7.3, the transitions between $J=1/2$ and $J=3/2$ are near 150 GHz, easily accessible by the KVARZ BWO synthesizer pump. The transitions between $J=3/2$ and $J=5/2$ are near 250 GHz, which we can probe with the klystron based system. The strongest pump transitions involve the $J=3/2, F=5/2\leftarrow J=1/2, F=3/2$ levels, and we found that pumping this transition in either $\Lambda$-doublet state yielded the strongest probe signals.

NO has a dipole moment of 0.16 D, which is an order of magnitude smaller than the dipole moments for H$_2$S and CH$_4$F. Because of such a small dipole moment and the splitting of the rotational levels into $\Lambda$-doublet and hyperfine states, the transitions of NO are much weaker than those in any of the studies presented above. Since the future of this double resonance may involve double resonance measurements of CO, which has a dipole moment of 0.10 D, these experiments of NO are a good diagnostic of the sensitivity limitations of the apparatus in preparation for a CO-He double resonance study. In
addition, because the NO dipole moment is small, coherent effects are very weak in the double resonance data since the Rabi frequency is an order of magnitude smaller than those in the H$_2$S and CH$_3$F experiments. Therefore, the pump could be operated at full power in this experiment, which was fortuitous given the relatively weak probe signals. We typically had to average the time resolved data for 2 to 200 seconds ($\sim 10^4$ to $10^6$ sweeps). Also, weak probe signals meant that we could get reliable data only at low He buffer gas pressures, typically 1 to 4 mTorr.

Because the pump frequency was less than the probe frequency, we could employ a dichroic filter to prevent pump radiation from entering the detector. The same filter used in the CH$_3$F experiment in Chapter 5 (176 GHz cutoff frequency) was again used in this experiment. We also attempted to both pump and probe the $J=3/2\leftrightarrow J=1/2$ transitions, but since both radiation sources were tuned near 150 GHz, we had to use a wire grid polarizer to reflect pump power away from the detector. However, given the weak probe absorption signals and the fact that we could not attenuate the pump power and still get adequate probe signals, we were unable to extract time resolved probe signals because the amount of pump power passing through the polarizer was too great.

All the data presented below were acquired at a cell temperature of 4.2 K. At this temperature, the $J=1/2$ and $J=3/2$ levels are thermally isolated from levels at higher energy. The energy gap between the $J=3/2$ and $J=5/2$ levels is 8.3 cm$^{-1}$ ($\sim 12$ K), which is roughly $3kT$ at 4.2 K. Since the probe absorption signal is proportional to the difference between the lower and upper probe level populations, as shown in Eq. 2.23, probe signals for $J=5/2\leftrightarrow J=3/2$ transitions monitor only the population in the $J=3/2$ levels because of this thermal isolation. Therefore, after pumping excess population from $J=1/2$, $F=3/2$ into the $J=3/2$, $F=5/2$ level, we could monitor changes in the populations of each of the three hyperfine states in each $\Lambda$-doublet level by using six different probe transitions.
We found that the inelastic processes in NO-He which lead to rotational relaxation rates are, like those for \( \text{H}_2\text{S}-\text{He} \), fairly slow. Thus we square wave amplitude modulated the pump at a 4 kHz rate to insure the system had enough time to return to equilibrium for the slowest collision processes. With the addition of the CAMAC system for the digitization of time resolved signals, discussed in Chapter 4, we had more flexibility with digitization rates. For this experiment, 0.5 and 1 \( \mu \)s/point were sufficient.

7.2.2 Time Resolved Data

As mentioned above, we tuned the pump source to the \( J=3/2, F=5/2 \leftarrow J=1/2, F=3/2 \) transition in the lower \( \Lambda \)-doublet at 150.176 GHz, adding excess population to the \( J=3/2, F=5/2 \) level. To monitor the redistribution of this excess population among the hyperfine levels for the \( \Lambda \)-doublet levels of \( J=3/2 \), we measured the time resolved signals of six probe transitions. These transitions included \( J=5/2, F=7/2 \leftarrow J=3/2, F=5/2; J=5/2, F=5/2 \leftarrow J=3/2, F=3/2; \) and \( J=5/2, F=3/2 \leftarrow J=3/2, F=1/2 \) in both the upper and lower \( \Lambda \)-doublet levels of \( J=3/2 \), shown in Fig. 7.3. Examples of the six time resolved probe traces are shown in Figs. 7.5 and 7.6 for the lower and upper \( \Lambda \)-doublet levels, respectively. As previously discussed, since the cell temperature was 4.2 K, we assume no collisional excitation to the \( J=5/2 \) such that each of the probe signals in Figs. 7.5 and 7.6 represent the time dependence of the populations of each lower probe level.

The population of \( J=3/2, F=5/2 \) in the lower \( \Lambda \)-doublet level (the upper state of the pump transition) increases when the pump is turned on at \( t=0 \) and subsequently decreases when the pump is turned off at \( t=125 \mu s \), as shown in Fig. 7.5. After the pump has been on for \( \sim 25 \mu s \), the population reaches a steady state value, where the rate of population increase due to the pump is balanced with inelastic rates which remove population from the level. After the pump is turned off, the population returns to equilibrium via inelastic
Figure 7.5. Time resolved probe signals of three hyperfine states of the lower Λ-doublet level of $J=3/2$ (in order of increasing energy). The $F=5/2$ level is directly populated by the pump radiation, and thus has a factor of 10 larger probe signal than the others.
Figure 7.6. Time resolved probe signals of three hyperfine states of the upper Λ-doublet level of $J=3/2$ (in order of increasing energy).
collisions. Note that the rate at which population increases is faster than the rate of decrease because of the rate associated with the pump radiation.

The populations of the $F=3/2$ and $F=1/2$ levels in the lower Λ-doublet also increase when the pump is turned on, as shown in Fig. 7.5. These signals are significantly weaker (by a factor of ~10) than that for the $F=5/2$ level, meaning that a very small amount of population is transferred into these levels. The increased probe signal for the $F=3/2$ level suggests population transfer from the $F=5/2$ level when the pump is on. It is unclear without further analysis whether the probe signal increase in the $F=1/2$ level is due to population transfer directly from the $F=5/2$ level ($\Delta F=2$) or due to two $\Delta F=1$ transitions ($F=5/2\rightarrow 3/2$ and $F=3/2\rightarrow 1/2$). Physically, these $\Delta J=0$, Λ-doublet conserving processes correspond to a reorientation of the $J$ vector (change in $M_J$) relative to the $I$ vector, as shown in Fig. 7.4. As will be discussed below, the interaction between NO and He cannot change nuclear spin.

For the probe signals involving the upper Λ-doublet level, shown in Fig. 7.6, the populations of the hyperfine levels behave quite differently under the influence of the pump. The population of the $F=5/2$ level increases while the populations of the $F=3/2$ and $F=1/2$ levels decrease. This decrease is presumably due to inelastic collisions connecting these levels to the pump depleted $J=1/2$, $F=3/2$ level. The increase of the $F=5/2$ signal suggests that $\Delta F=0$, Λ-doublet changing inelastic rate dominates $\Delta J=1$ rates for this level. It is also direct evidence that the $\Delta F=\Delta J$ propensity is valid, since the $F=3/2$ and 1/2 levels do not exhibit a similar increase.

Figure 7.7 diagrams the proposed propensities for the hyperfine dependent processes based on the qualitative examination of our data. However, to acquire information about cross sections, and to prove that the propensities in Figure 7.7 are realistic, we must impose more rigorous analysis methods in conjunction with a physically
Figure 7.7. Proposed propensities for the dominant inelastic processes involving the $J=3/2$ levels (dashed arrows) under the influence of a $J=3/2, F=5/2 \rightarrow J=1/2, F=3/2$ pump in the lower $\Lambda$-doublet level (solid arrow).
realistic model. In any event, this data represents the first laboratory observation of hyperfine dependent inelastic collisions at low temperatures.

