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ELECTRON SPIN RESONANCE STUDIES OF HYDROGEN AND DEUTERIUM ATOMS IN KRYPTON-HELIUM CONDENSATES

A Dissertation
Presented to the Faculty of the Graduate School
of Cornell University
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by
Ethan Paul Bernard
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ELECTRON SPIN RESONANCE STUDIES OF HYDROGEN AND DEUTERIUM ATOMS IN KRYPTON-HELIUM CONDENSATES

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Cornell University 2009

Krypton-helium condensates are formed by directing a jet containing krypton and helium gases into the surface of superfluid helium. The resulting condensate is a gelatinous aggregate formed of compact spheroidal krypton nanoclusters containing approximately 1000 atoms each. When hydrogen is added to the gas mixture and the jet is passed through an electrical discharge immediately prior to condensation, the resulting gel contains stabilized atomic hydrogen radicals in concentrations as high as $10^{19}$ cm$^{-3}$. We show using continuous wave electron spin resonance (ESR) that the stabilized atomic hydrogen is predominantly located on the surfaces of the krypton nanoclusters. Two-pulse electron spin resonance envelope modulation (ESEEM) studies of similarly condensed deuterium atoms indicate that they are similarly located. Modeling of the dipolar broadening of the continuous wave ESR spectra shows that the average krypton cluster is no larger than 4 nm in diameter and suggests that no more than one radical can be stabilized on each facet of the krypton clusters. Specialized microwave resonators and a scheme for quantifying electron spins using longitudinally detected ESR (LODESRS) are also discussed.
BIOGRAPHICAL SKETCH

Ethan Bernard was born to loving parents Lois and Ed in 1977. He soon wanted to know how everything worked, and was fortunate to have a father that did. He learned to design and build things under time and material constraints by “playing Legos” with his brother David. Painfully shy through high school, he spent much of his time tinkering with gadgetry in the family garage and with computers alongside his friend Kris Rosenberg. He changed his major to physics in his fourth year at Oregon State University and benefitted tremendously from the quality of their “Paradigms in Physics” program. It was there while collaborating with David Vediner that he discovered the joy and importance of teamwork in the process of understanding science. He went to graduate school intending to become a physics professor but has since learned the futility of planning the distant future so specifically.
To all who have taught me. Thank you for your patience and generosity.
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This work would not have been possible without the expertise and generosity of many people.

David Lee was a thoughtful and caring mentor who brought optimism to our group and the wisdom and experience to justify it. He worked hard to maintain funding and eagerly discussed new ideas. Vladimir Khmelenko developed much of the equipment and techniques needed to form impurity-helium condensates, including the insert shown in chapter 1 and most of the resonant microwave cavity described in chapter 6. He was a gentle teacher and effective coworker who shared his knowledge generously. Peter Borbat designed and built most of the microwave section of the pulse ESR spectrometer. He was always available for consultation and happy to bring his expertise in ESR and microwave techniques to bear on any problem. Roman Boltnev produced much of the data and analysis of the CW ESR work in chapter 2 and also collaborated on the x-ray project. Valery Kiryukhin and Nina Krainyukova lead the experimental and theoretical portions of the x-ray work discussed in chapter 1. Sergey Kiselev preceded me as graduate student and laid much of the foundation for the cryostat setup and the CW ESR experiments.

Jack Freed taught an excellent class in magnetic resonance and loaned us the (expensive) TWT amplifier used in the pulse spectrometer. Jeevak Parpia loaned us equipment including the sampling scope (with manuals!) used in the pulse spectrometer. Jarno Jarvinen and Carley Paulsen brought brains and youthful spirit to our lab, engaged us in vigorous discussions of physics, and piloted the beer drinking project. My committee members Carl Franck and Jim Sethna posed thoughtful A-Exam questions and gave constructive criticism of this thesis. Eric Smith shared his expertise in low temperature techniques and troubleshooting. Chris Henley guided my thinking about exchange interactions. Stan Carpenter, Bob Kenyon, Barry Robinson, John Sinnott and the other
Clark technical staff offered much good advise and kept things running smoothly. Dave Wise made many quartz tubes for our condensation inserts. Bob Snedeker taught me to fear communism and machine parts. Jeff Koski’s fine craftsmanship of the ESR and x-ray condensation inserts showed us why some jobs are best left to professionals.

I have enjoyed the camaraderie and support of many friends in Ithaca and am especially grateful to my housemates Marko Nania and Andrew Fefferman who sympathetically toiled at their own physics doctorates. NASA funded me as part of our group for three years and NSF supported us subsequently. Teaching assistantships at Cornell, an adjunct appointment at Wells college and my generous parents allowed for enough savings to support my final two years of pro bono work in the lab.
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CHAPTER 1

KRYPTON-HELIUM CONDENSATES

Impurity-helium condensate (IHC) is formed when a jet containing a mixture of helium and one or more impurity gases is directed into the surface of superfluid helium [1]. The impurities are a small fraction (0.1–5%) of the gas mixture, and are restricted to gases with boiling temperatures below 120 K. The jet cools as it approaches the superfluid helium, and the impurities freeze and condense into a low density gel that sinks (except in the case of H₂) into the liquid helium. The gas mixture cools from above 100 K to the 1.5 K temperature of the superfluid helium in about 1 ms as it crosses the 2 cm distance from the jet orifice to the liquid surface. The superfluid helium is maintained at 1.5 K by forcing it to boil under vacuum. Gels have been condensed from HD, D₂, Ne, N₂, O₂, Ar and Kr. X-ray scattering and ultrasound absorption measurements show the gels to be loose aggregates of clusters with porosities of 90–99% and a wide range of pore sizes extending up to at least 860 nm. The clusters are compact spheroids 5–10 nm in diameter and contain enough spatial order to produce broad Bragg peaks. In the smallest of these clusters approximately 25% of the atoms are in contact with the helium. The surface of the clusters attracts helium through van der Waals forces and one or two layers of helium solidifies on the cluster surfaces. Figure 1.1 shows two examples of impurity-helium condensates.

The condensates can also be formed from gas mixtures containing atomic radicals. These are made by passing a gas mixture containing molecular dimers through a radio frequency electric discharge immediately prior to condensation. Figure 1.2 shows the design of the apparatus used to dissociate and condense dissociated gas mixtures. Many (most, in the best cases) of the resulting radicals become immobilized in the molecular impurity composing the condensed gel. In gels containing the largest concentrations of
Figure 1.1: A composite image of impurity-helium condensates. The beaker on the left contains a sample condensed from a gas mixture of hydrogen, deuterium and helium in the proportions 1:4:100. The sample on the right was condensed from a mixture of deuterium, krypton and helium in the proportions 1:5:1200. The sample on the right is viewed from below the surface of the liquid helium, which obscures the conical portion of the collection beaker. Note the higher optical density of the krypton containing sample. These samples were condensed over a period of ten minutes, as were all the samples discussed in this thesis.
Figure 1.2: The cryostat insert used to produce radical-containing impurity-helium condensates. A gas mixture is supplied through the top of the center capillary of the quartz insert. It travels down the capillary and through the region between the discharge electrodes, where any molecules in the gas are dissociated. The gas then exits the 0.8 mm diameter orifice of the quartz capillary and strikes the surface of the superfluid helium in the quartz beaker. The electrodes are cooled by liquid nitrogen that fills the open space in the quartz insert. The vacuum can insulates the insert from the cold helium gas in the cryostat. This design is by Vladimir Khmelenko.
atomic radicals, the chemical energy density in the mass of the condensed impurity is comparable to dynamite [2].

The exceptionally high thermal conductivity of superfluid helium stabilizes the gels against the heat produced by the occasional recombination of atomic radicals within the clusters. If the superfluid is drained from the gels, heat from a recombination event speeds the diffusion of nearby atomic radicals, encouraging further recombination. The drained gel destroys itself in a series of small explosions over the course of a minute. If superfluid is removed from a gel without atomic radicals, surface tension slowly pulls the clusters together into a fine powder. The energy stored in the surface tension of the as-prepared gels is 2–5 times smaller than the latent heat of fusion of the bulk impurity.

This thesis concerns samples condensed from dissociated gas mixtures of H₂, Kr and He, with the ratio of krypton to helium fixed at 1:200. We have discovered that krypton is exceptionally effective at concentrating and stabilizing atomic hydrogen and deuterium. The concentration of stabilized hydrogen radicals in hydrogen-krypton condensates is about 10¹⁹ cm⁻³—higher than in any other macroscopic material. For comparison, this is 40% of the density of an ideal gas at standard pressure and temperature. This concentration can be maintained indefinitely provided that the samples remain immersed in superfluid helium. This thesis focuses on the question of the location of the hydrogen atoms relative to the krypton clusters in the sample and the overall scale of the clusters. Two pieces of evidence lead us to conclude that most of the atomic radicals are adhered to the surfaces of the krypton clusters. First, the spectroscopic parameters of the continuous wave electron spin resonance lines of our hydrogen atoms do not match those published for hydrogen atoms within bulk krypton. Second, pulse ESR measurements show a degree of magnetic interaction between the electron spins of the deuterium atoms and the nuclear spins of ⁸³Kr that is consistent with the positioning of the atoms at the
surface of the clusters. Unfortunately, the complication of nuclear quadrupole interactions prevents this method from definitively excluding the possibility that most of the atoms are stabilized within the bulk of the clusters. The dipolar broadening of the CW ESR lines is unusually small for the concentrations of electron spins within our samples; this leads us to conclude that the typical cluster size is at most 20 Å in radius, somewhat smaller than previously measured [3].

1.1 X-ray scattering studies krypton-helium condensates

Our survey of the structures of noble gases condensed by the IHC method included x-ray measurements of a sample condensed from a gas mixture of 0.5% krypton in helium [3]. The sample remained continuously submerged in superfluid helium following preparation and throughout the x-ray measurements. A measure of the x-ray absorption of the sample indicated an overall density of $3 \cdot 10^{19}$ atoms / cm$^3$, which is about 700 times less than the density of bulk krypton. However, this measure assumed that the portion of the sample beaker traversed by the x-ray beam was fully occupied by the sample. The Kr density could be many times higher if the sample only partially filled the beaker. The x-ray powder patterns from this sample showed strongly broadened Bragg peaks indicating that the krypton possessed a strongly truncated or distorted crystal structure.

The patterns were fit under the assumption that the sample was composed of krypton clusters with internal atomic structures that minimized or nearly minimized their configurational energies. In other words, we assumed that the clusters were annealed as they condensed in the cooling gas jet. The optical spectra of the analogous jets of atomic nitrogen samples indicate that clusters do form within the jet [4].

Bulk noble gases (except helium) condense to FCC structures when fully annealed
at low temperature, although the HCP phase is only slightly higher in energy. For clusters smaller than $\sim 10^4$ particles, the surface energy contributes substantially to the overall structure and the surfaces of the clusters assume faceted spheroidal shapes that maximize the number of nearest neighbor interactions among their atoms. Clusters possessing "magic numbers" of atoms corresponding to completely filled surface layers are especially stable and have been observed to dominate the distribution of clusters in many systems [5]. For the smallest noble gas clusters, of several hundred atoms each, the lowest energy configurations are decahedral and icosahedral forms. These have a five-fold symmetry achieved by the intersection of five regions of FCC structure at five symmetrically positioned twinning faults [6, 7]. The energy cost of these faults is more than compensated for by the presentation of low energy FCC(111) facets at the cluster surfaces. These structures are also seeds for larger structures formed by adding FCC
Table 1.1: Distribution of the hico clusters from the best fit to the powder scattering data. The cluster radius is that of a sphere of the density of bulk krypton containing the indicated number of atoms.

<table>
<thead>
<tr>
<th>Fraction of clusters</th>
<th>Atoms per cluster</th>
<th>Cluster radius in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24</td>
<td>861</td>
<td>21.3</td>
</tr>
<tr>
<td>0.24</td>
<td>1343</td>
<td>24.7</td>
</tr>
<tr>
<td>0.24</td>
<td>1975</td>
<td>28.1</td>
</tr>
<tr>
<td>0.28</td>
<td>2777</td>
<td>31.4</td>
</tr>
</tbody>
</table>

or HCP layers to the facet surfaces; these larger structures are theoretically predicted to minimize the configurational energy up to $10^4$ atoms.

A library of scattering patterns was computed from the magic numbered clusters of the icosahedral (ico), decahedral (dec), and hexagonally covered icosahedral (hico) forms and used to fit the powder scattering data. The best fit was achieved using a distribution of four cluster sizes of the hico form, as shown in figure 1.3. The distribution of sizes is listed in table 1.1. These results indicate that krypton-helium condensates, like other impurity-helium condensates, are loose aggregates of compact spheroidal clusters. Fitting the scattering data with energetically unfavorable cluster structures, such as spherical FCC particles containing stacking faults, produced very poor results. This is strong evidence that the krypton atoms coalescing within the helium jet have sufficient time to settle into low energy configurations—an important point to consider when thinking about the structure of clusters containing krypton and hydrogen atoms.
CHAPTER 2

CW ESR MEASUREMENTS OF HYDROGEN AND DEUTERIUM ATOMS

This thesis concerns krypton-helium condensates doped with hydrogen and deuterium atoms. We call these by various names such as "radicals", "unpaired atoms" or just "atoms", and will make a point of specifically indicating if they are part of a molecule. Unlike their corresponding molecular dimers, H and D atoms each have an unpaired electron spin. The electron spin coupling to magnetic fields is more than 600 times larger than the strongest nuclear couplings.