7.3 Analysis

7.3.1 Numerical Bloch Equation Analysis

To untangle the underlying physics of our time resolved data, and to extract inelastic cross sections, we employed a numerical model based on a combination of the optical Bloch equations (Eq. 2.37) and the Master equation (Eq. 2.24). The density matrices from which the Bloch equations are derived can be recast in terms of individual state-to-state inelastic rates rather than the total depopulation rate $1/T$. These density matrices obey the following set of coupled differential equations

$$
\frac{d}{dt} \rho_{mn} = \sum_q \left[ \left( -k_{mq} \rho_{mn} + k_{qm} \rho_{qm} \right) - \frac{i}{2} \left( \Omega_{qm} \rho_{qm} - \Omega_{mq} \rho_{qm} \right) \right]
$$

where the diagonal elements $\rho_{nn}$ represent populations, the off-diagonal elements $\rho_{nm}$ represent coherences, $\Omega$ is the Rabi frequency, $\Delta \omega_{nm}$ is the detuning for the $n \leftrightarrow m$ transition, and $k_{mq}$ is the inelastic rate for the $q \leftrightarrow m$ transition. Using the definitions from Eqs. 2.35 and setting $\Delta \omega_{nm}=0$, the density matrices are recast in terms of rotational populations, $n$, and the imaginary part of the bulk polarization, $P$, for the $U \leftrightarrow L$ transition as
\[
\begin{align*}
\frac{d}{dt} P_{\mu} &= \frac{\Omega}{2} (n_L - n_U) - \frac{P}{T_2} \frac{1}{\mu} \\
\frac{d}{dt} n_L &= -\Omega \frac{P}{\mu} + \sum_q k_{\mu q} n_q \\
\frac{d}{dt} n_U &= \Omega \frac{P}{\mu} + \sum_q k_{q \mu} n_q \\
\frac{d}{dt} n_i &= \sum_q k_{i q} n_q
\end{align*}
\tag{7.14}
\]

where $\mu$ is the transition matrix element for the pump transition and $n_i$ are any populations not connected to the pump transition. The inelastic rates $k_{\mu q}$ comprise a matrix, sometimes called the Redfield matrix\textsuperscript{18}, where the diagonal elements $k_{qi}$ are given by

\[
k_{qi} = -\sum_{i \neq j} k_{ij}.
\tag{7.15}
\]

Equations 7.14 are functionally equivalent to the Bloch equations presented in terms of $T_2$. We could have used this same formalism for the H\textsubscript{2}S study presented in Chapter 6, but it was more convenient for the analysis of a large number of data files to use Eqs. 6.1, which can be solved analytically.

For the analysis of the 4.2 K double resonance data, the model must include the populations of all the $J=1/2$ and $J=3/2$ energy levels, as well as all the inelastic rates which connect them. Thus there are a total of 10 time dependent populations to include, in addition to $P_\mu$, and 90 inelastic rates connecting the energy levels. With 11 coupled differential equations, an analytical solution is not possible, so we employ numerical techniques to model the flow of population under the influence of the pump. The time dependence for each population can be solved by a first order Taylor expansion about a small $\Delta t$, where
Generalizing Eqs. 7.14 by

$$\frac{d}{dt} n_i(t) = \sum k_n n_i(t). \quad 7.17$$

where \(i=0, \ldots, 10\) and \(n_i(t) = \bar{P}/\mu\). Eq. 7.16 can be rewritten as

$$n_i(t) = n_i(t - \Delta t) + \Delta t \left( \sum k_n n_i(t - \Delta t) \right). \quad 7.18$$

Equation 7.18 is then solved numerically for the time dependence of the population of each energy level given the values of the inelastic rates.

The time resolved probe signals \(S_i(t)\), which are proportional to the populations of each of the six lower probe levels, are each represented by

$$S_i(t) = a_i + b_i n_i(t). \quad 7.19$$

where \(a_i\) is a DC offset with no physical meaning and \(b_i\) is a multiplicative constant which depends on the probe radiation power, the radiative transition moment, the number of molecules along the probe path in the cell, additional constants in the probe absorption coefficient (see Eq. 2.20), and analog-to-digital conversion factors. For each probe signal at a given He buffer gas pressure, we assume that only the probe power and the transition moment differ among the six probe transitions. For all data files, we maintained equal NO backing pressures in the injector, allowing us to assume that the number of molecules along the probe path are equal at a given He pressure. We therefore reduce the six \(b_i\) constants to
one multiplicative fitting constant, $b$, by weighting each probe signal by the calculated transition moment and the measured probe power. As a result, we are fitting both for the rates of population transfer (the slope of population increase and decrease in a data file) and for the steady state probe signal levels, which also depend strongly on the inelastic rates.

To fit the time resolved data with this numerical Bloch equation formalism, we employ the Levenberg-Marquardt non-linear least squares fitting routine in a computer program written in the C language. However, without some additional constraints, the 90 different hyperfine and $\Lambda$-doublet dependent inelastic rates (reduced to 45 by detailed balance) are far too many adjustable parameters for a reasonable fit to six time resolved traces. The goal then for this RET model, like in the ambient infrared-millimeter wave double resonance study of Everitt and De Lucia, is to reduce these 45 rates to only a few adjustable physical parameters. To do so requires an appropriate formalism for hyperfine dependent inelastic collisions.

7.3.2 Hyperfine Resolved Inelastic Collisions

The previous NO-He theory and experiments presented above in Section 7.1.2 do not pertain to the issues of hyperfine resolved inelastic collisions, and we have been unable to find any such studies in the literature for NO. Therefore, we look to studies of the collision dynamics of other open shell molecules. In particular, the hyperfine resolved inelastic collisions of OH have been widely studied theoretically because of the observation of OH masers in the interstellar medium. It has been proposed that collisional pumping through specific channels followed by radiative decay may be the mechanism for some of the observed maser emissions.

The general approach for solving the hyperfine dependent inelastic cross sections theoretically is to first calculate the S-matrix without nuclear spin dependence and then recouple the solution with the specific hyperfine states. This approach is valid because the
interaction between molecule and atom is electrostatic and will not affect the nuclear spin.

A subsequent tensorial recoupling involving the initial and final $F$ hyperfine states leads to the prediction of $\Delta F$ propensity rules independent of the details of the intermolecular interaction. This approach has its origins in the prediction of $\Delta M$ propensities in atomic $^{27}$ and $^1\Sigma$ molecular collisions. $^{28}$ The presentation below will follow the general outline of the recoupling used by Alexander and co-workers. $^{23, 29}$

Typically one might try to solve the quantum scattering problem of hyperfine dependent collisions by the following coupling scheme:

\[
\mathbf{F} = \mathbf{J} + \mathbf{I} \\
\hat{\mathbf{F}} = \mathbf{F} + \ell
\]

where $\ell$ is the orbital angular momentum of the collision partners and $\hat{\mathbf{F}}$ is a total angular momentum. An alternative coupling, justified by the spectator role of the nuclear spin during the collision, is

\[
\mathbf{j} = \mathbf{J} + \ell \\
\hat{\mathbf{j}} = \mathbf{j} + \mathbf{I}
\]

where $\mathbf{j}$ is an intermediate angular momentum which is conserved during the collision.

Inelastic cross sections are determined by the $T$-matrix, defined in terms of the $S$-matrix by

\[
T_{\mu,\mu'}^{\nu,\nu'} = \delta_{\mu,\nu} \delta_{\nu',\nu} - S_{\mu,\nu'}^{\nu,\nu'}
\]

and, in general, $^{30}$

\[
\sigma_{m \rightarrow n} = \frac{\pi}{k_n^2} \sum_{\nu} \langle 2\hat{\mathbf{j}} + 1 \rangle |T_{m,n}^{\nu}|^2.
\]

185
From the recoupling scheme above, the hyperfine dependent T-matrix (for transitions within the \(^3\Pi_1\alpha\) fine structure state) is given by

\[
T_{j\ell F', J'\ell' F''}^j = (-1)^{j'-j} \frac{1}{F' + F''} \left[ (2F + 1)(2F' + 1) \right]^{1/2} \times \sum_j (2j + 1) \left\{ J, I, F \choose j, \ell, j \right\} \left\{ J', I, F' \choose j', \ell', j \right\} T_{j\ell F, J'\ell' F'}^{j'},
\]

where \(\varepsilon\) designates the \(\Lambda\)-doublet parity and \(\{:::\}\) are \(6-j\) symbols.\(^{31}\) For the purposes of the scattering calculation, the irreducible components of the T-matrix of order \(K\) are defined by

\[
\langle J\ell F || T^K || J'\varepsilon' F' \rangle = (2K + 1)(-1)^{-F'} \sum_j \left( -1 \right)^{-j} \left( 2j + 1 \right) \left\{ F, F' \choose \ell, j \right\} \left\{ K, K_j \right\} T_{j\ell F, J'\varepsilon' F'}^{j'},
\]

and, applying equation 7.24,

\[
\langle J\ell F || T^K || J'\varepsilon' F' \rangle = (-1)^{j'-j} \left[ (2F + 1)(2F' + 1) \right]^{1/2} \left\{ J, J' \choose F, F' \right\} \left\{ K, K_l \right\} \langle J\ell F || T^K || J'\varepsilon' F' \rangle
\]

the hyperfine dependent T-matrix elements are equated to the hyperfine independent T-matrix elements. Redefining the hyperfine independent T-matrix elements in terms of a tensor opacity \((P)\), which physically represents the fraction of collisions which lead to a particular inelastic process, yields

\[
P^K_{j\ell, J'\varepsilon'} = \frac{1}{2K + 1} \sum_{\ell' F'} \left| \langle J\ell F || T^K || J'\varepsilon' F' \rangle \right|^2
\]
and the inelastic cross sections (averaged over $M$-degeneracy) are expressed, by imposing Eq. 7.26, as

$$\sigma_{J_F \rightarrow J'_F} = \frac{\pi}{k^3} (2F' + 1) \sum_k \left\{ \begin{array}{ccc} J & J' & K \\ F' & F & I \end{array} \right\}^2 P_{k,F,F'}^K$$

Equation 7.28 is therefore an expression for the $F$ dependent inelastic cross sections from which propensity rules for $\Delta F$ processes can be determined independent of the details of the intermolecular potential.

It has been shown that the magnitude of the tensor opacity decreases sharply with increasing tensor order $K$. Physically, $K$ represents the total amount of angular momentum transferred during the collision. By conservation of angular momentum, the triangle rule

$$K = |J - J'| = |\ell - \ell'|$$

holds for all collisions. Using algebraic expressions for the 6-j symbols, branching ratios for particular allowed $\Delta F$ processes can be determined for a particular value of $K$. Specifically, for OH, a propensity for $\Delta F = \Delta J$ inelastic collisions is predicted. Since the same equations hold for NO, the propensity for $\Delta F = \Delta J$ collisions is expected regardless of the details of the intermolecular potential. Table 7.1 lists the coefficients for the tensor opacities in Eq. 7.28 for the $J=1/2$ and $J=3/2$ states in the three lowest orders of $K$ ($K=0,1,2$). One observes that the $\Delta F = \Delta J$ entries in Table 7.1 are indeed the largest.
Table 7.1. The relative magnitudes of various ΔF cross sections for inelastic collisions involving the J=1/2 and 3/2 levels of NO.
For the purposes of the numerical Bloch equation analysis of the NO-He time resolved data, the 45 individual state-to-state rates can be described by four sets of tensor opacities which govern the A-doublet changing and conserving processes for \( J=3/2 \rightarrow J=3/2 \) and \( J=3/2 \rightarrow J=1/2 \) transitions within the \( |\Omega|=1/2 \) fine structure state. We selected only those opacities of order \( K=1 \) for the sake of the simplest possible model (\( K=0 \) corresponds to purely elastic processes only). Using higher order opacities increases the number of adjustable fit parameters and in diagnostic tests, we found that the addition of more terms yielded inconsistent results for several data sets. Each tensor opacity is related to a base inelastic rate by

\[
R_{J \epsilon \rightarrow J' \epsilon'} = c \epsilon^K_{J \epsilon ightarrow J' \epsilon'}.
\]  

7.31

where \( c \) is a proportionality constant determined by combining Eqs. 4.3 and 7.28. The four base rates given by Eq. 7.31 are then the adjustable fit parameters for the numerical optical Bloch model. From the fitted values of the rates, we calculate hyperfine resolved state-to-state rates by

\[
k_{J' \nu \rightarrow J' \nu'} = (2F' + 1) \sum_K \begin{pmatrix} J & J' & K \end{pmatrix}^2 R_{J \epsilon \rightarrow J' \epsilon'}.
\]

7.32

Inelastic cross sections are then calculated from the pressure dependence of the state-to-state rates by Eq. 5.7.

Two additional assumptions were employed in the fitting routine. First, we assumed that \( e \rightarrow e \) and \( f \rightarrow f \) rates are equivalent, and that \( e \rightarrow f \) and \( f \rightarrow e \) rates are equivalent. This assumption is justified for Hund's case (a) by electronic symmetry arguments.\(^3\) Second, we constrained the \( \Delta J=0 \) inelastic rates between the \( J=1/2 \) levels to be equal to the rates between the \( J=3/2 \) levels, because the A-doublet and hyperfine splittings are very
small compared to $kT$. In reality, these rates may not be equal, but for the purposes of our fit, the $\Delta J=0$ rates in $J=1/2$ did not significantly affect the results for rates involving the $J=3/2$ levels.

7.4 Results and Discussion

Using the numerical Bloch equation analysis routine described above, we fit the six time dependent probe signals simultaneously for the four base rates. Unfortunately, the analysis routine requires that the six probe data files were taken at roughly the same pressure. Coupled with the difficulty of acquiring some of the weaker probe responses, we were able to perform the simultaneous fit at only four different pressures between 1 and 2 mTorr. Probe signals at higher pressures tended to be very weak and noisy, and these data could not be fit consistently. Data at more pressures would be desirable for reducing the statistical uncertainty, but these four pressure points still yielded reliable cross sections. Figure 7.8 shows the pressure dependence of the four base rates, as well as a linear fit of the pressure dependence. Included in the linear fit was the transit rate analysis described in Chapter 6 above, which fixes the zero pressure intercept. The error bars shown in Fig. 7.8 were determined both from the statistical error in the fit and from the large pressure deviations common to these data. Table 7.2 lists the slopes of the pressure dependence for the four base rates, as well as their corresponding cross sections calculated using Eq. 5.7. Employing Eqs. 7.32 and 5.7, we calculated the state-to-state cross sections for all 45 downward cross sections, and using detailed balance (Eq. 2.25) we calculated the 45 upward cross sections. All downward and upward inelastic cross sections for initial states in $J=3/2$ are listed in Table 7.3.

As discussed in Section 7.1.2 above, the near homonuclear character of NO and the conservation of parity during collisions suggest that the dominant propensities for NO-He should be that when $\Delta J=\text{odd}$, the $\Lambda$-doublet state changes and when $\Delta J=\text{even}$, the $\Lambda$-
Figure 7.8. Pressure dependence of the base rates for the $J=3/2 \to J=3/2$ $\Lambda$-doublet conserving (solid circles) and changing (open circles) and the $J=3/2 \to J=1/2$ $\Lambda$-doublet conserving (solid squares) and changing (open squares) processes with linear fits for the pressure dependence.
Table 7.2. Slopes and calculated cross sections (with statistical uncertainties) from the pressure dependence of the four base inelastic rates derived from the fit of the numerical model to the data.

<table>
<thead>
<tr>
<th>Inelastic Process</th>
<th>Rate Constant (MHz/Torr)</th>
<th>Cross Section (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J=3/2, \text{elf} \rightarrow J=3/2, \text{elf} )</td>
<td>18.5±3.0</td>
<td>31.8±5.2</td>
</tr>
<tr>
<td>( J=3/2, \text{elf} \rightarrow J=3/2, \text{fe} )</td>
<td>0.29±0.03</td>
<td>0.50±0.05</td>
</tr>
<tr>
<td>( J=3/2, \text{elf} \rightarrow J=1/2, \text{elf} )</td>
<td>2.29±0.57</td>
<td>3.94±0.98</td>
</tr>
<tr>
<td>( J=3/2, \text{elf} \rightarrow J=1/2, \text{fe} )</td>
<td>3.31±0.72</td>
<td>5.70±1.24</td>
</tr>
</tbody>
</table>
Table 7.3. Tabulated hyperfine resolved inelastic cross sections for initial states in $J=3/2$. 

<table>
<thead>
<tr>
<th>Final State</th>
<th>$F=5/2$</th>
<th>$3/2$</th>
<th>$1/2$</th>
<th>$1/2$</th>
<th>$3/2$</th>
<th>$5/2$</th>
</tr>
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<tbody>
<tr>
<td>$J=3/2$, $f$, $F=5/2$</td>
<td>0.41(0.04)</td>
<td>0.12(0.01)</td>
<td>0</td>
<td>0</td>
<td>7.62(1.25)</td>
<td>X</td>
</tr>
<tr>
<td>$J=3/2$, $f$, $F=3/2$</td>
<td>0.078(0.007)</td>
<td>0.26(0.02)</td>
<td>0.22(0.02)</td>
<td>14.11(2.31)</td>
<td>X</td>
<td>5.08(0.83)</td>
</tr>
<tr>
<td>$J=3/2$, $f$, $F=1/2$</td>
<td>0</td>
<td>0.11(0.01)</td>
<td>0.27(0.03)</td>
<td>X</td>
<td>7.06(1.16)</td>
<td>0</td>
</tr>
<tr>
<td>$J=3/2$, $c$, $F=1/2$</td>
<td>0</td>
<td>7.06(1.16)</td>
<td>X</td>
<td>0.28(0.03)</td>
<td>0.11(0.01)</td>
<td>0</td>
</tr>
<tr>
<td>$J=3/2$, $c$, $F=3/2$</td>
<td>5.08(0.83)</td>
<td>X</td>
<td>14.12(2.31)</td>
<td>0.22(0.02)</td>
<td>0.27(0.03)</td>
<td>0.079(0.007)</td>
</tr>
<tr>
<td>$J=3/2$, $c$, $F=5/2$</td>
<td>X</td>
<td>7.63(1.25)</td>
<td>0</td>
<td>0</td>
<td>0.12(0.01)</td>
<td>0.42(0.04)</td>
</tr>
<tr>
<td>$J=1/2$, $f$, $F=3/2$</td>
<td>5.70(1.23)</td>
<td>2.53(0.55)</td>
<td>0.63(0.14)</td>
<td>0.44(0.11)</td>
<td>1.75(0.44)</td>
<td>3.94(0.99)</td>
</tr>
<tr>
<td>$J=1/2$, $f$, $F=1/2$</td>
<td>0</td>
<td>3.16(0.69)</td>
<td>5.06(1.10)</td>
<td>3.51(0.88)</td>
<td>2.19(0.55)</td>
<td>0</td>
</tr>
<tr>
<td>$J=1/2$, $c$, $F=1/2$</td>
<td>0</td>
<td>2.19(0.55)</td>
<td>3.51(0.88)</td>
<td>5.06(1.10)</td>
<td>3.16(0.69)</td>
<td>0</td>
</tr>
<tr>
<td>$J=1/2$, $c$, $F=3/2$</td>
<td>3.94(0.99)</td>
<td>1.75(0.44)</td>
<td>0.44(0.11)</td>
<td>0.63(0.14)</td>
<td>2.53(0.55)</td>
<td>5.70(1.23)</td>
</tr>
</tbody>
</table>
doublet state is conserved.\(^3\) In addition, the angular momentum recoupling theory in
Section 2.3.2 predicts that \(\Delta F = \Delta J\) processes should be dominant. Inspection of the cross
sections presented in Tables 7.2 and 7.3 show that our results agree with these predicted
propensities. Specifically, from Table 7.2, the \(\Delta J = 0\) \(\text{elf}^\text{conserving cross section of 31.8}
\text{Å}^2\) is nearly two orders of magnitude larger than the \(\Delta J = 0\) \(\text{elf}^\text{changing cross section of 0.50}
\text{Å}^2\). The \(\Delta J = 1\) \(\text{elf}^\text{changing cross section of 5.70 \text{Å}^2}\) is larger than the \(\Delta J = 1\) \(\text{elf}^\text{conserving cross section of 3.94 \text{Å}^2}\), though by less than a factor of two. The possibility
of low energy resonances in these cross sections might complicate the physics of these
processes, however our results clearly indicate that the expected propensities are obeyed at
4.2 K.