The electron occupies an S orbital that has a density maxima the nucleus. This leads to the "Fermi contact term" A that couples the orientation of the spin 1/2 electron to the orientation of the spin 1/2 proton or the spin 1 deuteron. Magnetic fields also couple to the orientation of the electrons and protons, lowering their energy when their magnetic dipole moments align with the magnetic field. For protons, the angular momentum aligns with the magnetic moment; for electrons and $^{83}$Kr (among a few other curious nuclei), the directions of $\vec{\mu}$ and $\vec{S}$ or $\vec{I}$ are antiparallel. For the magnetic fields of approximately 3000 G used in our X-band electron spin resonance experiments, the coupling energies order as electron-field coupling $\gg$ electron-nucleus coupling $\gg$ nucleus-field coupling. The Hamiltonian of an electron in a magnetic field and isotropically coupled to a single nucleus is

$$\mathcal{H} = (g_e\mu_B m_S - g_I\mu_I m_I)B_0 + 2\pi\hbar A \vec{I} \cdot \vec{S}$$  \hspace{1cm} (2.1)

where $B_0$ is the magnetic field, $\mu_B$ is the Bohr magneton, $m_S$ and $m_I$ are the respective projections of the electronic and nuclear angular momenta along the field, and $g_e$ and $g_I$ are the respective $g$-factors of the electron and the nucleus. Note the nonstandard


\[ d = \frac{1}{2}, \frac{1}{2} \]
\[ c = \cos \theta \left[ \frac{1}{2}, -\frac{1}{2} \right] + \sin \theta \left[ -\frac{1}{2}, \frac{1}{2} \right] \]
\[ b = -\frac{1}{2}, -\frac{1}{2} \]
\[ a = \cos \theta \left[ -\frac{1}{2}, \frac{1}{2} \right] - \sin \theta \left[ \frac{1}{2}, -\frac{1}{2} \right] \]

Figure 2.1: The hyperfine structure of hydrogen, as calculated from equation 2.3. The arrows show the allowed excitations under 9 GHz microwave radiation with field \( \vec{B}_1 \) perpendicular to \( \vec{B}_0 \).

definition of the nuclear \( g \)-factor relative to the Bohr magneton:

\[ g_e = 2 \frac{\mu_e}{\mu_B} \quad g_I = 2 \frac{\mu_p}{\mu_B} \quad (2.2) \]

where \( \mu_e \) and \( \mu_p \) are the respective magnetic moments of the electron and nucleus. Note also that \( g_e \) is sometimes just called \( g \) and that the \( g \)-factors and magnetic moments of the particles are positive with this writing of the Hamiltonian.
For hydrogen atoms, the electron-field and electron-nucleus couplings give rise to the hyperfine structure shown in figure 2.1. This is derived in many quantum mechanics texts and has a structure given by the Breit-Rabi equation [8]:

\[ E(F, M) = \frac{-hA}{4} - \mu_B g_f MB_0 \pm \frac{hA}{2} \sqrt{1 + 2Mx + x^2} \]  \hspace{1cm} (2.3)

where \( E \) is the energy of the level, \( F \) is the total angular momentum quantum number of the hydrogen atom, \( M \) is the projection of \( F \) along the magnetic field and

\[ x = \frac{(g_I + g_e) \mu_B B_0}{hA} \] \hspace{1cm} (2.4)

The eigenstates of the coupled system indicated by \( F \) and \( M \) can be expressed in terms of the states of the uncoupled spins, as is shown in figure 2.1. The mixing angle \( \theta \) that determines the admixtures of the states is given by the relation \( \tan(2\theta) = 1/x \).

When an ensemble of hydrogen atoms thermalizes within a magnetic field, their level populations become unequal. Our samples are held at 1.35 K while a \( B_0 \) field of 3000 Gauss is adjusted to allow one of the two transitions under 9 GHz microwave radiation. Under these conditions the populations of the “a” and “b” levels exceed those of the corresponding “d” and “c” levels by 16%. Applying microwave radiation with a field \( \vec{B}_1 \) perpendicular to \( \vec{B}_0 \) stimulates transitions that equalize the level populations, resulting in a net absorption of microwaves. Most CW ESR experiments, including this one, use a microwave resonator such as a symmetric cavity to increase the microwave amplitude and enhance absorption. We measure our samples with the standard CW ESR technique in which the microwave frequency is held constant while \( B_0 \) is slowly swept. A small 100 kilohertz modulation field is applied in addition to \( B_0 \); this causes changes in the microwave absorption that are detected with a lock-in amplifier to reveal the derivative of the absorption line with respect to \( B_0 \). All the spectra described here are measured with a microwave power too small to noticeably affect the level populations.
and with a modulation field much smaller than the measured linewidths. An extensive description of the classic CW ESR experiment is given by Poole [9].

The quantity of state mixing due to the hyperfine coupling $A$ in our experiments is indicated by $\sin(\theta)$ and $\cos(\theta)$, as shown in figure 2.1. In our system $\theta \simeq 0.07$. The mixing has two effects on the CW experiment: The obvious splitting of the resonance lines by approximately 508 Gauss and a reduction of one of the dipolar line broadening mechanisms, as is discussed in chapter 5. The magnetic moment of the states is almost entirely due to the electron spin. In states "b" and "c" a small fraction of the electron moment is set against the rest; this reduces the magnetic moment of those states by $2\sin^2(\theta) \simeq 1\%$ relative to that of the free electron. This has a negligible effect on the broadening calculations of chapter 5 and the echo modulation calculations of chapter 4.

The magnetic field positions of the low-field and high-field lines of hydrogen atoms stabilized in frozen noble gases typically differ from those of free hydrogen by factors of less than $10^{-2}$. These correspond to similarly small changes in the $g$ and $A$ factors of the hyperfine constants. If the field and frequency of an ESR experiment are accurately measured, the resulting hyperfine constants can be used to identify the trapping sites of the radicals by comparison to previously studied spectra. Changes in the $g$ and $A$ values of matrix stabilized hydrogen atoms stem from distortions to the electronic wavefunction of the radical caused by the surrounding matrix [10]. In general, if the surrounding matrix is repulsive the wavefunction will be compressed toward the proton and the $A$ term will increase. Similarly, van der Waals attraction can stretch the electronic wavefunction toward the surrounding matrix, reducing $A$. The $g$-factors change when the electronic wavefunction of becomes distorted to a non-spherical shape, which occurs because the matrix interaction is not spherically symmetric. This introduces small admixtures of orbital angular momentum to the hydrogen wavefunction; these components have $L > 0$.
and correspondingly different L-S couplings than the S wavefunction. A complete theory of the interaction of hydrogen atoms with noble gas matrices is given by Adrian [11].

2.1 Prior CW ESR studies of hydrogen atoms within krypton

Vaskonen et al. have studied the CW ESR spectra of frozen krypton doped with HCl [12]. When the HCl is dissociated with ultraviolet light, ESR lines corresponding to hydrogen atoms trapped in interstitial and substitutional sites appear. The \( g \) and \( A \) spectroscopic factors of these sites differ substantially, allowing the lines to be easily distinguished and identified. The interstitial signal shows numerous small satellite lines due to a strong superhyperfine interaction between the hydrogen atoms and their \(^{83}\text{Kr}\) nearest neighbors, indicating substantial overlap of the electronic wavefunction of the hydrogen atoms with the krypton nuclei around this highly strained trapping site. The ultraviolet irradiation preferentially generates interstitially trapped hydrogen atoms, but these convert to substitutionally trapped atoms or recombine with other radicals over time. The timescale of this conversion shortens rapidly with higher temperatures and is about 10 minutes at 27 K.

Electron spin resonance studies of hydrogen radicals trapped in krypton films quench-condensed on cold (6.5 K) surfaces by Dmitriev produce different results [13]. Hydrogen atoms in this system show CW ESR lines composed of symmetrically overlapping sharp (\( \sim 0.1 \) G peak-to-peak) and broad (\( \sim 1.5 \) G peak-to-peak) components. When annealed to 25 K the broad component vanishes, leaving only a sharp line with \( g \) and \( A \) factors consistent with the substitutionally positioned hydrogen atom. The broad line is attributed to hydrogen atoms positioned near defects in the quenched lattice that
slightly modify the $g$ and $A$ values. These defects anneal out of the film upon warming. Both of these experiments indicate that the substitutional site is the lowest energy position of a hydrogen atom within bulk solid krypton. This is an obvious consequence of the strong repulsion of the H-Kr potential (figure 3.1) below 3.3 Å and the 2.86 Å spacing allowed for the hydrogen atom in the unstrained interstitial site.

2.2 The hyperfine constants $g$ and $A$ of hydrogen within krypton-helium condensates.

We measured the low-field and high-field CW ESR spectra of samples condensed from dissociated gas mixtures containing hydrogen, krypton and helium in the ratios 1:50:10,000, 1:5:1000 and 1:1:200. The freshly prepared samples were continuously submerged in superfluid helium at 1.35 K for several hours while many CW ESR spectra were recorded. The samples were then drained of superfluid helium and warmed with helium gas to 14.5 K over the course of a few minutes. These annealed samples were then flooded with superfluid helium and returned to 1.35 K for further measurement.

We doubly integrated the CW ESR lines to measure the total microwave absorption of the sample during each sweep of $B_0$. These were compared to similar microwave absorption measurements of a ruby standard obtained periodically during the experiment. The standard consists of a single crystal of ruby (Cr$^{3+}$ ions in crystalline Al$_2$O$_3$) fixed near the bottom of the CW ESR microwave cavity resonator, a few millimeters below the sample beaker. The $Q$ spoiler (detail "o" in figure 6.2) replaces the ruby standard in the pulse ESR cavity resonator described in chapter 6. The ruby standard was calibrated against absorption measurements of a known mass of copper sulfate crystal at room temperature. This calibration chain and knowledge of the sample temperature
gives the number of hydrogen atoms within the microwave cavity. This can be converted to concentration by dividing by the 0.36cm³ volume of the sample beaker within the volume of the resonant cavity. We also make minor corrections to account for the uneven distribution of the microwave field $\vec{B}_1$ within the cavity.

The measured hydrogen atom concentrations were larger than the largest published macroscopic concentration of stabilized hydrogen atoms, which were contained in a matrix of HD and D₂ [14]. The concentrations in the H:Kr = 1:50 and H:Kr = 1:5 samples fell about 20% in the first hour of the experiment to a stable plateau. For the most concentrated sample, made from the H:Kr = 1:50 mixture, we measured a concentration of $1.3 \cdot 10^{19}$cm⁻³, corresponding to 1 H atom per 44 Kr atoms. The concentration in the H:Kr = 1:1 sample decayed continuously with a second-order rate equation implying that the hydrogen atoms were diffusing through the matrix and recombining; since we annealed the sample we do not know if all of the atoms would have eventually recombined or if there was a small stable subpopulation. We found the rate constant of the decay to be $3.7 \cdot 10^{-23}$cm³s⁻¹. This is more than an order of magnitude smaller than the rate of $5.5 \cdot 10^{-22}$cm³s⁻¹ measured for hydrogen atoms trapped in a matrix of predominantly H₂ [2].

The dramatically large concentrations and slow reaction rates suggest that the hydrogen radicals in these samples are not contained within molecular hydrogen; if they were they would recombine very quickly. Superfluid helium is highly repulsive to hydrogen atoms, like other 1S block elements, so radicals cannot reside there. We are left with placing the hydrogen atoms in contact with the krypton, either on the surface of the krypton clusters or within the clusters. To this end we analyze the lineshapes.

In all of the samples, the high-field hydrogen lines of the fresh samples produced symmetric derivative lineshapes, suggesting that the hydrogen atoms were of a single
population characterized by one set of hyperfine coupling constants. Both high and low-field lines of the fresh samples (figures 2.2 and 2.3, respectively) show substantial magnetic dipolar broadening, which is the subject of chapter 5.

The low-field hydrogen lines each show a main resonance line with a shoulder feature on the high-field wing. The relative magnitude of the shoulder feature varies between samples and it accounts for 2–5 % of the doubly integrated low-field signal. Most interestingly, the relative spacing of the shoulder feature relative to the main line grows as the proportion of hydrogen in the condensed gas mixture increases. To better understand this, we shifted the magnetic fields of all our measurements to a common scale using a correction of 1 Gauss / 2.8025 MHz to account for small (~ 10^-3) changes in microwave frequency between spectra. The common scale corresponds to 9072.751 MHz for the low-field lines and 9072.724 MHz for the high-field lines. All the spectra shown have been shifted to the common scale. From figure 2.3 it is clear that it is the main line of the low-field spectra that is moving to lower fields as the proportion of hydrogen is increased in the condensed gas mixture. The line of the high-field spectra also moves, though to a much lesser extent.

We determined the field positions of the main lines from where their derivative spectra crossed a zero line inferred from the wings of each curve. We determined the line positions of the shoulder features of the low-field lines from the point where they most strongly inflected the signal; this method causes a small systematic error due to the changing curvature of the main line. We assumed that the high-field complement to the shoulder feature was buried within the main line and had an identical field position. The line positions and microwave frequency were used to invert the Breit-Rabi equation and calculate the g and A shifts in table 2.1. Algebraic details of the inversion of the Breit-Rabi equation are given in our prior CW ESR study of deuterium atoms within molec-
Table 2.1: Experimentally determined hyperfine constants $g$ and $A$

<table>
<thead>
<tr>
<th>Line and matrix</th>
<th>$g$ shift, ppm</th>
<th>$A$ shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main line, average of 1:1 samples</td>
<td>-20(60)</td>
<td>-0.0021(4)</td>
</tr>
<tr>
<td>Main line, average of 1:5 samples</td>
<td>-150(60)</td>
<td>-0.0027(4)</td>
</tr>
<tr>
<td>Main line, average of 1:50 samples</td>
<td>-180(60)</td>
<td>-0.0031(4)</td>
</tr>
<tr>
<td>Small line, average of 1:1 samples</td>
<td>-320(125)</td>
<td>-0.0068(8)</td>
</tr>
<tr>
<td>Small line, average of 1:5 samples</td>
<td>-390(125)</td>
<td>-0.0065(8)</td>
</tr>
<tr>
<td>Small line, average of 1:50 samples</td>
<td>-390(125)</td>
<td>-0.0065(8)</td>
</tr>
<tr>
<td>Free hydrogen atom</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H in H$_2$[15]</td>
<td>87(40)</td>
<td>-0.0023(3)</td>
</tr>
<tr>
<td>H in Kr(substitutional)[16]</td>
<td>-333(40)</td>
<td>-0.00606(2)</td>
</tr>
<tr>
<td>H in Kr(substitutional)[12]</td>
<td>-477</td>
<td>-0.00803</td>
</tr>
<tr>
<td>H in Kr(interstitial)[16]</td>
<td>-1292(155)</td>
<td>+0.0047(20)</td>
</tr>
</tbody>
</table>

ular deuterium [17]. The shifts obtained as described reproduced those from a complex computational fitting procedure that simultaneously fit the low-field and high-field spectra. Table 2.1 shows a clear match between the spectroscopic constants of the shoulder feature and those of hydrogen atoms substitutionally positioned within bulk krypton. The spectroscopic constants of the main lines do not match those of any line reported in systems of hydrogen and krypton. As the proportion of hydrogen is increased, the spectroscopic constants of the main line increasingly resemble those of hydrogen atoms within molecular hydrogen.

More than 90% of the hydrogen atoms are lost to recombination during the annealing process; those that remain form a line centered about the position previously held by the shoulder feature, as can be seen in figures 2.5 and 2.4. The sharp features of the high-field lines of the annealed spectra are closely aligned with the corresponding line
Figure 2.2: CW ESR high-field hydrogen lines of fresh samples condensed from gas mixtures containing H$_2$, Kr and He in various ratios. Top set: Curves from three samples condensed from gas mixtures H$_2$:Kr:He = 1:50:10,000, Middle set: Curves from two samples condensed from gas mixtures H$_2$:Kr:He = 1:5:1000, lower set: Curves from two samples condensed from gas mixtures H$_2$:Kr:He = 1:1:200. The innermost line in the top set corresponds to the sample featured in chapter 5.

positions in the fresh sample. The lines of our annealed samples are similar to those seen by Dmitriev in quench-condensed films prior to annealing; they contain a sharp line due to atoms substitutionally trapped within crystalline bulk krypton and a broad line due to atoms trapped at disordered sites.