James et al. have measured total depopulation cross sections for the \(J = 1/2\) state of
NO in collision with He down to 7 K.\(^4\) Equivalent total depopulation cross sections out of
\(J = 1/2\) can be calculated from our 4.2 K data using the \(\Delta J = 1\) base rates in Table 7.2.

detailed balance, and averaging over the initial and summing over the final \(L\)-doublet states by

\[
\sigma_{J = 1/2 \rightarrow J = 3/2} = \frac{1}{2} \left( \sigma_{1/2, e \rightarrow 3/2, e} + \sigma_{1/2, e \rightarrow 3/2, f} \right) + \frac{1}{2} \left( \sigma_{1/2, f \rightarrow 3/2, e} + \sigma_{1/2, f \rightarrow 3/2, f} \right)
\]

The depopulation cross sections of James et al. down to 7 K are plotted in Fig. 7.9 along
with the 4.2 K cross section from our data. Our 4.2 K value of 9.64 (1.58) \text{Å}^2 shows
satisfactory agreement with the general downward trend in the cross sections of James, et
al., as expected for an upward process as temperature decreases. As the temperature
decreases, there is less kinetic energy available for rotational energy transfer into higher
lying states (see Fig. 2.2). The downward trend of the cross sections in Fig. 7.9 is what
we would expect for a rotational energy gap of \(\sim 5 \text{ cm}^{-1}\).
Figure 7.9. Comparison of total depopulation cross sections for the $J=1/2$ level measured by James et al. (open circles) and determined in this study (solid circle) as a function of temperature. Also included are pressure broadening cross sections measured during this study (solid squares) and those of Willey et al. (open squares).
Figure 7.9 also shows the measured pressure broadening cross sections of Willey. 
et al. as well as broadening cross sections measured during this study. We find that the 4.2 K depopulation cross section is much smaller than the broadening cross section, again suggesting that elastic collisions are playing a dominant role in low temperature broadening. It is interesting to note that at 300 K, the depopulation cross section of James et al. is larger than the pressure broadening cross section, implying that there may be problems with their 300 K measurement. The broadening cross section should set an upper limit on the magnitude of any inelastic cross section. This discrepancy certainly merits further investigation.

In summary, we have demonstrated that we can measure propensities for various inelastic processes involving hyperfine and A-doublet levels in NO with the low temperature millimeter wave double resonance apparatus. These results represent the first direct laboratory observation of such inelastic collisions at low temperatures. We have also successfully developed a numerical model to analyze the double resonance data in the context of the optical Bloch equations and an angular momentum recoupling scheme which allows us to fit for all the possible inelastic processes in the two lowest J states of NO by four adjustable parameters.

References


CHAPTER 8

QUANTUM SCATTERING THEORY CALCULATIONS

8.1 CO-He Diagnostic Calculations

8.1.1 Introduction

As mentioned in Chapter 2 above, PESs have been developed for only the simplest collision systems. As the complexity of a molecule is increased (i.e., a larger number of atoms), the development of molecule-atom or molecule-molecule PESs becomes computationally prohibitive. Therefore, in order to understand low energy collisions of systems for which no PES has been developed, we have performed diagnostic quantum scattering theory calculations using the PES of the simpler CO-He system. In these calculations, we vary physical parameters such as the well depth of the CO-He PES and the rotational energy level spacing of CO to gain a qualitative understanding of low energy scattering processes for different collision systems. Because resonances dominate low energy cross sections, the problem really lies in understanding the behavior of these resonances with respect to the well depth and rotational energy level spacing.

This investigation was inspired by the work of Palma and Green,1 who performed calculations of CO-He scattering with modified versions of the PES of Thomas, et al.2 They investigated the dependence of low energy pressure broadening on the interaction potential well depth by repeating the earlier MOLSCAT calculations of Green3 with the well either halved or removed entirely. For the halved well, they calculated fewer low energy resonances in the broadening cross sections, and these resonances were much smaller in
magnitude than those of the full well calculations. Not surprisingly, the removed well (purely repulsive potential) yielded no resonance structure. While the Palma and Green study was initially an attempt to explain possible disagreements between the best experimental and theoretical results of the time, their findings can be generalized to qualitatively explain the behavior of other collision systems. However, the changes made in the PES were too large to draw any quantitative conclusions about the changed characteristics of the low energy resonances.

In the present investigation, we have performed calculations of cross sections for low energy CO-He collisions, this time using the “XCfit” PES of Le Roy et al. This PES, based on an exchange-coulomb model, was determined from a fit to the experimentally measured infrared ro-vibrational transitions of the CO-He dimer. The XCfit potential was “hard-wired” into the MOLSCAT version 12 computer program instead of entered in an appropriate input file, to preclude interpolation errors sometimes typical of the MOLSCAT program. The $J=1\rightarrow 0$ pressure broadening and shift cross sections as well as various inelastic cross sections were calculated by running MOLSCAT on the Cray T90 at the Ohio Supercomputer Center. The cross sections span energies from 0 to 6 cm$^{-1}$, a range over which the close-coupling approximation is very efficient for CO-He. Cross sections were calculated with an energy resolution of 0.03125 between 0 and 4 cm$^{-1}$ and 0.0625 between 4 and 6 cm$^{-1}$, except in the vicinity of some resonances, for which an even finer energy grid was required. We have completed two investigations thematically similar to the Palma and Green study where, in addition to modifying the depth of the potential well, we altered the rotational constant of CO. These changes were purposefully chosen to be small (on the order of a few percent) so that we could observe corresponding small changes in the energy and magnitude of the resonances in the low energy cross sections with hopes that quantitative information could be extracted. Calculations for normal well depth and rotational constant were performed by Beaky et al. and are shown in Fig. 2.4 above.
8.1.2 Calculations with Modified Well Depth

In order to generalize the CO-He system to other collision systems, we first investigate how the low energy cross sections change as the depth of the attractive well is changed. In practice, we changed the depth of the well by simply changing the overall energy scaling of the entire PES to avoid discontinuities in the surface. We chose to scale the PES by \(+2\%\) and \(-2\%\) to investigate small changes in the cross sections. Figures 8.1 shows a comparison between inelastic and broadening cross sections for normal and increased wells. Figure 8.2 shows a comparison between the same cross sections for normal and decreased wells.

Figures 8.1 and 8.2 show that changing the well depth changes the characteristics of the low energy resonances. When the well depth is increased, as in Fig. 8.1, the resonances shift lower in energy and become greater in magnitude. The energy shifts are uniform for all resonances and are equal to 0.1875 cm\(^{-1}\) (within the resolution of the calculation). The changes in magnitude are greater for resonances at lower energy, with typical increases of \(\sim 15\%-20\%\). In Figure 8.2, we see exactly the opposite behavior when the well depth is decreased. The resonances shift higher in energy by 0.1875 cm\(^{-1}\), and they decrease in magnitude.

8.1.3 Calculations with Modified Rotational Constant

To investigate how the resonances change for different rotational energy level spacings of molecules, we changed the CO rotational constant \((B_r)\), which is normally 1.92265 cm\(^{-1}\). Again, to observe small changes in the cross sections, we changed \(B_r\) by \(+5\%\) and \(-5\%\). Figure 8.3 shows a comparison between the inelastic and broadening cross
Figure 8.1. Calculated CO-He pressure broadening and inelastic cross sections vs energy for normal and 2% increased potential wells.
Figure 8.2. Calculated CO-He pressure broadening and inelastic cross sections vs energy for normal and 2% decreased potential wells.
Figure 8.3. Calculated CO-He pressure broadening and inelastic cross sections vs energy for normal and 5% decreased rotational constant.
Figure 8.4. Calculated CO-He pressure broadening and inelastic cross sections vs energy for normal and 5% increased rotational constant.
sections for normal and decreased $B_e$. Figure 8.4 shows a comparison between the same cross sections for normal and increased $B_e$.

Figures 8.3 and 8.4 show that, like the well depth changes above, changes in the rotational constant alter the characteristics of the low energy resonances. When $B_e$ is decreased, as in Fig. 8.3, some resonances shift lower in energy and become greater in magnitude. Specifically, the pressure broadening resonances at 1.09, 3.16, and 5.50 cm$^{-1}$ and the resonance in the $J=1\rightarrow0$ inelastic cross section at 5.50 cm$^{-1}$ shift by 0.1923 cm$^{-1}$, corresponding to exactly the change in the rotational energy level spacing between $J=0$ and $J=1$. The broadening resonance at 4.69 cm$^{-1}$ shifts by 0.3846 cm$^{-1}$, the change in energy level spacing between $J=1$ and $J=2$. The resonances in the $J=1\rightarrow0$ inelastic and the broadening cross section at 1.6 cm$^{-1}$ are unshifted. The increase in the magnitude of the shifted cross sections is greater at lower energies, with typical increases again of ~15-20% in this range of energies. Figure 8.4 shows that some resonances shift higher in energy and decrease in magnitude when $B_e$ is increased. The energy shifts are equivalent to those in Fig. 8.3.

8.1.4 Discussion

Before describing the specific mechanisms responsible for changes in the energy and amplitude of a resonance, it is necessary to review some fundamental concepts of resonance phenomena. In simplest terms, a resonance occurs at a specific relative kinetic energy of the collision system which is coincident with the excitement of a bound state in the potential well. A simple picture of the excitation of the bound state is shown in Fig. 8.5. The effective potential, $V_{eff}$, is given by

$$V_{eff}(R) = V(R) + \frac{\hbar^2}{2\mu} \frac{\ell(\ell+1)}{R^2}.$$  (8.1)
Figure 8.5. Effective potential as a function of intermolecular separation ($R$) shown with an example of relative kinetic energy ($E$) which excites a quasi-bound state.
where \( V(R) \) is the potential energy at some specific orientation angle of the collision system, \( \mu \) is the reduced mass of the collision partners, and \( \ell \) is their orbital angular momentum. At some specific relative kinetic energy \( E \), there is maximal probability of tunneling through the centrifugal barrier into one of the allowed bound states of the potential well. The energies of the allowed bound states are similar in character to the energy levels of an anharmonic oscillator, but they depend explicitly on the details of the PES, prohibiting generalized predictions.

The simple example shown in Fig. 8.5 illustrates the formation of a "shape" resonance, which, as the name implies, depends only on the geometric shape of the PES. The case shown in Fig. 8.5, where the relative kinetic energy \( E \) is smaller than the centrifugal barrier maximum, is classified as a decaying-orbiting resonance by von Seggern and Toennies.\(^{11}\) It is also possible to form shape resonances at energies just above the centrifugal barrier, whereby the system is weakly coupled to the potential well and resonances are classified as virtual-orbiting.\(^{12}\)

When the wavefunctions of the bound and continuum states represent different internal rotational states, the cross sections exhibit what is known as Feshbach resonances.\(^{13,14}\) In this case, a second order coupling between open channels leads to a "virtual excitation" during the formation of the quasibound state. The net effect of the collision can be either elastic or inelastic. For example, the steps before, during, and after the formation of a Feshbach resonance in CO-He can be

\[
\text{He-CO}(J=0) \rightarrow \text{He-CO}(J=1) \rightarrow \text{He-CO}(J=0) \quad (8.2)
\]

for an elastic collision, or
He-CO\((J=0)\) → He-CO\((J=2)\) → He-CO\((J=1)\)  \hspace{1cm} (8.3)

for an inelastic collision. Since energy and total angular momentum are conserved, any change in the internal rotational state of a molecule is accompanied by a change in the relative kinetic energy and the orbital angular momentum. Erlewein et al., in calculations of \(N_2\)-He inelastic cross sections, show that each resonance is associated with the final value of a particular orbital angular momentum state, suggesting that the resonances are associated with orbiting in the final internal rotational state of the molecule.\(^{15}\)

When we consider the changes in the resonances due to increasing or decreasing the depth of the potential well, as shown in Figs. 8.1 and 8.2, we can understand the energy shifts of all the resonances, which appear to be equivalent, in terms of shifts in the energies of the allowed bound states shown in Fig. 8.5. Increasing the well depth shifts the bound states lower in energy, and subsequently a smaller value of relative kinetic energy is required to excite the quasi-bound state. Figure 8.6 demonstrates this effect schematically. Energy \(E' < E\) represents the relative kinetic energy required to excite a lower energy quasi-bound state.

The increase in the magnitude of the resonances when the well depth is increased can also be understood from the simple picture in Fig. 8.6. We assume that the cross section is proportional to the square of the classical turning point \(r\):

\[
\sigma \propto r^2. \hspace{1cm} (8.4)
\]

At lower kinetic energy \(E'\), the classical turning point \(r'\) is greater than \(r\), and thus the cross section is larger:
Figure 8.6. Two effective potentials for normal (solid line) and increased well depth (dashed line), shown as a function of intermolecular separation ($R$). Relative kinetic energy ($E' < E$) excites a quasi-bound state at classical turning point $r' > r$. 
Similarly, decreasing the potential well will have the opposite effect, where \( r' < r \) and \( \sigma' < \sigma \). While the actual formalism is much more complicated, this simple explanation at least allows us to qualitatively understand the changes in the amplitudes of the resonances.

When the rotational constant of CO is changed, the internal rotational energies of CO are shifted. As mentioned above, Feshbach resonances involve a rotational excitation during the formation of the quasibound complex, therefore changes in the CO rotational energy levels correspond exactly to changes in the energies of the Feshbach resonances. If \( B_r \) is decreased, the energies of the rotational states of CO are decreased, as well as the energies of the Feshbach resonances, as shown in Fig. 8.3. Since the relative kinetic energy required to excite the quasi-bound state shifts lower in energy when \( B_r \) is decreased, we observe the expected increase in the amplitude of the resonance by the same argument presented above.

The \( J=1 \rightarrow 0 \) downward inelastic and the pressure broadening cross sections each exhibit a resonance at 1.6 cm\(^{-1}\) which does not shift when the rotational energy levels of CO are changed. Clearly these resonances do not depend on the internal rotational energy levels of CO for temporary transfer of kinetic energy to rotational energy during the collision, and therefore these resonances are shape resonances. The resonance in the downward inelastic need not rely on couplings to other rotational states because, by conservation of energy, the downward inelastic process are possible at any kinetic energy. Thus, a downward inelastic process can lead to a shape resonance, while resonances in the upward inelastic cross sections are always Feshbach resonances.
8.1.5 Larger changes in well depth and rotational constant

We have shown that small changes of the well depth and rotational constant allow us to observe incremental, yet fundamental and predictable changes in the resonance structure. This leaves open the question of what happens for larger changes in the well depth or $B_r$. Figures 8.7 and 8.8 show the same calculated pressure broadening sections for the cases of well depth increased by 5% and $B_r$ increased by 12%, respectively. Figure 8.7 also shows the same broadening cross sections in Fig. 8.1 (normal well and well increased by 2%), and Fig. 8.8 shows the same broadening cross sections in Fig. 8.4 (normal $B_r$ and $B_r$ increased by 5%) for comparison.

As expected, Fig. 8.7 shows that the resonances continue to uniformly shift lower in energy as the potential well is made deeper. The magnitude of the resonances also become larger, particularly at the lowest energies. Most notable for the 5% increased well depth is the broad resonance at 0.44 cm$^{-1}$, which is one of the most prominent features of the broadening cross sections. In the case of the normal well, this resonance is buried in the “baseline” of the cross sections. In the 2% increased well, it becomes more noticeable, yet not dominant. The behavior of this resonance illustrates the difficulty of preparing a generalized formulation of the behavior of the low energy resonances, in that the mere existence of this particular resonance is hardly predicted in the normal well case.