At this point we propose a model of the progress of the hydrogen atoms in our sam-
Figure 2.3: CW ESR low-field hydrogen lines of fresh samples condensed from gas mixtures containing \( \text{H}_2 \), Kr and He in various ratios. Top set: \( \text{H}_2:\text{Kr}:\text{He} = 1:50:10,000 \) Middle set: \( \text{H}_2:\text{Kr}:\text{He} = 1:5:1000 \), lower set: \( \text{H}_2:\text{Kr}:\text{He} = 1:1:200 \). The rightmost line in the top set corresponds to the sample featured in chapter 5.

In the fresh samples, most of the hydrogen atoms lie on the faceted surfaces of the krypton clusters, where they produce the main line features of the ESR spectra. Molecular hydrogen formed from hydrogen atoms that did not survive recombination also lies on the faceted surfaces. In the \( \text{H}:\text{Kr} = 1:50 \) and \( \text{H}:\text{Kr} = 1:5 \) samples the coverage of the cluster surfaces by hydrogen atoms and molecules is sparse, so most of the environment on the cluster surfaces around the hydrogen atoms is filled by helium. This helium evidently prevents diffusion and recombination of the hydrogen atoms in these samples.
Figure 2.4: CW ESR high-field hydrogen lines of three annealed samples, one from each set shown in figure 2.2 and displayed analogously. The dashed line indicates the average field position of main lines shown in figure 2.2.

In the H:Kr = 1:1 samples, the abundance of molecular hydrogen dominates the environment around the hydrogen atoms on the cluster surfaces. This environment shifts the spectroscopic constants substantially relative to the samples with less H2. The hydrogen atoms can tunnel through the blanketing layer of hydrogen, approach each other and recombine, although at a rate slow compared to that in pure H2. In all of the samples, a small population of hydrogen atoms becomes trapped in the bulk of the krypton clusters during the formation process, producing the shoulder feature. When the samples are annealed, the clusters agglomerate and lose most of their surface area, while the hydrogen
Figure 2.5: CW ESR low-field hydrogen lines of three annealed samples, one from each set shown in figure 2.3 and displayed analogously. The dashed line indicates the average field position of the eight shoulder features shown in figure 2.3.

Atoms on the surface are sufficiently mobile that most of them recombine. Those that remain become trapped in the bulk of the annealed sample, often at disordered sites. The variety of signals from the annealed samples is a product of variation within the annealing process, which is largely uncontrolled because it is driven by the release of heat from the recombining hydrogen atoms.

This model, in combination with the x-ray work described in chapter 1, leads us to imagine that our fresh sample is composed of faceted spheroidal clusters with atomic
Figure 2.6: An idealized FCC cluster with hydrogen atoms, shaped as a truncated octahedron with Kr(111) and Kr(100) surfaces populated by hydrogen and helium atoms. Krypton is shown in dark gray, hydrogen atoms in light gray, and helium in white. Superfluid helium and possible H$_2$ is not shown. There are 2735 Kr atoms in the cluster. This is a very low energy structure for this size of cluster, though theoretically not the lowest [3].

hydrogen atoms studding their surface. The remaining sites are occupied by molecular hydrogen or helium, depending on the ratio of hydrogen to krypton in the condensed gas mixture. Such a cluster is shown in figure 2.6. How the hydrogen atoms come to be located on the cluster surfaces is discussed in chapter 3.
CHAPTER 3

A SIMPLE THEORETICAL MODEL OF HYDROGEN AND HELIUM ATOMS
ADSORBED TO KRYPTON CLUSTER SURFACES

We now describe a modest theoretical model for predicting the behavior of the hydrogen and helium atoms adhered to the krypton clusters in our material. This gives estimates of the binding energies of hydrogen and helium atoms to the cluster surfaces and suggests the possibility of observing bound hydrogen with Raman spectroscopy. We also estimate the tunneling rate between attractive sites for hydrogen adhered to the krypton surfaces.

3.1 Binding energies and Raman spectroscopy

The potential energy of a system composed of two atoms as a function of their interatomic distance is a fundamental problem in quantum chemistry. Two-atom potentials between hydrogen, helium, and krypton that agree closely with experiments have been computed by Tang and Toennies [18, 19]. From these basic potentials (shown in figure 3.1), it is straightforward to approximate the potential of a single hydrogen or helium adatom interacting with a krypton surface by simply summing the two-body potentials between the adatom and the krypton atoms. The positions of the krypton atoms near the adatom are assumed to be unaffected by the presence of the adatom, which is reasonable considering that interactions between krypton atoms are an order of magnitude stronger than those between krypton and hydrogen or helium atoms. This approximation also assumes that the electronic wavefunction of the adatom is only slightly perturbed by the interaction with the krypton, so that the interatomic potential remains independent of the number of krypton atoms with which the adatom is interacting. This is a sound assumption because the energy scale of electronic excitations of hydrogen and helium
Figure 3.1: Potential energy curves as a function of internuclear distance between hydrogen and krypton atoms (lower curve) and helium and krypton atoms (upper curve). From the tabulations by Tang and Toennies [18][19].

($\sim 10^5$ K) is far larger than that of the potentials.

As described in chapter 1, x-ray scattering has shown that the krypton clusters within our samples assume forms that minimize their configurational energy. All of these clusters contain faceted surfaces to maximize the number of bonds between the Kr atoms. In general, these surfaces will be of the FCC(100) and FCC(111) forms, which maintain 8 and 9 bonds per each surface atom, respectively. There may also be low energy HCP surfaces; these also maintain 8 or 9 bonds per surface atom. The 9-bond HCP surface is identical to the FCC(111) surface, and the 8-bond HCP surface is similar enough to FCC(100) that they are identical for our purposes. Some of the low energy cluster types
only present the FCC(111) surface to the helium, as is the case for the hico clusters shown in table 1.1 that best fit our x-ray data.

Each type of surface hosts a single type of attractive site that can potentially bind hydrogen and helium atoms. The Kr(100) sites neighbor four Kr atoms while the Kr(111) sites neighbor three. The Kr(100) sites number one per Kr surface atom and like the surface atoms they are spaced at 4.04 Å. The Kr(111) sites number two per Kr surface atom and are spaced at 2.33 Å, which is shorter than the 2.65 Å distance at which the potential between helium atoms becomes strongly repulsive. We assume that the helium adatoms form a triangular lattice that binds half of the Kr(111) sites, as shown in figure 2.6.

There are three orthogonal directions that the hydrogen or helium adatoms can move within the potential: one perpendicular to the surface and two parallel to the surface. We will assume that the zero-point energies of these three motions of the adatom add to the total zero-point energy, even though we do not have the case of a separable potential. We then calculate the binding energy of the adatom as

\[ E_b = E_w + E_{zp\perp} + E_{zp\parallel} \]  

(3.1)

where \( E_b \) is the binding energy, \( E_w \) is the energy of the attractive well, \( E_{zp\perp} \) is the zero-

Table 3.1: Energies used in calculating the binding energy of H and He to Kr surfaces.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>H-Kr(100)</th>
<th>H-Kr(111)</th>
<th>He-Kr(100)</th>
<th>He-Kr(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{zp\perp} )</td>
<td>75 K</td>
<td>78 K</td>
<td>28 K</td>
<td>28 K</td>
</tr>
<tr>
<td>( E_{zp\parallel} )</td>
<td>57 K</td>
<td>78 K</td>
<td>19 K</td>
<td>26 K</td>
</tr>
<tr>
<td>( E_w )</td>
<td>-272 K</td>
<td>-204 K</td>
<td>-122 K</td>
<td>-92 K</td>
</tr>
<tr>
<td>( E_b )</td>
<td>-140 K</td>
<td>-48 K</td>
<td>-75 K</td>
<td>-38 K</td>
</tr>
</tbody>
</table>

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point energy of the motion perpendicular to the surface and $E_{zp\parallel}$ is the zero-point energy of the motion parallel to the surface.

The potentials in the direction perpendicular to the surfaces along a path passing through the potential wells are a good fit to the analytically solvable Morse form, which is

$$U(r) = D \left(1 - \exp\left(-a(r-r_0)\right)\right)^2 - D; \quad (3.2)$$

where $D = -U(r_0)$ is the energetic depth of the potential, $r_0$ is the location of the potential minimum, and $a$ parameterizes the width of the potential well. The energy of the Morse potential is

$$E_n = \hbar \omega_0 \left((n+1/2) - \chi(n+1/2)^2\right) - D; \quad \chi = \frac{\hbar \omega_0 D^{-1}}{4}; \quad \omega_0 = a(2D/m)^{1/2} \quad (3.3)$$

where $n$ is the quantum number describing the motion of the particle in the well [20]. Through equation 3.3 we estimate the zero-point energies of the perpendicular degrees of freedom for each atom and surface type, as shown in table 3.1.

Contributions to the zero-point energy due to motions parallel to the krypton surface are more difficult to estimate because of the complex form of the potential. The potentials are highly anisotropic at parallel displacements more than one Ångstrom from the well minima. For simplicity, we assume that the two degrees of freedom parallel to the Kr surface each possess a zero-point energy corresponding to that of a simple harmonic oscillator. The spring constant of the oscillator is an average of two spring constants obtained from the strongest and weakest potential curvatures along directions parallel to the Kr surface at the location of the well. The perpendicular zero-point energies are listed in table 3.1. This method probably overestimates the zero-point energies of the adatoms, particularly for the hydrogen atoms. This is because the adatoms move away from the surface due to the asymmetric shape of the potential in the parallel direction.
Table 3.2: Approximate zero-point energies of the first three vibrational modes of hydrogen adatoms in the direction perpendicular to krypton surfaces.

<table>
<thead>
<tr>
<th>Energy level</th>
<th>H-Kr(100)</th>
<th>H-Kr(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>75 K</td>
<td>78 K</td>
</tr>
<tr>
<td>$E_1$</td>
<td>189 K</td>
<td>178 K</td>
</tr>
<tr>
<td>$E_2$</td>
<td>256 K</td>
<td>203 K</td>
</tr>
</tbody>
</table>

For hydrogen, the maximum of the adatom wavefunction density is displaced from the well minimum by 0.16 Å for Kr(100) surface and 0.19 Å for the Kr(111) surface. In both cases, the curvature of parallel motions in the potential is softer away from the surface. Furthermore, we will show in later calculations that the hydrogen atom on the Kr(111) surface is not bound to a single attractive site, so it can lose a substantial amount of zero-point energy by delocalizing. These errors in overestimation of the parallel zero-point energy are less significant for the helium atoms.

At this point we consider if there is a vibrational transition between two bound states of the hydrogen atoms on the Kr surfaces. The energies of the higher modes of the perpendicular motion are calculated from equation 3.3 and shown in table 3.2. For the Kr(100) surface, the extra 114 K energy of the second mode is not enough to break the 140 K binding energy, so the vibrating hydrogen atom should remain bound to the surface. For the Kr(111) surface, the extra 100 K of energy will remove the atom, unless the perpendicular zero-point energy has been overestimated by a factor of three. In principle, the excitations to the first excited state of the perpendicular motion of the hydrogen are observable in the Stokes spectrum of a Raman spectroscopy experiment, and they will be much higher in energy than the corresponding transitions in helium. However, the broadening of the transitions may be severe due to interactions with the superfluid helium above the hydrogen atoms.
In the earliest stage of the formation of our samples, the gas jet contains a mixture of unbound krypton, hydrogen and helium atoms. The strongest interactions among these atoms are between krypton pairs, which exceed the other interactions by an order of magnitude [18, 19]. As the jet begins to cool, only the krypton atoms can coalesce into clusters [21]. These present a large surface to the hydrogen and helium atoms in the jet. After further cooling, the hydrogen and helium begin to bind to the krypton surfaces, with the high density of the helium ensuring that no binding sites remain unfilled. An important question is the order of the addition of the hydrogen and helium atoms. If the hydrogen atoms bind to the clusters at a higher temperature than the helium atoms, there is likely to be a time during sample formation when the hydrogen atoms are bound to the clusters, but many of the sites on the clusters are vacant. The hydrogen atoms can then diffuse on the cluster surfaces and potentially recombine with each other, as shown in figure 3.2.

3.2 Tunneling of hydrogen atoms on krypton surfaces

Diffusion across the surface may proceed through either thermal activation or quantum tunneling. The binding energies of table 3.1 show that the hydrogen atoms will bind before the helium atoms. This does not necessarily imply that the hydrogen will be able to move about the cluster surfaces unimpeded by helium, because the helium density in the jet exceeds that of the hydrogen by $10^2$–$10^3$. Nevertheless, this raises the question of how fast hydrogen atoms might tunnel between binding sites on the krypton surface. Similar tunneling of hydrogen on Cu(100) and Ni(100) surfaces has been observed in ultra-high vacuum experiments [22, 23].

To estimate the tunneling rate of hydrogen on krypton surfaces, we must approxi-
Figure 3.2: Left pane: A hydrogen atom adsorbed to a 100 krypton surface coated with a helium monolayer. The hydrogen (light gray) and helium (white) atoms each bind four krypton atoms (dark gray). The hydrogen atom can tunnel along the path of the arrow to a neighboring binding site if a vacancy is present in the helium monolayer. Right pane: A hydrogen atom adsorbed to a Kr(111) surface coated with a helium monolayer. Only half of the binding sites on the surface are occupied. The hydrogen atom can tunnel along the path of the arrow only if two adjacent helium atoms are missing from the monolayer.

mate the path of the reaction coordinate from one binding site to its neighbor. Symmetry indicates that the path will lie in a plane that includes both of the binding sites and is perpendicular to the Kr surface. The potentials in the planes of the reaction paths of the Kr(100) and Kr(111) surfaces are shown in figures 3.3 and 3.4, respectively. On both surfaces, the potential between the sites is strongly dominated by the two krypton atoms symmetrically positioned about the center of the path. A reasonable estimate for the path of the reaction coordinate is a path of constant radius that pivots around the axis between the two dominant atoms, with the radius of the path chosen to minimize the potential along the path. The potential in the plane of the reaction coordinate is then best considered in angular coordinates about the pivot axis. An actual tunneling atom would sample the potential in a region surrounding the tunneling path. To account for
Figure 3.3: The potential in the plane of the tunneling reaction coordinate above the Kr(100) surface. Darker shades indicate lower energy. The line in the inset shows the path of the x-axis of the graph. The potential is calculated from interactions with only the atoms of the topmost layer of the krypton. The dashed lines show the region radially integrated to form a one-dimensional potential.

This, we radially integrated a region around the path between classical turning points found by modeling the radial portion of the potential with a simple harmonic oscillator. These boundaries are shown as the dashed lines in figures 3.3 and 3.4. The radial integration was probably unnecessary since the integrated potential was of only slightly different shape and size than the potential along the path of the reaction coordinate. Consequently, we assumed that integration in the direction normal to the plane of the path of the reaction coordinate (out of the page in figures 3.3 and 3.4) was unnecessary. The radially integrated potential for the Kr(100) surface is shown as curve "b" in figure 3.5.

We have reduced the three-dimensional problem of tunneling between the binding sites to a one-dimensional problem of tunneling along the reaction coordinate. The sim-
Figure 3.4: The potential in the plane of the tunneling reaction coordinate above the Kr(111) surface. Darker shades indicate lower energy. The line in the inset shows the path of the x-axis of the graph. The potential is calculated from interactions with only the atoms of the topmost layer of the krypton. The dashed lines show the region radially integrated to form a one-dimensional potential.

The simplest way to estimate the tunneling rate through an arbitrary potential barrier is the WKB approximation. This requires us to find the classical turning points of the potential along the reaction coordinate. We used both Morse and quartic “Mexican hat” functions to approximate the potential along the reaction coordinate. These are shown as curves “a” and “c” in figure 3.5. The ground state energies $E_g$ of the two approximations are found using equation 3.3 and numerical solutions to the quartic potential given by Aquino [24]. These energies both indicate that the hydrogen atom sits high in the potential along the reaction coordinate of the Kr(100) tunneling path. For the Kr(111) surface, the path is only $2/3$ as long as that of the Kr(100) surface, and the tunneling barrier is only $30\%$ as high. Both Morse and quartic approximations predict energies higher than the barrier, indicating that the hydrogen is unbound along the path of the reaction coordinate on the
Figure 3.5: Potential energy along the 100 reaction coordinate. a) Morse approximation to curve "b". b) Radially averaged potential energy. c) Quartic approximation to curve "b". d) Ground state energy of a hydrogen atom in Morse potential "a". e) Ground state energy of a hydrogen atom in quartic potential "c".

Kr(111) surface. To complete the WKB calculation for the Kr(100) surface, we use a tunneling attempt frequency of $E_g/h$, giving tunneling times of 75 and 130 ps between each pair of sites, and dwell times for the hydrogen of 1/4 this value.

The results of the tunneling calculations indicate that hydrogen tunnels rapidly across the surfaces of our condensing clusters. Each cluster facet hosts ~ 50 attractive sites; the hydrogen atoms should be able to fully sample these sites in only tens of nanoseconds even if they are transiently occupied by helium. In contrast, the time available to the hydrogen for exploring the cluster surfaces is probably many microseconds,
since the transit time during sample formation from the orifice of the discharge tube to the surface of the helium surface is $\sim 1$ ms. Even if our estimated tunneling rates are high by a factor of ten, it is hard to imagine that more than one hydrogen atom can ever become stabilized on the same cluster facet. This point is critical to the discussion of the dipolar line broadening in chapter 5.
CHAPTER 4

PULSE ESR MEASUREMENTS OF HYDROGEN AND DEUTERIUM ATOMS
IN KRYPTON MATRICES

4.1 Electron spin echoes and spin echo decay

The pulse ESR spectrometer described in chapter 6 was used to study a single sample condensed from a mixture of hydrogen, krypton and helium that passed through an RF discharge as described in chapter 1. The condensed gas contained H₂, Kr and He in the ratios 1:5:1200. Although not deliberately introduced into the sample, a trace quantity of deuterium atoms was also stabilized in the krypton matrix.

We performed a pulse ESR experiment in which a pair of microwave pulses are applied at the 9 GHz Larmor frequency of the electron spins. The magnetic field of the microwaves is perpendicular to \(\vec{B}_0\) and the two pulses are separated by a time \(\tau\). Prior to the first pulse, the electron spin magnetization is 16% polarized along \(\vec{B}_0\) due to the thermalization of the sample. The first microwave pulse exerts a torque on the spins; its duration and amplitude are chosen to turn them through an angle \(\pi/2\) so that they lie in the transverse plane, perpendicular to \(\vec{B}_0\). The electron spins precess at their Larmor frequency in the transverse plane following the first pulse; they dephase after about 200 ns due to slight variations in precession frequency. Once the spins are incoherent the sample produces no macroscopic magnetization even though each individual spin continues to precess. (The spins can precess in the transverse plane for tens of milliseconds before thermalizing and realigning with \(\vec{B}_0\).) The second microwave rotates each spin through an angle \(\pi\) about an axis in the transverse plane, mirroring the direction of the spins about this axis. This inverts the phase acquired in the period \(\tau\) between the pulses, so that spins that precessed faster than the average spin are now lagging in phase.
Figure 4.1: The two-pulse electron spin echo experiment. Microwave pulses "1" and "2" are applied by the spectrometer and separated by a time \( \tau \). The "spin echo" is a microwave pulse produced by the sample after another period \( \tau \) has elapsed. Incrementing \( \tau \) reveals the echo envelope modulation pattern.

relative to the average spin. Each spin precesses at the same frequency after the second pulse that it precessed after the first pulse, so that at a time \( 2\tau \) after the first pulse all of the phase differences among the spins cancel out. The moments of the refocused spins add constructively to produce a macroscopic magnetization precessing in the transverse plane that induces a detectable spin echo in the microwave resonator. This is illustrated in figure 4.1. A quantum mechanical treatment of the spin echo phenomenon shows it to be more robust than the previous classical explanation suggests. Although angles of \( \pi/2 \) for the first pulse and \( \pi \) for the second pulse give the strongest spin echo, almost any pair of pulses will produce an echo and it is common experimentally to use pulses of equal rotation angle. In general, the echo scales as \( \sin^2(\theta_{\text{2nd}}/2) \), where \( \theta_{\text{2nd}} \) is the rotation angle of the second pulse. This is derived quantitatively as part of the ESEEM phenomenon (follow the \( \Psi \) and \( G \) terms) in appendix A.3.

Rapidly repeating the spin-echo experiment using a fixed value for \( \tau \) allows measurement of the thermal recovery of the spins along the axis of \( \vec{B}_0 \). In many samples the recovery of the polarization to thermal equilibrium is exponential ("Bloch type") and
characterized by a time constant $T_1$. If a series of many $\pi/2 - \pi$ pulse experiments is repeated on such a sample, with a time $T_{\text{rec}}$ allowed for thermal recovery between each experiment, the resulting echo amplitudes follow the form [25]

$$A(T_{\text{rec}}) = A(T_{\text{rec}} = \infty) \cdot (1 - \exp(-T_{\text{rec}}/T_1)).$$  \hspace{1cm} (4.1)

Figure 4.2 shows that the hydrogen atoms in our sample do not have a precisely exponential polarization recovery, and that this recovery occurs over tens of milliseconds. All of the other measurements on the hydrogen atoms of this sample were made with a recovery time of 400 ms between pulse experiments to guarantee full polarization recovery. We also performed pulse ESR measurements on a trace population of deuterium atoms in this sample. These recovered about ten times slower than the hydrogen atoms, and we allowed five seconds of recovery time between each pulse experiment.

In practice, the second microwave pulse only partially refocuses the spins into an echo. This is because the two-pulse echo only refocuses static magnetic field inhomogeneity. The magnetic field at the electron causes it to precesses in the transverse plane at an angular frequency $\gamma_B B(t)$. If $B(t)$ varies with time, the angle accumulated in the period $\tau$ preceding the second pulse may not match that accumulated in the period $\tau$ following the second pulse. If the time varying components of $B(t)$ are identical for the whole ensemble of electron spins, the effect will be to move the direction of the refocused echo in the transverse plane. This rarely occurs unless the applied magnetic field is changing. More commonly, $B(t)$ varies in time and from one spin to the next. In this case the electron spins will not completely align at time $2\tau$ and the echo will be reduced in amplitude, if it appears at all. The time dependent variation of the precession rate of individual spins is termed “spin-diffusion” in magnetic resonance literature. This is because if the field fluctuations are due to a random process the precession frequency of individual spins will diffuse similarly to a one-dimensional random walk. The spin echo experiment becomes increasingly sensitive to the effects of fluctuating magnetic fields
Figure 4.2: The effect of the repetition rate of the $\pi/2-\pi$ pulse sequence on the echo amplitude. Rapidly repeating the pulse sequence prevents complete thermal recovery of the sample before each $\pi/2$ pulse, reducing the size of the echo. The upper and lower curves shown correspond to $T_1$ times of 19 ms and 45 ms, respectively, and are calculated from equation 4.1.

as $\tau$ increases because there is more time for variations in angle between electron spins to accumulate. In many systems, $B(t)$ is uncorrelated between spins and fluctuates randomly due to thermal fluctuations in the orientations of electrons and nuclei surrounding the precessing spin. The dipolar couplings between the magnetic species are also randomly modulated by thermal phonons. The Bloch equations empirically describe the echo decay as decreasing exponentially with $2\tau$, following a time constant $T_2$. This fits the behavior of many systems. The trace quantity of deuterium atoms in our samples behaves in this way; the much larger quantity of hydrogen atoms does not.

Electron spin echoes from hydrogen atoms trapped in krypton matrices decay with a faster-than-exponential envelope over the range $0 < \tau < 2\mu$s. At longer pulse sepa-
Figure 4.3: The effect of the rotation angle of the second microwave pulse on the spin echoes from hydrogen atoms trapped in a krypton condensate. a) Echoes produced using a $\pi/2 - \pi$ pulse sequence. b) Echoes produced using a $\pi/2 - \pi/6$ pulse sequence.

Reorientation periods their decay is approximately exponential. This is shown in figure 4.3. In concentrated samples such as ours, a major source of changing magnetic fields within the sample is the reorientation of the electron spins due to the second microwave pulse. When the second microwave pulse rotates the electrons through an angle $\pi$, the magnetic coupling between each precessing electron and any nearby precessing neighbors immediately changes sign. By analogy to spin diffusion, this effect is called “instantaneous diffusion” in ESR literature because the spectral frequencies of the precessing electrons instantly change with the application of the second microwave pulse. This effect depends on the degree of reorientation of the electron spins by the second pulse. Consequently, the rate of dephasing scales as $\sin^2(\theta_{2nd}/2)$, just like the amplitude of the echo. Instantaneous diffusion dominates the decay of the electron spin echo signals from the hydrogen atoms in our samples. This is clear from the dramatic reduction in
echo decay that results when the second pulse is shortened so that it turns the electron spins through an angle of only $\pi/6$, as shown in figure 4.3. For this reason it is advantageous to use a $\pi/2 - \pi/6$ pulse sequence to measure a long range of $\tau$. Atomic radicals trapped in molecular deuterium matrices also show a faster-than-exponential echo decay curve, which is similarly dominated by instantaneous diffusion. The molecular deuterium matrix is similar to krypton in that it is composed of a loose aggregate of spheroidal clusters, each containing 5–50 trapped radicals. This suggests that the unique shape of the echo decay curve is a consequence of the unusual distribution of the electron spins within our samples.

In contrast to the high concentration of stabilized hydrogen atoms, the trace concentration of deuterium atoms stabilized in our krypton samples is not affected by instantaneous diffusion. The echo decay under the application $\pi/2 - \pi$ and $\pi/2 - \pi/6$ sequences shows simple exponential decay with a $T_2$ time of 10.4 $\mu$s, as shown in figure 4.4.

4.2 Electron spin echo envelope modulation (ESEEM)

Random thermal reorientation of magnetic nuclei near electron spins is not the only mechanism by which nuclei affect electron spin echoes. Nuclear motion can also be induced by the changing orientation of the electron spins. Nuclei near electron spins precess in a magnetic field that is a sum of the external field $\vec{B}_0$ and the field cast by the dipole moment of the electron. In general, this field has a component perpendicular to $\vec{B}_0$ that is due entirely to the electron. In a two-pulse experiment, the first microwave pulse changes the direction of the electron spin and its field over a timescale short compared to the nuclear precession. The nuclei then precess about the new magnetic field and their
moments produce a changing field at the position of the electron. This field speeds or slows the precession of the electron, ultimately affecting the spin echo. In general, the electron spin echoes are strongest when \( \tau \) is an integer multiple of the nuclear precession period, so the electron spin echo envelope is modulated at the Larmor frequency of the nearby nuclei. Higher harmonics also appear in ESEEM spectra, especially when the nuclei are close to the electron spin [26]. Rowan et al. gave the first full explanation of the effect, a complete derivation of which is given in appendix A [27].

The magnetic species in our samples are unpaired electron spins, protons within atomic hydrogen, protons within molecular hydrogen, and the \(^{83}\text{Kr}\) isotope, which is naturally abundant at 11.5\%. The protons within atomic hydrogen are effectively locked against precession by the strong hyperfine coupling (\( \sim 1420 \text{ MHz} \)) to their surrounding electron spins. Any molecular hydrogen present in the sample can take either ortho (parallel protons) or para (antiparallel protons) forms. The magnetic ortho hydrogen is relaxed to magnetically inert para hydrogen through the action of the strong magnetic field gradients produced by the unpaired electron spins. This insures that after a few seconds any \( \text{H}_2 \) neighboring the atomic radicals is magnetically inert. Thus the only ESEEM signals that our samples can produce are due to \(^{83}\text{Kr}\).

The echo modulation scales as \( r^{-6} \) with the distance of the nucleus from the electron and is strongly dependent on the angle between \( \vec{r} \) and \( \vec{B}_0 \). To a good approximation, the motions of multiple nuclei surrounding a single electron are uncorrelated, so the resulting echo modulation is simply a product of that due to each nucleus. The ESEEM modulation pattern is conveniently insensitive to many parameters of the experiment. It is independent of the lengths of the first and second microwave pulses, although the second pulse (and the microwave resonator that concentrates it) must have a bandwidth larger than the Larmor frequency of the nuclei under study, as discussed in chapter 6.
Figure 4.4: Spin echo decay from the population of trace deuterium atoms in our sample. a) Electron spin echoes obtained with a $\pi/2 - \pi$ pulse sequence. b) Echoes obtained with a $\pi/2 - \pi/6$ sequence. The lines correspond to a $T_2$ time of 10.4 $\mu$s. Weak $^{85}$Kr ESEEM modulation causes the fluctuations of the echoes.

The modulation is also independent of the CW ESR lineshape provided that the pulses have sufficient bandwidth to excite the entire resonance line, which is the case in this work.

4.3 Simulating ESEEM signals

The ESEEM modulation functions are simulated by modeling the electron spin as positioned among $N$ krypton atoms, which are indexed by $i = 1 \ldots N$ and located at positions $\vec{r}_i$ relative to the radical. The modulation functions for individual $^{85}$Kr atoms, $E^i_2(\vec{r}_i, \theta_i, \tau)$, are multiplied to compute the ESEEM signal for a particular arrangement $\sigma$ of isotopes.
and a particular direction \( \hat{B}_0 \) of the applied magnetic field. These signals are averaged over isotopic distribution and field direction to simulate the ESEEM signal from our randomly oriented samples.

\[
E(\tau) = \left\langle \prod_{i}^{N} E^2_{\tau}(\vec{r}_i, \theta_i, \tau) P(i,a) \right\rangle_{a,\hat{B}_0} \quad \left\langle P(i,a) \right\rangle_{i,a} = 0.115 \quad (4.2)
\]

The random variable \( P(i,a) \) equals one for \( ^{83}\text{Kr} \) atoms and zero for the magnetically inert isotopes of krypton; \( a \) indexes elements of an ensemble of random arrangements of the isotopes. The average of \( P(i,a) \) corresponds to the natural abundance of the \( ^{83}\text{Kr} \) isotope. The angle between \( \vec{r}_i \) and \( \hat{B}_0 \) is \( \theta_i \).