Another important feature of the resonances in the case of the 5% increased well depth is that when they are shifted lower in energy, they also become narrower. This effect is not obvious in the case of the 2% well depth increase, at least at the resolution of the energy grid used in the calculations. Figure 8.9 shows the same broadening cross sections on an expanded energy axis to illustrate the changes of one particular resonance as the well depth is increased. The resonance at 1.6 cm$^{-1}$ in the normal well case becomes slightly narrower with a 2% increase in the well depth, and close inspection reveals that there may
Figure 8.7. Calculated CO-He pressure broadening cross sections vs energy for normal, 2%, and 5% increased potential wells.
Figure 8.8. Calculated CO-He pressure broadening cross sections vs energy for normal, 5%, and 12% increased rotational constants.
Figure 8.9. Calculated CO-He pressure broadening cross sections vs energy for normal, 2%, and 5% increased potential wells on an expanded energy axis.
be some additional structure to this resonance. For the 5% increased well, it is plainly obvious that there are in fact two resonances instead of one.

The decreased width of the resonances can be understood qualitatively by considering the steady state solutions of tunneling through a square, one-dimensional barrier, an analysis which has also been used to qualitatively define the lifetime of an α-particle in a nucleus. The width of a resonance, \( \Gamma \), as mentioned above is inversely proportional to the lifetime, \( \tau \), of the quasi-bound complex:

\[
\Gamma = \frac{\hbar}{\tau}.
\]  

The lifetime of the quasi-bound state is related to the probability of tunneling, \( T \), through the centrifugal barrier, which is modeled by a simple square potential for the sake of a qualitative analysis, and \( E \), the relative kinetic energy of the collision partners by

\[
\tau = \frac{\hbar}{TE}.
\]  

The tunneling probability \( T \), for a square potential barrier of height \( V \) \((V>E)\) and width \( a \), is

\[
T = \left[ 1 + \frac{\sinh^2 \frac{ka}{4}}{E \left( \frac{1 - \frac{E}{V}}{V} \right)} \right]^{-1}
\]  

where \( \hbar = \sqrt{2\mu(V-E)} \). Substituting Eqs. 8.7 and 8.8 into Eq. 8.6, we obtain

\[
\Gamma = E \left[ 1 + \frac{\sinh^2 \frac{ka}{4}}{E \left( \frac{1 - \frac{E}{V}}{V} \right)} \right]^{-1}.
\]  

For a given \( V \) and \( a \), the resonance width has a functional dependence with respect to \( E \) shown in Fig. 8.10, verifying that resonances at lower energy will have narrower widths.
Figure 8.10. Model functional dependence of resonance width on relative kinetic energy ($E$) relative to the height of a square potential barrier.
Figure 8.8 shows that when the rotational constant is further increased, the resonances shift even higher in energy and become even smaller in magnitude. The only exception concerns the supposed shape resonance in the broadening cross section at 1.6 cm\(^{-1}\). For this particular rescaling of \(B_r\), the shape resonance and the narrow resonance previously at 1.09 cm\(^{-1}\) for the normal \(B_r\) case overlap, creating what appears to be a much larger resonance than expected. This effect is merely a coincidence in the choice of \(B_r\) rescaling, and it is expected that the narrow resonance has shifted higher in energy and lower in magnitude.

8.1.6 Conclusions

The point of this exercise has been to qualitatively predict the general characteristics of low energy resonances in broadening and inelastic cross sections in relation to physically meaningful parameters such as the well depth or rotational energy level spacing. We have found that by introducing incremental changes to these parameters, we can, not only qualitatively, but quantitatively predict the dependence of these resonances on collision energy. Since there are many interesting collision systems for which PESs have not or cannot be developed, a better understanding of the relationship between the resonances and well depth or rotational constant for a known system such as CO-He allows us to predict the behavior of low energy resonances for different collision systems.

For instance, the rotational energy levels of SO\(_2\) are much more closely spaced than those of the lighter CO molecule. Based on the analysis of the calculations where we decreased the rotational constant of CO, we expect that some of the resonances in the SO\(_2\)-He cross sections should be lower in energy and larger than for CO. In addition, there should be many more resonances, since there are many more available open channels in SO\(_2\). Also, additional resonances will appear at higher energies, so long as potential well can support them. Molecules with sparser energy levels, such as H\(_2\)S or H\(_2\)O should
exhibit resonances which are smaller in magnitude and higher in energy. There should be fewer resonances as well, since there are fewer available open channels at low energy. Calculations of low energy H$_2$O-He pressure broadening cross sections indeed show this to be true.$^{17}$

Similarly, we expect collision systems for which the PES has a deeper well, such as CH$_3$F-He or CH$_3$Cl-He should have larger resonances at lower energies. In addition, there should exist more resonances because the deeper well supports more accessible bound states. Both of these systems have potential wells which are 2-3 times deeper than the CO-He well.$^6$ $^{18}$ The deeper well at least partially explains why the experimentally measured broadening cross sections of CH$_3$F-He at the lowest temperatures are significantly larger ($\sim$150-200%) than the CO-He broadening cross sections.$^{19}$

8.2 H$_2$S-He Calculations

8.2.1 Introduction

Until now, the CO-He system was the only collision system for which reliable low temperature pressure broadening and shift cross sections had been both calculated by quantum scattering theory and measured in the laboratory.$^3$ $^7$ $^{10}$ Very recently a new PES for the H$_2$S-He collision system became available, with which we have performed calculations using the MOLSCAT code.$^9$ We have previously measured the H$_2$S-He pressure broadening and shift cross sections for two transitions ($1_{1,0} \leftrightarrow 1_{0,1}$ reported in Chapter 4 above and $2_{2,0} \leftrightarrow 2_{1,1}$) over a temperature range of 1 to 600 K. We have also measured inelastic cross sections, as discussed in Chapter 6. The new H$_2$S-He PES now allows us to compare all of these experimentally measured cross sections with theoretical predictions, which will serve to test the validity of the experimental results, the PES, and the quantum scattering theory.
The $\text{H}_2\text{S}$-$\text{He}$ PES was calculated by Dr. David Woon of the Molecular Research Institute using \textit{ab initio} methods similar to those employed in the development of $\text{H}_2\text{O}$-$\text{He}$ PESs.\cite{woon1,woon2,woon3} The PES was derived using fourth order Møller-Plesset perturbation theory techniques with mixed valence triple-zeta basis functions implemented in the MOLPRO \textit{ab initio} package.\cite{woon4} A second PES was developed from the first by employing a counterpoise correction to offset basis superposition errors.\cite{woon5} A total of 153 potential energy points were computed between 4.5 and 8.5 bohr (1 bohr=0.529177 Å) at 17 different orientations of $\theta$ and $\phi$, defined by a coordinate system where the origin is at the center of mass of $\text{H}_2\text{S}$, the $z$-axis is the symmetry axis, and the $x$- and $y$-axes lie perpendicular to and parallel to the triatomic plane, respectively. For compatibility with the MOLSCAT routines, the PES was fit by the equation

$$V(R,\theta,\phi) = \sum_{\lambda,\mu} V_{\lambda,\mu}(R)\left(1 + \delta_{\mu,0}\right)^{-1}[Y_{\lambda,\mu}(\theta,\phi) + (-1)^\mu Y_{\lambda,-\mu}(\theta,\phi)]$$  \hspace{1cm} (8.10)

where $V_{\lambda,\mu}$ is a radial function, $Y_{\lambda,\mu}$ is a spherical harmonic, and $\delta_{\mu,0}$ is a Kronecker delta function. We used 15 terms for the fit, up to $\lambda=6$ and $\mu=4$, and only even values of $\mu$ were required due to the symmetry of $\text{H}_2\text{S}$. Contour plots of the counterpoise corrected PES are shown in Figs. 8.11 ($\phi=0$) and 8.12 ($\phi=\pi/2$).

Using these new PESs, pressure broadening, pressure shift, and state-to-state inelastic cross sections were calculated by the MOLSCAT program over an energy range of 0.05 to 700 cm$^{-1}$. Two sets of independent calculations were performed for the two nuclear symmetry species of $\text{H}_2\text{S}$ (ortho for the $1_{1,0} \rightarrow 1_{0,1}$ transition and para for the $2_{2,0} \rightarrow 2_{1,1}$ transition). For any given collision energy, at least one closed channel was included to account for possible virtual excitations.\cite{woon6} The close coupling approximation was employed for collision energies less than 50 cm$^{-1}$,\cite{woon7} and the coupled states approximation was used for higher energies.\cite{woon8} The coupled differential equations in the
Figure 8.11. Contour plot of the counterpoise corrected H₂S-He PES at φ=0. Each contour line represents a constant potential energy (in cm⁻¹).
Figure 8.12. Contour plot of the counterpoise corrected H₂S-He PES at $\phi=\pi/2$. Each contour line represents a constant potential energy (in cm⁻¹).
quantum scattering theory were solved for each total angular momentum by implementation of the hybrid modified log derivative-Airy integrator of Alexander and Manolopoulos.27

8.2.2 Results

Figure 8.13 shows the calculated pressure broadening cross sections for the \(1,0,0\rightarrow1,0,1\) transition as a function of collision energy for both the counterpoise corrected and uncorrected PESs. Figure 8.14 shows the pressure shift cross sections for both PESs. As expected, the broadening cross sections display characteristic resonance structure at energies below \(10\,\text{cm}^{-1}\). Above \(50\,\text{cm}^{-1}\), the broadening cross sections begin to increase slightly with increasing energy. The shift cross sections are negative at most energies, and tend to zero with increasing energy above \(10\,\text{cm}^{-1}\).