In randomly oriented samples like impurity-helium condensates, the angular average over the orientation of \( \hat{B}_0 \) blurs most of the information about the geometric arrangement of the nuclei around the electron spins, so that the ESEEM modulation can be considered a measure of the number and proximity of magnetic nuclei around the atomic radicals. In our case, we wish to determine if our radicals are adhered to the faceted surfaces of the krypton clusters or embedded within the bulk of the clusters. To simulate the ESEEM signal due to atoms situated on the krypton surface, the vectors \( \vec{r}_i \) point from the attractive minimum of the hydrogen-krypton potential above the cluster surface to the positions of the surrounding krypton nuclei. This predicts similar modulation patterns for both \( \text{Kr}(100) \) and \( \text{Kr}(111) \) surfaces. Our simulations of signals from atoms positioned on cluster surfaces are produced by equally weighting these two surfaces. The displacements of the radicals away from the potential well minima, caused by the Morse-like shape of the potentials in the direction normal to the cluster surface, only slightly reduce the simulated modulation. This effect is small relative to the uncertainty in the simulation introduced by the nuclear quadrupole coupling, which is discussed below. To simulate the ESEEM signal due to atoms substituted within the krypton clusters, the vectors \( \vec{r}_i \) point from the substitutional site of the atomic radical to the surrounding krypton nuclei. The radical trapping site is modeled as an unstrained FCC crystal with a
4.04 Å nearest neighbor spacing. In both surface and bulk models the effects of krypton nuclei more than 10 coordination spheres distant from the electron spins are ignored.

A formula due to Shubin [28] relates the ESEEM modulation signal from a nucleus of arbitrary spin to that from a spin 1/2 nucleus of equivalent \( \gamma_i \):

\[
E_I(\vec{r}_i, \theta_i, \tau) = \frac{1}{2I+1} U_{2I}[E_{\frac{1}{2}}(\vec{r}_i, \theta_i, \tau)]
\]  

(4.3)

where \( U_n \) are Chebyshev polynomials of the second kind. This allows \( E_{\frac{1}{2}}(\vec{r}_i, \theta_i, \tau) \) to be calculated from the modulation of a single spin 1/2 nucleus:

\[
E_{\frac{1}{2}}(\vec{r}_i, \theta_i, \tau) = \frac{K}{2}(1 - \cos(\omega_\alpha \tau))(1 - \cos(\omega_\beta \tau))
\]

(4.4)

\[
K = \left( \frac{B}{\omega_\alpha \omega_\beta} \right)^2 \quad \omega_L = \frac{g_n \mu_n |E_0|}{\hbar} \quad \omega_\alpha = \left[ \left( \frac{A}{2} \pm \omega_L \right)^2 + \left( \frac{B}{2} \right)^2 \right]^{rac{1}{2}}
\]

(4.5)

\[
A = g_n \mu_n g_e \mu_B (3 \cos^2(\theta_i) - 1)/\hbar(\vec{r}_i)^3 \quad B = 3 g_n \mu_n g_e \mu_B (\cos(\theta_i)\sin(\theta_i))/\hbar(\vec{r}_i)^3
\]

(4.6)

where \( g_e \) and \( g_n \) are the g-factors of the electron and nuclear spins, and \( \mu_B \) and \( \mu_n \) are the Bohr and nuclear magnetons.

The strong and non-exponential echo decay caused by instantaneous diffusion complicates the analysis of the shallow modulation visible in the hydrogen atom spectra shown in figure 4.3. Future spectra of this sample will need to be measured with the three-pulse stimulated echo sequence, which keeps the effect of the instantaneous diffusion constant as the echo modulation proceeds [26]. The simple exponential decay of the deuterium atom spectra is probably due to thermal motion of the abundant hydrogen atoms. This decay can be divided out to reveal the modulation, as is more commonly done when dividing out echo decay caused by the thermal motion of nuclei [29]. Dividing out the \( T_2 \) decay of the deuterium gives curves "d" and "e" in figure 4.5, which unfortunately show a great deal of noise.
Figure 4.5: $^{83}$Kr modulation of deuterium signals and simulated ESEEM signals. 
a) Simulated modulation for deuterium atoms positioned at the cluster surface, with no quadrupole coupling. 
b) Simulated modulation for deuterium atoms positioned in the cluster bulk with strong quadrupole coupling. 
c) Simulated modulation for deuterium atoms positioned at the cluster surface with moderate quadrupole coupling. 
d) Data from $\pi/2 - \pi/6$ pulse sequence. 
e) Data from $\pi/2 - \pi$ pulse sequence. The simulated modulation for deuterium atoms positioned in the cluster bulk without quadrupole coupling (not shown) is identical in shape to curve “a”, but has troughs 2.5 times as deep.

4.4 The complication of electric quadrupole interactions

The two-pulse ESEEM experiment described so far would be a very straightforward way to determine the position of the atomic radicals within the krypton clusters. Unfortunately, a $^{83}$Kr nucleus can experience torque from electric field gradients in addition to magnetic fields. Any nucleus of spin $I \geq 1$ has a nonspherical charge distribution that results in an electric quadrupole moment that couples to electric field gradients present at the nucleus. The electric field gradient is zero at substitutional or interstitial positions
within the FCC structure of bulk solid noble gases due to the cubic and octahedral symmetries of these sites. Since the ESEEM signal is dominated by the nuclei immediately neighboring the hydrogen or deuterium radicals, the asymmetry at those nuclei due to the radicals can affect the ESEEM signal. Cluster surfaces can also produce quadrupole coupling to the nuclei in the surface layer.

Nuclear quadrupole interactions have a strong effect on our ESEEM signals despite the fact that $^{83}$Kr nuclei have small quadrupole moments and that there are no covalent or ionic bonds producing strong field gradients within our samples. This is a consequence of the four spherical closed electron shells surrounding the $^{83}$Kr nuclei. Any electric field gradient applied to the atom distorts these shells into shapes that enhance the field gradient at the nucleus. This effect is linear with the applied gradient and is called Sternheimer antishielding [30]. The electric field gradient seen by $^{83}$Kr nuclei is enhanced by a factor of $\sim 80$ by its surrounding electrons [31]. This is why nuclear quadrupole couplings have a strong effect on the ESEEM spectra of $^{83}$Kr in krypton-helium condensates while quadrupole couplings are negligible in the analogous spectra of deuterium nuclei within molecular deuterium-helium condensates. The unshielded quadrupole moments $Q$ of $^{83}$Kr and deuterium nuclei are 0.253 and 0.286 barn, respectively.

The effects of quadrupole coupling on the ESEEM spectra are understood by considering the Zeeman and quadrupolar contributions to the energy of the nucleus. Following the discussion by Slichter, the gradient of the electric field at the nucleus is a $3 \times 3$ tensor $V$, with each component given by

$$V_{\alpha\beta} = \left( \frac{\partial^2 V(\vec{r})}{\partial \alpha \partial \beta} \right)_{r=0}$$

(4.7)

where $V(\vec{r})$ is the voltage at the nucleus due to all sources other than the nucleus and $\alpha$ and $\beta$ are the axes $x, y, z$ [30]. The tensor $V$ can be written in the coordinate system
Figure 4.6: Energy levels for the simplified case (equation 4.10) of a symmetric electric field gradient aligned parallel to $\vec{B}_0$ for a spin 9/2 nucleus. $R = \frac{e^2 q Q}{\hbar \omega_L}$ is the relative coupling and $\omega_L$ is the Larmor frequency.

$x', y', z'$ of its principle axes so that it has only nonzero components $V_{x'x'}, V_{y'y'}$ and $V_{z'z'}$. If we neglect the electron density within the nucleus then $V_{x'x'} + V_{y'y'} + V_{z'z'} = 0$ because the electric field is divergenceless. Only two variables are needed to characterize $\mathbf{V}$:

\[
q = \frac{V_{z'z'}}{e} \quad \eta = \frac{V_{x'x'} - V_{y'y'}}{V_{z'z'}}
\]

(4.8)

where $e$ is the electron charge and $z'$ is chosen to be the strongest principle axis of $\mathbf{V}$. The magnitude of the field gradient is indicated by $q$ and the asymmetry of the gradient by $\eta$. With these we write the quadrupole Hamiltonian

\[
\mathbf{H}_{\text{Quad}} = e^2 q Q \frac{(3I_x^2 - I^2 + \eta(I_x^2 - I_y^2))}{4I(2I - 1)}
\]

(4.9)

where $Q$ is the quadrupole moment of the nucleus.
The strongest principle axis $\zeta'$ usually coincides with the direction to the source of the asymmetry surrounding the $^{83}\text{Kr}$ nucleus. If a hydrogen atom is positioned substitutionally within an FCC lattice, $\zeta'$ of any neighboring magnetic nuclei will point toward the hydrogen atom. Similarly, for a magnetic nucleus positioned at the surface of a lattice $\zeta'$ will be normal to the surface. If multiple sources of asymmetry are present, such as a neighboring hydrogen atom and a lattice surface, the direction of $\zeta'$ is not easily predicted. The krypton clusters within our samples are randomly oriented, so in general $\zeta'$ is uncorrelated with the direction of $\vec{B}_0$, which is aligned with $\vec{z}$. Only in the special case where $\zeta'$ aligns with $\vec{B}_0$ and $\eta \ll 1$ do the Zeeman and quadrupolar Hamiltonians commute, with the energy determined by the quantum numbers $I$ and $I_z$:

$$\mathcal{H}_{\text{aligned}} = e^2 q Q \frac{3 I_z^2 - I^2}{4I(2I-1)} - \hbar \gamma B_0 I_z$$  \hspace{1cm} (4.10)

Figure 4.6 shows the effect on the Zeeman energy levels in this case.

In general, as intuition would suggest, randomly oriented systems whose nuclei experience quadrupole interactions that are comparable to or smaller than the Zeeman energy show ESEEM modulation that damps after a few oscillations, resembling an underdamped harmonic oscillator [32, 33, 26]. The average of the echo amplitude over $\tau$ is not influenced by quadrupole coupling, which simply causes the changes in echo amplitude to become less pronounced at larger $\tau$. This has been confirmed numerically by Kim et al. for a system closely analogous to ours involving the $^{87}\text{Sr}$ nucleus, which is a spin 9/2 particle with Larmor frequency and quadrupole coupling very similar to those of $^{83}\text{Kr}$ [32]. Figure 4.7 shows numerical simulations of the stimulated echo modulation due to a single $^{87}\text{Sr}$ nucleus randomly oriented about each electron spin. The ESEEM experiments of both the $^{87}\text{Sr}$ system and ours concern nuclei weakly coupled to the electron spin; specifically, in equation 4.5 the magnitude of $A$ is much smaller than that of $\omega_r$. In the small $A$ limit, the higher harmonics of the nuclear Larmor frequency vanish in the primary (two-pulse) echo ESEEM signal and it becomes identical to the stimu-
Figure 4.7: Simulated damping of stimulated echo ESEEM due to nuclear Quadrupole coupling in the $^{87}$Sr system. This also models the damping of the primary echo ESEEM in our system if the frequencies listed are scaled by 0.83. Used with the permission of the American Chemical Society [32].

lated (three-pulse) echo ESEEM signal [26]. This allows us to use the simulations of the quadrupole damping in the $^{87}$Sr system shown in figure 4.7 as a proxy for a numerical simulation of the quadrupole damping in our system. The relevant scaling parameter of the quadrupole damping is the ratio $R$ of the quadrupole coupling to the nuclear Larmor frequency. Therefore the quadrupole couplings $e^2 q Q$ listed in figure 4.7 can be scaled by $\omega_{L}^{33Kr}/\omega_{L}^{87Sr} = 0.83$ to indicate the couplings of an analogous simulation for $^{33}$Kr.

The dominant source of electron density (and electric field gradients) in our samples is the krypton atoms. Each $^{33}$Kr atom neighboring a hydrogen or deuterium radical substituted in the bulk of the clusters experiences a field gradient due to the krypton atom missing at the position of the radical. If we ignore the small electron density of the radical, the quadrupole coupling $e^2 q Q$ of the $^{33}$Kr atom should be approximately that
of a $^{83}$Kr atom within a Kr$_2$ dimer. (We are equating the magnitude of the electric field gradient neighboring a vacancy in bulk krypton with that neighboring a single krypton atom.) Cleveland and Meersmann found no value for the quadrupole coupling within Kr$_2$ in a 2008 literature search; they have estimated it at 1 MHz by scaling the value from a Kr-Ar molecule [34, 35]. This suggests that the quadrupole damping of ESEEM modulation signals from radicals positioned within the cluster bulk is slight, about that shown in curve "b" of figure 4.7.

For $^{83}$Kr atoms in the surface layer of the cluster facets, three (Kr(111)) or four (Kr(100)) missing krypton atoms contribute to the field gradient at the $^{83}$Kr nucleus. Adding the field gradients due to the missing atoms as vectors estimates $e^2qQ$ as 2.6 MHz for the Kr(111) surface and 2.8 MHz for the Kr(100) surface. This will cause moderate quadrupole damping of the ESEEM modulation, as shown in curve "d" of figure 4.7. We note that comparison of our data to the $^{87}$Sr simulation is limited to the effects of the damping on the depth of the modulation, which is determined entirely by $R$. We cannot compare the modulation frequency shifts in the simulation to our data because these are dependent on the asymmetry parameter $\eta$, which was only simulated for the case of $\eta = 0.2$ in the $^{87}$Sr system and is unknown (although likely small) in our system [32].

We constructed damped ESEEM modulation curves by multiplying our simulated undamped curves by an exponential decay. To simulate the signal for deuterium atoms on the surface of the clusters, the exponential decay was chosen so that the modulation depth of the second trough was reduced to 3/8 of its undamped depth, in accordance with curve "d" of figure 4.7. This result is shown as curve "c" in figure 4.5; it roughly agrees with the data shown as curves "d" and "e". Analogous damped modulation curves for deuterium atoms substituted in the cluster bulk were not calculated but would be
strongly modulated, with a depth approximately the size of the full vertical scale of figure 4.5, in blatant disagreement with the data. Though compelling, this cannot be used to conclusively exclude the possibility of bulk placement of the deuterium atoms, because there is another case that can produce shallow ESEEM modulation.

The interpretation of shallow $^8$Kr modulation as evidence that the deuterium in our samples is positioned on the cluster surfaces requires consideration of other scenarios that could lead to shallow modulation. The assumptions of the model culminating in equation 4.2 used to calculate the ESEEM signals were easily satisfied by this experiment. The parameters of this model are the geometric positioning of the electron spins relative to the nuclei and the form of their magnetic coupling. The substitutional positioning of the radicals within the krypton structure is certain. As discussed in chapter 1, both FCC and HCP structures are likely present in the krypton clusters; this doesn’t affect the interpretation of the ESEEM measurements because the ESEEM signals from atoms substitutionally positioned within FCC and HCP structures are nearly identical. The magnetic interactions each electron spin its neighboring nuclei are transmitted through dipolar (field-mediated) and superhyperfine (direct contact) couplings. The case of strong superhyperfine coupling (where the electron spin wavefunction of the atomic radical is sufficiently dense at the krypton nucleus to dominate its orientational energy) can be excluded by the lack of satellite lines in our CW ESR spectra. Significant superhyperfine coupling at the 4.04 Å nearest neighbor distance of the substitutional site is also physically unrealistic because this is within the attractive range of the hydrogen-krypton potential. Small superhyperfine couplings do not affect the modulation depth of the ESEEM signal. Unfortunately, we cannot exclude a priori the possibility of strong nuclear quadrupole coupling—this is the one parameter that adds substantial ambiguity to the interpretation of our ESEEM signals.
Suppose the quadrupole interaction is so strong that the echo signal from any electron spin with an $^{83}$Kr nearest neighbor does not modulate. Then only atoms having no $^{83}$Kr nearest neighbors contribute to the modulation of the echo envelope. These will modulate very weakly, because the nuclei closest to the electron spins contribute most strongly to the modulation. Furthermore, the statistics of the isotopic distribution will bias these modulating spins toward surface populations, since only 23.1% of radicals in the bulk have no $^{83}$Kr nearest neighbors, but 61.3% and 69.3% of the atoms on the Kr(100) and Kr(111) surfaces have no $^{83}$Kr nearest neighbors. The resulting modulation will oscillate very weakly even if there is a substantial bulk population.

We simulated the case where the deuterium radicals are located within the bulk of the krypton clusters and the quadrupole coupling is so strong that those radicals with $^{83}$Kr nearest neighbors produce a critically damped modulation signal. The remainder of the atoms are modulated only by $^{83}$Kr positioned at symmetric bulk sites beyond the first coordination shell, which produce a weak but undamped modulation signal. This case is shown as curve “b” in figure 4.5. It is clearly a poor match to the data of curve “d” but perhaps a better match to the data of curve “e”. If it is the case that the radicals are in the bulk of the clusters and the quadrupole coupling is so strong that it is obliterating most of the $^{83}$Kr modulation, then our estimate of $e^2 qQ$ for the nuclei in the bulk must be low by at least a factor of six. This is unlikely, but not impossible.

No amount of quadrupole coupling can explain the precipitous drop in both the $\pi/2 - \pi/6$ and $\pi/2 - \pi$ data over the first 0.6 $\mu$s. Instantaneous diffusion cannot explain the drop either, as this would cause the drops in the two data sets to occur over very different timescales. We also cannot explain why the $\pi/2 - \pi/6$ and $\pi/2 - \pi$ data are so different. We note that the hypothesis of two deuterium populations with different $T_1$ relaxation times can be excluded by the fact that we allowed sufficient time in
our measurements for the electron spins to fully thermalize. As for using ESEEM measures-
ments to determine the position of the radicals, the obvious thing to do is study the
relative modulation of fresh and annealed samples. Whatever the quadrupole coupling,
the modulation depth will increase by a factor of 2–3 if the atoms move from the surface
into the bulk during the annealing process.
CHAPTER 5
DIPOLAR BROADENING OF THE CW ESR LINESHAPE

To understand the lineshapes of the CW ESR absorption spectra of an impurity-helium condensate, we must consider the sources of magnetic fields that are present within these materials. In addition to the homogenous applied magnetic field of \( \sim 3200 \) Gauss, there are inhomogeneities in the applied magnetic field of \( \sim 0.05 \) Gauss across the size of the sample. Magnetic moments due to atomic radicals and magnetic nuclei also contribute to the distribution of magnetic fields inside the condensates. Within the H-Kr-He and D-Kr-He samples, the fields due to the electron spins are far larger than the fields from the \(^{83}\text{Kr}\) nuclei. Each electron spin produces a dipolar magnetic field that is experienced by the other electrons in the sample. The electron spins can also interact by an exchange coupling, but this is probably a very rare occurrence in our samples.

In the case of the high-field line of the samples condensed from mixtures of H\(_2\):Kr:He in the ratios of 1:50:10,000, the environment surrounding the atomic hydrogen is largely devoid of H\(_2\), as evidenced by the progression of line positions seen in figures 2.2 and 2.3. The high-field line position is relatively insensitive to the molecular surroundings of the H atoms. This is because shifts in line position due to \( g \) and \( A \) for the three environments (H in bulk Kr, H on the Kr surface with neighboring He, and H on the Kr surface with neighboring H\(_2\)) in this system tend to add for the low-field line but cancel for the high-field line. This is a fortuitous consequence of the correlation of \( g \) and \( A \) for these three environments and the magnitude of our applied magnetic field. Although there are multiple types of attractive sites on the cluster surfaces for hydrogen atoms, we proceed under the assumption that the high-field line positions of these sites coincide. The high symmetry of the line, and the fact that it retains its symmetry under high microwave power, strongly suggests (but does not prove) that this is the case. In
Figure 5.1: Measured CW ESR derivative spectra of the featured sample and two fitted curves. a) A Gaussian line scaled to match the measured data in peak-to-peak linewidth. b) A Lorentzian line scaled to match the measured data in peak-to-peak linewidth. c) Measured high-field hydrogen line. The lines have been shifted to zero field for clarity.

any event, broadening of the line due to variations in $g$ and $A$ would only strengthen the conclusions of this section.

The measured CW ESR line shapes of H-Kr samples possess very broad wings in comparison to the Gaussian and Lorentzian curves conventionally used to fit signals from solid samples. This is shown in figure 5.1, where the conventional curves are fitted to a "featured sample" condensed from a gas mixture of H:Kr:Hc = 1:50:10000. This sample also produced the rightmost line in the upper set of curves in figure 2.3; it was chosen because this line position suggests the sample contains the least amount H$_2$ near the H atoms. The shape and scale of the high-field line of the featured sample are almost entirely due to dipolar magnetic coupling among the electron spins. This provides an opportunity to compare this lineshape to that predicted by a model of spins adsorbed to
clusters of the ~25 Å radii indicated by the x-ray measurements discussed in chapter 1.

The distribution of electron spins within our samples is unusual in two ways. First, in our samples radicals are trapped in a loose aggregate of clusters possessing a narrow size distribution, with 5–50 spins per cluster. The cluster size is drawn from the x-ray scattering results discussed in chapter 1. The number of hydrogen atoms is found by doubly integrating the measured ESR lines, and the number of krypton atoms is known from the composition and quantity of gas used in forming the samples. Second, both pulse (chapter 4) and CW (chapter 2) ESR indicates these radicals are largely confined to the surfaces of the clusters. Numerically simulating the dipolar broadening of the hydrogen atoms allows us to determine if the unusual distribution of electron spins is responsible for the broad wings of our CW ESR line shapes. In our simulations we ignore magnetic interactions between electrons occupying different clusters; this is appropriate considering the large number of electrons in each cluster and the fact that liquid helium containing no spins occupies most of the volume immediately surrounding each cluster. This allows direct computation of the lines from an ensemble of systems each containing a small number of spins.

5.1 Simulating the dipolar broadening

In the simplest approximation, the electron spins interact only with the applied magnetic field $\vec{B}_0$, and the time-independent Schrodinger equation is:

$$\hbar \gamma B_0 \sum_i S_{z i} |\Psi_u\rangle = \mathcal{H}_u |\Psi_u\rangle = E_u |\Psi_u\rangle = \hbar \gamma B_0 \sum_i m_{z i} |\Psi_u\rangle$$

(5.1)

where $i$ indexes the spins and $|\Psi_u\rangle$ is an eigenstate of $\mathcal{H}_u$, with the "u" subscript indicating that this Hamiltonian is unperturbed by the dipolar broadening. The eigenstates
Figure 5.2: Simulated CW ESR absorption lines of an ensemble of clusters each containing 20 electron spins randomly positioned throughout the bulk of the clusters. Innermost line: Simulation including only the A term. Second innermost line: Simulation of deuterium atoms including A and B terms. Third innermost line: Simulation of hydrogen atoms including A and B terms. Outermost line: Simulation of atoms lacking nuclear hyperfine coupling including A and B terms. Lines are normalized to match their maximum absorption.

of the whole system are simply products of the eigenstates of the isolated spins:

\[ |\Psi_u\rangle = \prod_i^N |\Psi_{ui}\rangle \]

\[ m_{ci} = \langle \Psi_{ui}|S_z|\Psi_{ui}\rangle \quad (5.2) \]

Since we are concerned with hydrogen and deuterium radicals, where the electron spin wavefunction has total angular momentum \( S = 1/2 \), each spin can take on either the \( m_{ci} = +1/2 \) (up, \( |\uparrow\rangle \)) or \( m_{ci} = -1/2 \) (down, \( |\downarrow\rangle \)) eigenstate. The full list of system eigenstates is formed from equation 5.2 by listing the \( 2^N \) unique products of individual spin eigenstates. The CW ESR line is found by considering the energy differences
between states of the system $\Psi_u$ that are coupled by the transverse microwave field $\vec{B}_1$. These are states that differ by the orientation of a single electron spin. In the limit of small $\vec{B}_1$, corresponding to the usual CW ESR experiment, the transition requires an energy of exactly $\hbar \gamma_S B_0$, giving an infinitely sharp absorption line.

We now add a perturbative dipolar coupling between the spins. The dipolar Hamiltonian is

$$\mathcal{H}_{\text{dip}} = \hbar^2 \gamma_S^2 \sum_{i,j<i}^N \frac{(\vec{S}_i \cdot \vec{S}_j - 3(S_i^x S_j^x + S_i^y S_j^y))(\vec{S}_i \cdot \vec{r}_{ij})(\vec{S}_j \cdot \vec{r}_{ij})}{r_{ij}^3} = \hbar^2 \gamma_S^2 \sum_{i,j<i}^N \frac{(A + B + C + D + E + F)}{r_{ij}^3}$$

(5.3)

where

$$A = S_z S_z (1 - 3 \cos^2 \theta_{ij})$$

$$B = -\frac{1}{4}(S_i^+ S_j^- + S_i^- S_j^+)(1 - 3 \cos^2 \theta_{ij})$$

$$C = -\frac{3}{2}(S_i^+ S_z S_j^- + S_z S_i^- S_j^+ \sin \theta_{ij} \cos \theta_{ij} \exp(-i \phi_{ij}))$$

$$D = -\frac{3}{2}(S_i^- S_z S_j^+ + S_z S_i^+ S_j^- \sin \theta_{ij} \cos \theta_{ij} \exp(i \phi_{ij}))$$

$$E = -\frac{3}{4}(S_i^+ S_j^+ \sin^2 \theta_{ij} \exp(-2i \phi_{ij}))$$

$$F = -\frac{3}{4}(S_i^- S_j^- \sin^2 \theta_{ij} \exp(2i \phi_{ij}))$$

and $\theta_{ij}$ and $\phi_{ij}$ indicate the direction of $\vec{r}_{ij}$. The dipolar fields among the electrons spins in our samples are at most 20 Gauss, far smaller than $\vec{B}_0$ and thus justifying the use of perturbation theory. The energy perturbed to first order is

$$E_p = \hbar \gamma_S B_0 \sum_i^N m_{z,i} + \langle \Psi_u | \mathcal{H}_{\text{dip}} | \Psi_u \rangle$$

(5.4)

The total angular momentum along the z-axis is

$$M_z = \sum_i^N m_{z,i}$$

(5.5)

and is a constant of the motion of the unperturbed system. Therefore only the $A$ and $B$ terms, which connect eigenstates $|\Psi_u\rangle$ of equal $M_z$, can contribute to $E_p$ [36]. Qual-
itatively, the A term accounts for the fields that are produced and sensed by the z-components of the individual spins. These are static because the spins are precessing about the z-axis. The B term involves transverse components of the spins that oscillate at the 9 GHz Larmor frequency. If for any reason spins i and j precess at different Larmor frequencies, then their coupling by the B term will average to zero over a few precession periods. (absorption occurs over many periods because $B_0 \gg B_1$.) For a given magnetic field, hyperfine coupling to the state of the hydrogen nucleus causes the electron spin of the hydrogen atom to precess at one of two frequencies. Similarly, deuterium atoms will precess at one of three possible frequencies. These frequency separations are far larger than the distribution of frequencies due to all other sources, so among all pairs of hydrogen (or deuterium) atoms in a sample only one half (or one third) of them are affected by the B term. Thus the presence of nuclear hyperfine coupling changes the breadth of a CW ESR line in addition to splitting it. The effect of the B term is also reduced as frequency shifts due to the A term (the static magnetic fields) cause spins to lose the resonant precession that the B coupling requires. In a computation, a straightforward (though certainly not the most accurate) way to handle this is to first compute the precession frequencies of the spins in a sample due only to the A term couplings. Then the B couplings are calculated and multiplied by a devaluing factor $R$ constructed by analogy to the Lorentzian absorption line of a damped harmonic oscillator:

$$R(f_M/f_B) = \frac{1}{(f_M/f_B)^2 + 1}$$

(5.6)

where $f_M$ is the frequency mismatch between a pair of spins due to all of their A couplings and $f_B$ is the frequency of the coupling due to the B term. The effect of the inclusion of the B coupling is shown in figure 5.2. Including the B term always broadens the absorption curves; it also affects the shape of the absorption curves. Changes in both breadth and shape are more pronounced in clusters with smaller numbers of atoms and in clusters where the atoms only populate the surface. The lineshape simu-
Figure 5.3: a.) Simulated CW ESR absorption lines of an ensemble of clusters each containing 24 atoms randomly positioned on the cluster surface. b.) A Lorentzian curve fitted to match the amplitude and curvature of the peak of line “a”.

lation proceeds by randomly positioning a fixed number of randomly oriented spins on (surface population) or in (bulk population) a spherical cluster. The $A$ and $B$ couplings between the spins are computed at the position of each spin in the cluster, and the energy needed to invert each spin is calculated. This energy includes coupling to both the $S_z$ and $S_x$ components of the spin. In randomly orienting the spins this model assumes that the sample is not thermally polarized. Spins in the actual samples are polarized approximately 16% along the z-axis, but this has a negligibly small effect on the field distribution in the clusters. Numerous clusters are averaged to give a representative absorption curve. All of the couplings scale as $r^{-3}$, so the absorption curve can be scaled to simulate a cluster of any size. Two libraries of absorption curves were simulated,
one of clusters containing atoms throughout their bulk and another of clusters containing atoms only on their surfaces. The libraries contained curves for clusters containing 4–80 atoms. Over this range the absorption lines of clusters with atoms in their bulk are about twice as broad as those of clusters with atoms only on their surfaces.

The final computed line is determined by the distribution of cluster sizes and the relative concentration $C_R = [H]/[Kr]$ of hydrogen atoms to krypton atoms. The cluster size distribution is drawn from the x-ray scattering measurements of samples condensed from gas mixtures containing .5% Kr, as discussed in chapter 1. The number of krypton atoms is known from the quantity of condensed gas and the number of hydrogen atoms is known from the double integration of measured ESR signals. From these values bulk and surface densities of the atomic radicals are computed and the electron spins are distributed among the clusters according to a Poisson distribution. The contributions of clusters are summed across size and population and the resulting absorption line is smoothed and differentiated for comparison to measured data.