Figure 8.15 shows the calculated pressure broadening cross sections for the \(2,2,0\rightarrow2,1,1\) transition as a function of collision energy for both PESs, and Fig. 8.16 shows the pressure shift cross sections. These cross sections also have low energy resonances, which do not appear to be as resolvable as those in the \(1,0,0\rightarrow1,0,1\) cross sections. Again, the broadening cross sections slightly increase with increasing energy above \(50\,\text{cm}^{-1}\). The shift cross sections are positive at most collision energies, and they tend to zero with increasing energy. The magnitude of the \(2,2,0\rightarrow2,1,1\) shift cross sections are somewhat larger than those for the \(1,0,0\rightarrow1,0,1\) transition by about a factor of 2 below \(50\,\text{cm}^{-1}\).

In Figs. 8.13 through 8.16, we observe, at collision energies less than \(100\,\text{cm}^{-1}\), that the counterpoise corrected PES yields broadening and shift cross sections that are somewhat smaller in magnitude than those calculated with the uncorrected PES. Also, the low energy resonance structure for the corrected PES is shifted lower in energy and smaller in magnitude. The main reason for these differences is because the counterpoise corrected PES has a shallower attractive well (\(\sim10\%\)) and slightly different angular dependence. The
Figure 8.13. Calculated $\text{H}_2\text{S}$-$\text{He}$ pressure broadening cross sections as a function of collision energy for the $1_{0,0} \leftarrow 1_{0,1}$ transition. Cross sections were calculated using the counterpoise corrected (solid line) and uncorrected (dashed line) PESs.
Figure 8.14. Calculated H$_2$S-He pressure shift cross sections as a function of collision energy for the $1_{0,0}$→$1_{0,1}$ transition. Cross sections were calculated using the counterpoise corrected (solid line) and uncorrected (dashed line) PESs.
Figure 8.15. Calculated H$_2$S-He pressure broadening cross sections as a function of collision energy for the 2$_{2u}$-2$_{1,1}$ transition. Cross sections were calculated using the counterpoise corrected (solid line) and uncorrected (dashed line) PESs.
Figure 8.16. Calculated H₂S-He pressure shift cross sections as a function of collision energy for the 2₂₀←2₁₁ transition. Cross sections were calculated using the counterpoise corrected (solid line) and uncorrected (dashed line) PESs.
"correct" characterization of the PES should lie somewhere between the uncorrected and corrected versions. 28

Figure 8.17 shows several selected inelastic cross sections for the ortho species as a function of energy calculated using the corrected PES. These particular state-to-state cross sections are associated with inelastic processes involving the $l_{1,0} \leftarrow l_{0,1}$ transition. The downward $l_{1,0} \rightarrow l_{0,1}$ cross section has a prominent narrow resonance at 0.6 cm$^{-1}$, which corresponds to a resonance in the $l_{1,0} \leftarrow l_{0,1}$ pressure broadening cross sections. Below 3 cm$^{-1}$, the downward cross sections become very large, and down to 0.05 cm$^{-1}$, the minimum energy in the calculations, there is no evidence that the cross section will turn over and tend toward zero. The various upward inelastic cross sections in Fig. 8.17 have a low energy threshold imposed by the conservation of energy. Of these upward cross sections, only the $l_{1,0} \leftarrow l_{0,1}$ cross section has a significant resonance, which is near 6 cm$^{-1}$ and corresponds to a small, broad resonance in the pressure broadening cross section.

8.2.3 Discussion

In Figs. 8.13 and 8.15, we observe a fairly sparse low energy resonance structure in the broadening cross sections, and that resonances exist only at energies below 5 cm$^{-1}$. By contrast, for the CO-He system, previous calculations have predicted more and larger resonances which extend higher in energy than those in the H$_2$S-He cross sections. Figure 8.18 shows a comparison of the CO-He ($J=1 \leftarrow 0$) and H$_2$S-He ($l_{1,0} \leftarrow l_{0,1}$, from the counterpoise corrected PES) pressure broadening cross sections as a function of energy. The well depths of the CO-He and H$_2$S-He PESs are nearly equal in magnitude (~23 cm$^{-1}$). Therefore, based on generalizations inferred from the CO-He diagnostic calculations in the previous section, the sparser resonance structure in the H$_2$S-He cross sections must be due to the sparser rotational energy level spacing of H$_2$S.
Figure 8.17. Calculated H$_2$S-He state-to-state cross sections involving the $l_{1,0}$ and $l_{0,1}$ rotational levels as a function of collision energy, calculated using the counterpoise corrected PES only.
Figure 8.18. Comparison of the CO-He ($J=1\leftarrow0$, dashed line) and H$_2$S-He ($1_{1,0} \leftarrow 0_{0,1}$, solid line) pressure broadening cross sections as a function of energy.
The temperature dependence of these various H₂S-He were determined by numerically integrating the cross sections over energy, weighted by the Boltzmann factor, as shown in Eq. 2.17 above. The calculated temperature dependent cross sections, for both PESs, are then compared to experimental values. Figure 8.19 shows the comparison between calculated and measured pressure broadening and shift cross sections for the \( l_{1,0} \rightarrow l_{0,1} \) transition. Figure 8.20 shows the same calculated and measured cross sections for the \( 2_{2,0} \rightarrow 2_{1,1} \) transition. Figure 8.21 shows the comparison between various calculated state-to-state inelastic cross sections involving the \( l_{1,0} \) and \( l_{0,1} \) rotational levels (counterpoise corrected PES only) and the inelastic depopulation cross sections from Chapter 6.

The experimentally measured and theoretically predicted pressure broadening and shift cross sections show satisfactory agreement over a restricted range of temperatures. In all cases, the cross sections calculated using the counterpoise corrected PES are in better agreement with the experimental data at lower temperatures than those calculated by the uncorrected PES. For broadening cross sections above 20 K, the measured and predicted values for both transitions agree very well. Above \(~450\) K, there appears to be some deviation between the experiment and theory, but this deviation is related to extrapolation errors for the high energy cross sections. MOLSCAT calculations for energies above 700 cm\(^{-1}\) are computationally too expensive, requiring more than 100 open channels. Simple tests show that the value of the cross sections at 1000 cm\(^{-1}\) still have a significant impact on the temperature dependent cross sections between 400 and 600 K. For the shift cross sections of both transitions, agreement between experiment and theory is satisfactory above 20 K. Because the measured shift cross sections are close to zero and typically have larger statistical errors, this comparison does not provide as good a basis for evaluating the quality of the PES as the broadening cross sections.
Figure 8.19. Comparison of experimentally measured pressure broadening (solid circles) and pressure shift (open circles) cross sections with thermally averaged calculated cross sections as a function of temperature for the $1_{0.0} \leftarrow 1_{0.1}$ transition. Cross sections were calculated using the counterpoise corrected (solid line) and uncorrected (dashed line) PESs.
Figure 8.20. Comparison of experimentally measured pressure broadening (solid circles) and pressure shift (open circles) cross sections with thermally averaged calculated cross sections as a function of temperature for the $^2\Sigma^+_{0^+} - ^2\Pi_{1/2}$ transition. Cross sections were calculated using the counterpoise corrected (solid line) and uncorrected (dashed line) PESs.
Figure 8.21. Comparison of experimentally measured inelastic depopulation cross section for $1_{1,0} \rightarrow 1_{0,1}$ transition (solid circles) with thermally averaged calculated state-to-state cross sections as a function of temperature, calculated using the counterpoise corrected PES only.
However, at the lowest temperatures, there is significant disagreement between the predicted and measured broadening and shift cross sections for both transitions. The calculated broadening cross sections increase rapidly below 20 K because of the influence of the low energy resonances. At the lowest temperatures, the calculated broadening cross sections are at least a factor of 5 larger than the measured cross sections. The predicted shift cross section for the $1_{1,0} \rightarrow 1_{0,1}$ transition become positive below 10 K, where the measured cross sections are negative at all temperatures covered in the experiment. The predicted shift cross section for the $2_{2,0} \rightarrow 2_{1,1}$ transition, like the broadening cross sections, also becomes quite large at the lowest temperatures.