5.2 Magnetic susceptibility

We now digress to consider the magnitude of the macroscopic magnetization of the sample due to its susceptibility. The dipolar broadening simulations assume that spins are randomly oriented within the clusters of the sample. However, the energy difference between the aligned and anti-aligned states is not negligible compared to the thermal energy at 1.35 K. Boltzmann statistics (equation A.10) indicate that the fraction of spins aligned with $\vec{B}_0$ exceeds the fraction aligned against $\vec{B}_0$ by $P = 0.16$, giving the sample an overall magnetization along $\vec{B}_0$.

Dipolar magnetic fields scale with the distance from their sources as $r^{-3}$. If we
consider integrating the field due to spherical shells of magnetization centered about a point within the sample, the quantity of sample in each shell will scale as \( r^2 \). The combined integrand will scale as \( r^{-1} \) and the integral will not converge. This means the magnetic field at any point within a polarized sample is dependent on the shape and size of the entire sample! This is unlike the fields due to randomly oriented spins, which are dominated by the local distribution of spins because couplings to distant, highly populated shells average out more than couplings to sparsely populated nearby shells. A simple way to estimate the magnitude of the paramagnetic susceptibility is to assume that the sample is a homogenously magnetized sphere and to calculate the field at its surface. The field outside such a sphere is perfectly dipolar and equals that which would be produced if the total magnetization of the sphere were due to a point dipole positioned at its center. From this we find that the field at the surface of the sphere is

\[
\vec{B}_{pol} = \frac{\mu_0 N P \mu_e (3 \cos(\theta) \hat{r} - \hat{z})}{r^3}
\]  

(5.7)

where \( NP \mu_e \) is the dipole moment of the sphere due to \( N \) electron spins. Using the spin concentration \( \rho_e = 3N/(4\pi r^3) \) gives the scale-independent result

\[
\vec{B}_{pol} = \frac{\mu_0 \rho_e P \mu_e (3 \cos(\theta) \hat{r} - \hat{z})}{3}
\]  

(5.8)

The concentration of our strongest sample is \( 1.3 \cdot 10^{19} \text{cm}^{-3} \). The largest field magnitude (at \( \theta = 0, \pi \)) estimated by equation 5.8 is 0.16 Gauss, with most of the sample experiencing less than 0.08 Gauss. This is small enough to ignore when calculating the dipolar lineshapes.

### 5.3 Simulation results and comparison to data

Encouragingly, dipolar simulation of ensembles of clusters each equally populated with atoms and of uniform radius generates absorption lines with considerably larger wings
Figure 5.4: Simulated CW ESR absorption lines of an ensemble of clusters each containing a.) 16 hydrogen atoms randomly positioned on the cluster surface b.) 32 hydrogen atoms randomly positioned on the cluster surface, c.) 16 hydrogen atoms randomly positioned within the bulk of the cluster, d.) 32 hydrogen atoms randomly positioned within the bulk of the cluster. The radius of the clusters in “b” has been adjusted so that their electron spin surface density matches that of “a”. The radius of the clusters in “d” has been adjusted so that their electron spin bulk density matches that of “c”. Lines are normalized to match their maximum absorption.

than the Lorentzian lineshape, as shown in figure 5.3. For all atomic radical populations simulated, ranging from 4–80 atoms per cluster, the absorption curve is narrower by about a factor of two if the atoms only populate the cluster surfaces. This can be seen by comparing curves a.) and c.) of figure 5.4. Unfortunately, curves from bulk and surface populated clusters are very similar in shape, so lineshape alone cannot be used to determine if radicals occupy the bulk of the Kr clusters in our samples. For clusters
Figure 5.5: Comparison of the featured sample lineshape and two computed lineshapes. a) Measured high-field hydrogen line of the featured sample. b) curve “a” dilated by a factor of 8.3 in magnetic field. c) Computed lineshape of clusters populated on their surfaces using an H/Kr ratio of 1/44 and the cluster size distribution of table 1.1. d) Computed lineshape of clusters populated in their bulk using an H/Kr ratio of 1/44 and the cluster size distribution of table 1.1.

populated with atoms only on their surface, clusters of equal electron spin surface densities but different sizes produce different absorption curves, with the larger and more populous clusters giving a broader curve. Curves “a” and “b” of figure 5.4 illustrate this effect; while curves “c” and “d” show the (weaker) analogous effect for clusters populated by atoms in their bulk.

To test the accuracy of the simulation, we calculated the absorption lineshapes of clusters containing large numbers of atoms randomly positioned within their bulk. In the limit of very large numbers of atoms in the cluster bulk, the simulated linewidth should approach that of randomly dispersed spins in continuous media. A well accepted estimate of the peak-to-peak dipolar broadening in such a system has been calculated by
Kittel and Abrahams to be

\[ B_{pp} = \frac{\rho_e \text{Gauss cm}^3}{2.7 \cdot 10^{19}} \]  

(5.9)

where \( B_{pp} \) separates the peaks of the derivative spectrum and \( \rho_e \) is the spin density [37, 9]. Limited computational memory constrains our simulations to clusters of 3000 spins. Figure 5.6 shows simulations of clusters populated by 1000 and 3000 atoms with spin densities of \( 2.7 \cdot 10^{19} \text{cm}^{-3} \). Both curves have a dipolar linewidth of about 3/5 of that predicted by equation 5.9. This means that we are simulating enough atoms to represent the continuum limit, and that our simulation probably underestimates the actual dipolar broadening within our samples. This result strengthens the conclusions of the following sections. We note that the exclusion of the "B" term of equation 5.3 has no effect on our simulated lineshapes in the continuum limit.

Lineshapes were simulated using the cluster size distribution from table 1.1 and a value for \( C_R \) of 1 hydrogen atom per 44 krypton atoms, as is the case for the featured sample. Unfortunately, the value for \( C_R \) is very approximate because it relies on the absolute CW ESR signal calibration and the efficiency of sample beaker in capturing the krypton introduced into the cryostat. If a portion of the sample does not fall into the lower part of the sample beaker, hydrogen atoms within that portion will be uncounted, reducing the value of \( C_R \). This is probably why two samples formed under identical conditions to the featured sample have \( C_R \) values of 100 and 115, yet produce ESR lines very similar to those of the featured sample. These other samples complete the upper set of lines in figure 2.2. The ESR calibration assumes that the sample occupies the full volume of the beaker inside the microwave cavity. The lower part of the beaker is about twice as sensitive as the average sensitivity of the beaker due to the distribution of the magnetic field \( \vec{B}_1 \) of the excited microwave mode in the cavity. The hydrogen atoms of a sample occupying only the bottom the beaker will be overcounted. Experiments with krypton using a similar condensation apparatus found that only 30% of the admitted
Figure 5.6: Simulated lineshapes of clusters that approximate the continuum concentration of $2.7 \cdot 10^{19}$ cm$^{-3}$. a) Simulation with 3000 atoms per cluster. b) Simulation with 1000 atoms per cluster. The waviness of the curves is an artifact of the small number of clusters averaged in the simulation and a subsequent filtering process.

Krypton atoms are condensed into the sample beaker. The value $C_R = 1/44$ is derived by assuming that all of the admitted krypton is captured and that the sample fully occupies (but does not overfill) the beaker. This value is conservative in that it most likely underestimates the actual relative concentration of hydrogen atoms.

Figure 5.5 compares the high-field line of the featured sample to the computed lineshapes. The lines computed for the cases of both surface (curve c) and bulk (curve d) radical positions severely overestimate the linewidth. Curves (b) and (c) show that the peak-to-peak width of the line computed for the surface case is 8.3 times larger than
experiment and also of a very different shape. This presents a quandary: why does the simulation predict such a broad line even when the uncertain parameters of the simulation err on the side of producing a narrow line? We will consider four sources of this discrepancy: exchange narrowing, the concentration $C_R$, the size distribution of the clusters, and finally the regularity of the electron spin distribution.

One explanation of the narrow line of the featured sample is exchange narrowing among the hydrogen atoms bound to the cluster surfaces. Exchange narrowing occurs when there is overlap of the spatial wavefunctions of neighboring electron spins, allowing neighboring electrons to exchange position. This allows the electrons to see an averaged magnetic field and produce narrower ESR lines. Exchange coupling is extremely unlikely in our system because a large fraction of the hydrogen atoms would need to be paired with another hydrogen atom at a distance shorter than 8 Å to produce a noticeable effect [38]. Furthermore, the hydrogen atoms must interact through vacuum. The fifth nearest neighbor spacing between attractive sites on the Kr(111) surface of krypton clusters provides an appropriate spacing of 7 Å. At this spacing the lattice formed by the helium atoms occupies half of the surface sites and provides an open path clear of helium to allow for overlap of the electronic wavefunctions. While this is an appealing picture and is a stable arrangement of hydrogen atoms that allows for exchange, it is very improbable that this arrangement could result from the condensation process. This is because as the clusters cool hydrogen atoms bind to the krypton surfaces before the helium atoms, and the hydrogen can diffuse very rapidly and recombine in the time before the helium binds. The hypothesis that hydrogen atoms could diffuse on the krypton surfaces and form exchange coupled pairs without recombining is implausible without a mechanism to stabilize the pairs against recombination. Exchange narrowing also produces a characteristic lineshape that has a broad peak-to-peak separation and reduced wings [38]. This is exactly the opposite of what the featured sample shows.
Figure 5.7: Comparison of the featured sample lineshape and a fitted computed lineshape. a) Measured high-field hydrogen line of the featured sample. b) Computed lineshape of clusters populated on their surfaces using an H/Kr ratio of 1/158 and the cluster size distribution of table 1.1. The small fluctuations in the computed line are an artifact of the computation.

An obvious explanation of the narrow line of the featured sample is that we have grossly overestimated $C_R$. We computationally explored reducing the hydrogen atom concentration while keeping the other parameters constant, and found that a concentration of $C_R = 1/158$ produces a line of appropriate peak-to-peak width, shown in figure 5.7. At this concentration there are about 9 atoms per cluster, enough that magnetic interactions between different clusters can still be ignored. The lineshape computed using the reduced concentration shows a very different lineshape than that measured, suggesting that an overestimate of $C_R$ does not explain our discrepancy.

A third explanation of the linewidth discrepancy is the possibility that the actual cluster size is smaller than the distribution drawn from the x-ray scattering experiments.
on similar samples. This is especially plausible considering that the x-ray samples were condensed at 1.6 K, where the vapor pressure of helium is 5.7 Torr, while the CW ESR samples were condensed at 1.5 K, where the vapor pressure of helium is 3.6 Torr [39]. The latent heat of evaporation is approximately constant over this range. Reducing the cluster sizes while holding $C_R$ constant reduces the surface density of the electron spins on the clusters and also places fewer atoms on each cluster. This second factor limits the range of exploration to cluster radii that are at least 60% of those obtained from the x-ray fit. At this scale the computed line is still four times as broad as the measured line and a poor match in shape. If a smaller cluster size distribution is the sole cause of the linewidth discrepancy, the cluster sizes must be less than half the sizes given in table 1.1, so that there are at most two or three spins per cluster. In the extreme case where the clusters are typically 8 Å in radius, there is only one hydrogen atom per cluster and the clusters will no longer concentrate the electron spins into small groupings. Then the spins will be distributed through a medium that is approximately continuous because the scale of the pores between the clusters will be comparable to the typical spacing between the spins. In this case formula 5.9 is applicable; with the 0.54 G linewidth of the featured sample it indicates a concentration of $1.5 \cdot 10^{19} \text{cm}^{-3}$, very close to the $1.3 \cdot 10^{19} \text{cm}^{-3}$ value obtained by simply dividing the number of spins by the sample volume.

Before concluding that the Kr cluster radii are only one third of those measured in the x-ray experiment, we should question the assumption that the electron spins are randomly dispersed on the cluster surfaces. Random dispersal is reasonable if the hydrogen atoms cannot diffuse after they adsorb to the cluster surfaces. However, the tunneling rates calculated in chapter 3 imply that the hydrogen atoms are very mobile on krypton surfaces in the absence of helium, suggesting that no more than one hydrogen atom per cluster facet can survive the condensation process. If this is the case, the distribution of
the electron spins on the cluster surfaces will be much more regular and close proximity between electron spins will only be possible at the facet edges. Lineshapes of regularly distributed spins have not yet been simulated but are certainly narrower than those of randomly distributed spins.

We now have two explanations for the linewidth discrepancy. The spins are either adhered to smaller clusters than originally believed, or the spins are stabilized on the cluster surfaces in a regular arrangement rather than a random one. Diffusion and recombination of hydrogen atoms on the cluster facets is probably the only mechanism by which the electron spins can acquire a regular distribution on the cluster surfaces. (The possibility of a regular arrangement of sites at the cluster vertices that are especially attractive to the hydrogen atoms is not inconceivable; the following discussion still holds in this case.) The x-ray measurements discussed in chapter 1 indicate that the clusters are icosahedra, with 20 facets per cluster. The x-ray size distribution and the value \( C_R = 1/44 \) imply an average of 39 atoms per cluster. Since diffusion of the hydrogen atoms on the cluster surfaces during the condensation process is required to form a regular distribution of hydrogen atoms, it is impossible to form clusters that host a regular distribution of electron spins whose population exceeds the number of cluster facets. This point links the hypothesis of a regular distribution of hydrogen atoms to the relative concentration \( C_R \) and the cluster size distribution. If we accept the theoretically reasonable hypothesis of a regular spin distribution, we must also accept that either the actual value of \( C_R \) is half that originally calculated, or that the actual cluster radii are only 75\% of those listed in table 1.1. The second case is the most likely explanation of the discrepancy because we are much more confident in the concentration measurements of our sample than in the x-ray measurements of a sample formed similarly in another apparatus.
We conclude that the krypton clusters in the featured sample have typical radii smaller than 20 Å, making them the smallest reported structures formed by the impurity-helium condensation method. We also conclude that either the hydrogen atoms are arranged in a regular distribution on the cluster surfaces, or the clusters have extremely small typical radii of only 8 Å, with the former case being far more likely. It remains to be seen if simulations of clusters with regular distributions of electron spins on their surfaces produce lines that are comparable to those of the featured sample in both shape and width.
CHAPTER 6
HARDWARE

This chapter discusses some of the hardware used in the pulse ESR measurements presented in this thesis, with a focus on the parts that were specifically designed for these experiments. We also discuss the design and function of a longitudinal ESR (LODESR) detection scheme for quantifying free radicals at low temperatures. Our CW ESR spectrometer is an older (~ 1970) but otherwise unremarkable Varian machine of a type described thoroughly by Poole [9].