If we believe the experimentally measured broadening and shift cross sections, then we must question some element of the calculations to explain the low temperature deviation between experiment and theory. We are confident that the PES has been properly fit and that the calculations, which show good convergence, are being done correctly. Since the deviation is caused by the low energy resonances in the cross sections, we must then ask whether the problem is due to the quality of the PES or if there is something fundamentally incorrect in the formulation of low energy broadening and shift cross sections.\textsuperscript{29} Since similar, though smaller, deviations have been determined in the case of CO-He, the ultimate question revolves around whether such large, very low energy resonances and cross sections with large, low energy “baselines” are physical. Answering that question would require a fundamental reexamination of the theoretical formulation of low energy broadening, which is beyond the scope of this dissertation.

In Fig. 8.21, we observe problems with the agreement of the predicted and experimental inelastic cross sections. Below 10 K, the only state-to-state cross sections which contribute to the depopulation cross section are those due to the downward $1_{1,0} \rightarrow 1_{0,1}$ and the upward $1_{1,0} \leftarrow 1_{0,1}$ processes. At these temperatures, Eq. 6.8 states that the depopulation cross section is simply a sum of the $1_{1,0} \rightarrow 1_{0,1}$ and $1_{1,0} \leftarrow 1_{0,1}$ cross sections.
However, it is clear that a sum of these two predicted cross section yields depopulation cross sections much larger than those measured experimentally. Like the broadening cross sections, resonances at the lowest collision energies in the $1_{1,0} \rightarrow 1_{0,1}$ cross sections in Fig. 8.17 are to blame for this deviation. Again, the question remains as to whether such increasing low energy inelastic cross sections are physical.

Based on the principle of detailed balance (Eq. 2.25) and Eq. 6.8, we can plot what we might expect for the low temperature $1_{1,0} \rightarrow 1_{0,1}$ and $1_{1,0} \leftarrow 1_{0,1}$ state-to-state cross sections from the experimental depopulation cross sections below 10 K. Figure 8.22 shows these experimental state-to-state cross sections along with the same theoretical predictions from Fig. 8.21. By making this comparison, we observe that the predicted upward $1_{1,0} \leftarrow 1_{0,1}$ cross sections are not significantly different than the experimental values, while the major problems appear for the downward $1_{1,0} \rightarrow 1_{0,1}$ cross sections.

In conclusion, we cannot be certain why there are such significant low temperature deviations between the predicted and measured cross sections involving H$_2$S-He collisions. Thachuk, et al. discuss four possible sources of the disagreements between predicted and measured low temperature CO-He broadening and shift cross sections. First, there could be problems with the quality of the PES. In the case of H$_2$S-He, the PES used in our calculations is the first ever developed for this collision system, so it would not be surprising, given the long history of the development of simpler CO-He PESs, that this PES may have some minor flaws. Second, there could be problems with the actual MOLSCAT calculations. As mentioned above, though, we believe that the PES has been properly fit by Eq. 8.10 and that the calculations, which show good convergence, are being done correctly. Third, the application of kinetic theory to the broadening and shifting of spectral lines may be inadequate for collision processes at the very lowest energies. Given the similar low temperature disagreements between experiment and theory in the CO-He and H$_2$S-He studies, this may be a reasonable argument, however, to support the claim.
Figure 8.22. Comparison of predicted $1_{1,0} \rightarrow 1_{0,1}$ (solid line) and $1_{1,0} \leftarrow 1_{0,1}$ (dashed line) inelastic cross sections with the $1_{1,0} \rightarrow 1_{0,1}$ (solid circles) and $1_{1,0} \leftarrow 1_{0,1}$ (open circles) cross sections calculated from the depopulation cross sections at temperatures below 10 K.
would require a careful reexamination of pressure broadening theory, which, again, is beyond the scope of this dissertation. Fourth, there could be problems with the experiment. It has been suggested that the most crucial source of error is the transpiration correction employed in our low temperature pressure measurements, which may be incorrect for the conditions of these experiments. However, an incorrect transpiration correction, which depends non-linearly on temperature and cell pressure, would then cause the broadening, shift, and inelastic data to exhibit non-linear pressure dependence, which we do not observe. In any case, the disagreement between experiment and theory in the lowest temperature cross sections certainly merits further investigation in other collision systems.

References


CHAPTER 9

CONCLUSIONS

With the experimental and theoretical investigations presented in this dissertation, we have made significant steps toward a more complete understanding of RET processes, particularly those which occur at low temperatures. Specifically, the marriage of time resolved double resonance methods with the collisional cooling technique has enabled us to directly measure inelastic collision cross sections for low temperature molecules in the gas phase. These experiments, coupled with previous and ongoing low temperature pressure broadening measurements, provide stringent diagnostics of the quality of \textit{ab initio} PESs as well as crucial tests of the low energy quantum scattering theory. The main accomplishments of this work are summarized below.

First, we have investigated the transition between ambient and low temperature collision processes by measuring the temperature dependence of pressure broadening parameters for collisions of SO$_2$ and H$_2$S with N$_2$, O$_2$, H$_2$, and He. We have found that the foreign gas broadening of SO$_2$ follows the qualitative predictions of semiclassical, Anderson-like theories over a temperature range from 90 to 500 K, obeying the power-law temperature dependence of Eq. 4.7. Similarly, temperature variations of N$_2$, O$_2$, and H$_2$ broadening parameters of H$_2$S also obey Eq. 4.7. However, the H$_2$S-He broadening parameters deviate from the power-law temperature dependence at relatively high temperatures (~300 K). Further investigation of the low temperature H$_2$S-He broadening
cross sections show the onset of quantum resonance phenomena, associated with the formation of quasibound complexes, at temperatures below 20 K.

Second, we have developed a millimeter wave double resonance system used in conjunction with a LHe cooled collisional cooling cell. This system has yielded the first direct measurements of low temperature rotationally inelastic collision cross sections of gas-phase molecules in an equilibrium environment. In diagnostic measurements with the CH$_3$F-He system, we have observed that the transient absorption of coherent radiation must be properly modeled so that accurate inelastic cross sections can be extracted from the time resolved data. From measurements of total depopulation cross sections of H$_2$S-He between 1 and 40 K, we have investigated the relative contributions of inelastic and elastic collisions in low temperature pressure broadening cross sections. We have also observed propensities for hyperfine and $\Lambda$-doublet changing or conserving inelastic collisions in the NO-He system at 4.2 K.

Third, we have completed a series of quantum scattering calculations of pressure broadening, pressure shift, and state-to-state inelastic cross sections at low collision energies. Using a PES for the CO-He system, we have performed diagnostic calculations in order to generalize the results from CO-He scattering to systems for which no PES has been calculated. By changing the well depth of the PES and the rotational constant of CO, we are able to make qualitative and quantitative predictions of the behavior of resonances in the low energy cross sections. Using a new PES for the H$_2$S-He system, we have calculated cross sections which can be compared directly to experimental results. While the predicted cross sections agree with the measured cross sections at most temperatures, there is significant deviation at the lowest temperatures. Given similar deviations in comparisons of measured and calculated CO-He broadening and shift cross sections,\textsuperscript{1,2} we believe that there may be problems with the definitions of broadening and inelastic cross sections as provided by scattering theory for the lowest collision energies.
Though we have made a great deal of progress, the study of low temperature RET is only just beginning. Our low temperature double resonance system is applicable to many other collision systems, and future directions for this experiment should involve measuring inelastic cross sections using a variety of interstellar molecules. At the top of the list of collision systems to investigate is CO-He, both because of its importance in the interstellar medium and because CO-He quantum scattering calculations have already been completed, allowing us to compare experimental and theoretical results. Measurements of CO-He inelastic cross sections may help explain existing disagreements between measured and predicted low temperature broadening cross sections. Two other interstellar molecules, CH$_3$OH, which is an interstellar maser$^3$, and H$_2$CO, which is observed in anomalous absorption$^4$, can be easily studied by the double resonance system, and it is possible we can gain better insight into some interstellar phenomena by measuring low temperature inelastic cross sections for these molecules.

Another future direction for the double resonance experiment is to employ H$_2$ as a buffer gas in the collisional cooling cell. Pressure broadening and shift cross sections have already been measured between 8 and 600 K for several molecules (CO, H$_2$S, and CH$_3$F)$^5$-$^7$ in collision with normal H$_2$. A parahydrogen converter can be constructed so that we can compare collisions of molecules with para H$_2$ and normal H$_2$. It is believed that para H$_2$ collisions should behave similarly to He collisions.$^8$ Measurements of rotationally inelastic collisions of molecules with H$_2$ are more relevant to interstellar processes than collisions with He because H$_2$ is by far the most dominant interstellar molecule.

References


LIST OF REFERENCES
(in alphabetical order)


CRC Handbook of Chemistry and Physics, 62nd ed. (CRC Press, Boca Raton, FL, 1982).


J. M. Hutson and S. Green, MOLSCAT computer code. Version 12 (1993), distributed by Collaborative Computational Project No. 6 of the Science and Engineering Research Council (UK).


R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).