6.1 Pulse ESR spectrometer

We begin with the overall scheme of the homodyne pulse ESR spectrometer, shown in figure 6.1. With the exception of the LODESR circuit and the cryogenic insert, the design is very conventional. The microwave section of this spectrometer was designed and mostly built by Peter Borbat. Beginning at the microwave generator, the 9 GHz microwaves are split into two paths. One path enters a mixer as a reference frequency while the other is gated in magnitude and phase, and then amplified by a traveling-wave tube amplifier. The powerful (2 kW) pulses are guided by a circulator and sent through coaxial lines to a resonator at the bottom the cryostat, which is placed in the applied magnetic field $\vec{B}_0$. The microwave pulses induce precession in the electron spins which later produce small microwave pulses of their own called spin echoes, as shown in figure 4.1. These microwave pulses leave the cryostat through the same coaxial line that carried the original pulses. The circulator routes the spin echo pulses to a sensitive amplifier connected to the previously mentioned mixer, where they beat against the microwave frequency to produce low frequency in-phase and quadrature signals.
These are amplified and then sampled by a digital oscilloscope.

The microwave gating, traveling-wave tube amplifier gating, and oscilloscope triggering are orchestrated by pulses produced by a programmable pulse generator card (Pulseblaster, by SpinCore Inc.) within a desktop PC. We wrote a custom program (in C language) to control this card and also the oscilloscope. The measurement of each spin echo was downloaded from the oscilloscope memory and saved to the computer hard disk while the electron spins in the sample recovered their thermal polarization.

Our spectrometer was capable of producing microwave pulses from 16 to 512 ns in duration, with their separation and duration incremented in 8 ns steps. A 100 ms pause
following each echo measurement was needed to download the sampled echo through the GPIB bus to the computer. If the measured echo signals were part of an ESEEM experiment, the echoes were phase corrected according to the method of Astashkin et al., which allows for a signal-to-noise improvement by using the full echo rather than only its peak [40].

6.2 Pulse ESR microwave resonators

We now discuss the lower portions of the cryostat inserts used in the pulse ESR experiments. These portions receive the microwave pulses from the pulse spectrometer and concentrate them in a resonator that also admits the sample collection beaker. As described in chapter 1, a sample is condensed in the collection beaker at the top of the cryostat for a period of ten minutes. The beaker is then moved into the microwave resonator in the lower part of the cryostat, which is situated between the poles of a conventional electromagnet that provides the static field $B_0$. We have developed two styles of microwave resonator pulse ESR experiments, one based on a resonant microwave cavity and another based on a loop-gap resonator. We first discuss the motivation to use a resonator.

ESEEM experiments like those of chapter 4 are most effective if the duration of the microwave pulses is small compared to the Larmor precession periods of the modulating nuclei. This condition results in the deepest modulation and allows the microwave pulses to be treated as though they occurred instantaneously, greatly simplifying the modeling of the modulation pattern (see appendix A.3). For the loss of modulation depth due to the finite pulse length of the microwave pulses to be acceptably small, the nuclei should precess by no more than $\pi/6$ radians during a pulse of length $T_p$ that causes the
Figure 6.2: Pulse ESR portions of two cryostat inserts for studying impurity-helium condensates. I) Loop-gap resonator based insert with LODESR detection coils. II) Cavity resonator based insert. a, j) Coaxial microwave line. b, m) Teflon and quartz beakers. c) Microwave shield. d, e) LODESR coils and forms. f) Silver patterning. g) Microwave coupling loop. h, k) Sample. i) Loop-gap microwave resonator. l, n) Resonant microwave cavity and silica cavity insert. o) Q spoiler and pedestal. The coaxial line “a” runs outside of microwave shield “c”, above the plane of the page, and turns to penetrate the shield in the plane of the coupling loop “g”. The plane of the coupling loop in “II” is actually perpendicular to the plane of page.
Figure 6.3: Left: The loop-gap resonator based pulse ESR cryostat insert. Right: The cavity resonator based pulse ESR cryostat insert, designed primarily by Vladimir Khmelenko.
electron spins to precess by $\pi/2$ radians, which is the minimum angle needed to perform experiments with good sensitivity. The required pulse duration is $T_p = \pi/6B_0\gamma$ and the corresponding field amplitude is $B_1 = 3B_0\gamma/\gamma_S$. This indicates maximum pulse lengths of 6 ns for proton modulation, 40 ns for deuteron modulation, and 160 ns for $^{83}$Kr modulation.

Achieving the large $B_1$ microwave fields required by the above condition requires a very powerful microwave source. For the challenging case of proton ESEEM at 9 GHz, the required field is 15 Gauss. The power needed to produce this field in a waveguide of cross sectional area of one square centimeter is about 50 kW. This enormous power requirement can be circumvented by using a microwave resonator. A resonator of quality factor $Q$ increases the $B_1$ field inside the resonator by a factor of $\sqrt{Q}$ relative to the case of the waveguide. The resonator also provides a sensitivity increase of $\sqrt{Q}$ to microwave signals produced by the sample. For these reasons, using a higher $Q$ resonator is preferable so long as its bandwidth is large enough to contain the applied pulses. Using the resonator comes at the cost of dead-time, which is the period immediately following the application of the microwave pulses when a spin echo cannot be measured because the resonator is still responding (“ringing down”) measurably to the microwave pulse. The dead-time grows linearly with $Q$, except in the case of extremely strong samples, and is a major reason why free induction decays (signals due to electron spin precession immediately following the first microwave pulse) are difficult to study in ESR.

For a microwave frequency $F_0$, the resonator bandwidth is $F_0/Q$. The fourier transform of a uniform microwave pulse $B_1(t)$ of duration $T_p$ and amplitude $A$ at frequency $F_0$ is

$$
\tilde{B}_1(f) = A \frac{\sin \left( \frac{\pi(f - F_0)T_p}{\pi(f - F_0)T_p} \right)}{\pi(f - F_0)T_p}
$$

(6.1)

The amplitude of $\tilde{B}_1(f)$ is approximately constant over the range
\(|f - F_0| < 1/(2T_p)|
\]

so the pulse has a useful bandwidth of \(1/T_p\). Thus the optimal resonator will have \(Q = T_p F_0\).

The power required to sustain a field \(B_1\) in the resonator is

\[
P = \frac{kV B_1^2 F_0}{\mu_0 Q}
\]

(6.2)

where \(V\) is the volume of the resonator and \(k \sim 1\) accounts for the geometric details of the resonant mode. Combining the above equations gives the power requirement for the optimal resonator:

\[
P = \frac{kV B_1^2}{\mu_0 T_p} = \frac{54kV B_0^3 \gamma^3}{\pi \mu_0 \gamma_s^2}.
\]

(6.3)

This shows that nuclei of large \(\gamma\) impose a strong power requirement on pulse ESR experiments. For our cavity resonator, of volume 8.3 cm\(^3\), the minimum power required to observe modulation by protons is 2300 Watts. For our loop-gap resonator, the effective volume is about 5 cm\(^3\) and the required power is about 1400 Watts. (Note that the quartz dielectric in the resonators does not enter into this calculation.) In contrast, only 8 Watts of power is needed to observe deuterium modulation in the cavity resonator, and only 5 Watts is needed for the loop-gap resonator. Our traveling-wave tube microwave amplifier produces pulses of 2 KW; however transmission losses of the microwaves limits the power delivered to the resonator to about 400 W. Consequently we optimized our resonators for the observation of deuteron modulation, with quality factors of about 300. (We have observed modulation by protons in HD molecules with these resonators, but their small bandwidth prevents quantitative work.) Most of our measurements were made using the modified cavity resonator with a 16 ns pulse inducing a \(\pi/2\) angular precession of the electron spins. This required about 50 Watts of microwave power. \(^{83}\)Kr modulation was also observed with these pulses.

The first resonator is shown on the right of figure 6.3 and as part II of figure 6.2. It uses a cylindrical brass cavity as a microwave resonator and is a modification of a design
originally developed for CW ESR by Vladimir Khmelenko. A coaxial line (formed of copper and porous Teflon) delivers microwaves to a wire loop that shorts the coax and provides magnetic coupling to the TE$_{011}$ mode of the cavity. The cavity is filled with a toroidal insert of synthetic fused silica. This lowers the frequency of TE$_{011}$ mode of the cavity to 9 GHz without causing significant microwave damping or adding magnetic impurities. The smaller volume allows larger microwave fields $\vec{B}_1$ to be achieved with a given pulse energy. The silica also distorts the resonant mode so that $\vec{B}_1$ is parallel to the cylinder axis and relatively homogenous in the open hole of the insert, where the sample beaker sits. The resonator as described has a cryogenic $Q$ factor of about 3000, which is good for CW work (this style is used for all the CW measurements in our lab) but too large for pulse ESR. We deliberately spoil the $Q$ by placing a small quartz ring beneath the beaker; the ring is coated with a 0.5 $\mu$m layer of chromium that absorbs the microwaves. The ring is mounted on a small copper pedestal that can be screwed in and out of the cavity to adjust the damping. For pulse ESR measurements we set the $Q$ of the cavity to 300.

The second resonator is shown on the left of figure 6.3 and as Part I of the figure 6.2. It was developed with the aim of producing a resonator with a smaller effective volume so that a smaller $Q$ factor could be used and the dead-time of the spectrometer could be decreased. As the power requirements listed above indicate, this was only marginally successful. We developed a bridged loop-gap microwave resonator based on the design described by Pfenninger et al., but used three gaps and bridges instead of two [41]. The resonator consists of silver patterned onto a hollow quartz cylinder that closely fits the sample beaker. In the lowest mode of the resonator, which is the only one used, the three large silvered areas on the inner surface of the quartz provide the inductive elements of the resonator, while the gaps across the cylinder wall act as capacitive elements. In this mode an approximately homogenous magnetic field parallel
to the cylinder axis is produced in the volume enclosed by the resonator. The bridges on the outside are not strictly necessary for resonance, but they help to concentrate the electric field within the quartz, lowering the resonant frequency and reducing the chance of arcing across the gaps. This also increases the homogeneity of the magnetic field and reduces the sensitivity to any dielectric within the volume contained by the resonator, most importantly the beaker material.

Our resonator designs were prototyped by placing copper tape on the quartz bodies. The prototypes were studied by observing the power returned to a network analyzer connected to a coupling loop that was positioned near the resonator. We settled on a design with an inner diameter of 6.7 mm, an outer diameter of 8.9 mm, and a cylinder height of 7.2 mm. The silvering gaps are 0.81 mm wide and the bridges are 2.64 mm wide. The silvered layer is 2 μm thick and was formed by four successive chemical silvering deposition steps. This layer is several skin depths thick, yet thin enough to tolerate thermal cycling. When inside a microwave shield, this resonator shows a well isolated fundamental mode at about 8.9 GHz. The $Q$ factor is about a thousand if the resonator is critically coupled, but in our application the $Q$ is reduced to about 250 by overcoupling to the coupling loop.

Pfenninger et al. patterned the silver by hand-painting the quartz cylinders with an organic gold solution that was baked to leave a thin layer of metallic gold. This was then electroplated with silver to a thickness of several skin depths ($\delta \approx 650$ nm) to achieve good conductivity of the layer. We explored alternative ways to define the pattern based on electroless (chemical) silvering. We used proprietary aqueous silvering solutions (Peacock labs, Philadelphia, PA) that reduce silver nitrate to metallic silver, similar to the Brashear process. These deposit a strong and homogenous silver layer on quartz, but only if it is meticulously clean. In the simplest patterning method, we positioned
precisely cut pieces of masking tape on the quartz cylinder to mask areas where silver was not desired. An alumina blasting tool (using compressed nitrogen to propel fine alumina powder) was used to remove a thin layer of quartz from the exposed areas, leaving a microscopically rough but very clean surface. The cylinder was promptly submerged in distilled water until it was silvered. Any silver deposited on areas that were not prepared by the alumina blasting rubbed off by touch. This method produced the resonator shown in figure 6.4, which was the only loop-gap resonator used in our pulse ESR experiments.

A more accurate method of defining the silver pattern would use a rigid mask, such as that in figure 6.5. The positive mask shown could be placed over a completely silvered resonator and used to protect areas from abrasive blasting that would remove the silver. Alternatively, a negative mask could take the role of the masking tape in the first method. Unfortunately, the mask shown (originally intended to mask fine liquid droplets) was accidentally destroyed before these methods could be tested. A more accurately defined silver pattern would not have improved the performance of the tape masked resonator, which already had a $Q$ factor much higher than we needed. Loop-gap resonators produce approximately dipolar magnetic fields that interact with conductive material far outside of their enclosed volume. This is undesirable because it may change the properties of the resonance during an experiment. A conductive pipe placed around the resonator will shield the microwaves if its cutoff frequency exceeds the resonator frequency. This implies a diameter $d_{\text{shield}} < 1.84 \frac{c}{\pi F_0} \simeq 2$ cm; we used $d_{\text{shield}} = 1.27$ cm. Some microwaves still escape through evanescent propagation down the length of the shield; these can cause unwanted resonances inside the metal cryostat. We found aluminized plastic ribbon, which can be removed from polyester or polypropylene capacitors, to be an effective microwave absorber for damping these resonances.
Figure 6.4: Silvered quartz resonator produced by tape masking. The left edge of the bridge element facing the camera is the most distorted feature of the resonator.

Figure 6.5: The brass resonator mask.
The beaker is subject to many design considerations. It must be made of a material that does not show paramagnetic resonance at the positions of the hydrogen and deuterium hyperfine lines. The material must be nonconducting and must not chemically react with the radicals of the sample. The beaker should be impervious to superfluid helium and have a smooth surface that does not scratch the silver patterning on the resonator. Finally, to maximize the volume of sample contained in the resonator, the beaker walls should fit precisely within the resonator and should be as thin as possible. Beakers are conventionally made of quartz to satisfy the above conditions, although specialized expertise and equipment is required to produce thin walled quartz beakers of precise dimension. We explored Teflon as an alternative material and machined a beaker of 0.25 mm wall thickness, allowing for a sample volume larger than what was possible with the quartz beakers. Unfortunately, this beaker showed a broad paramagnetic resonance signal at the $g = 2$ line position and at lower fields, although the high-field hydrogen line was clean. It may be possible to reduce this signal by annealing the Teflon, but this comes at the risk of warpage. We had abundant signal strength and so choose to revert to using quartz beakers. Directly patterning silver on a quartz beaker to form a microwave resonator out of the beaker itself promises to form very efficient resonators. However, the problem of fixing the relative position of the resonator and coupling loop is more difficult in this case because the beaker must be free to move to and from the collection region. The resonator was seated on a Teflon pedestal with notches that closely fit the coaxial line where it enters the microwave shield. The pedestal was pressed firmly against the coaxial line by a spring-loaded Teflon plunger mechanism. This fixed the position of the resonator relative to the coupling loop that was soldered to the coaxial line, despite the large thermal contraction of the Teflon parts. The resonator mounting apparatus is not shown in figure 6.2.
6.3 Longitudinal ESR (LODESIR)

Quantifying the number of radicals trapped in our hydrogen-krypton samples is necessary if we are to understand their stability over time. It is particularly important when studying samples containing hydrogen and deuterium atoms trapped in H₂, HD or D₂ matrices, where quantum tunneling allows both diffusive recombination and chemical reactions to change the number of radicals. In CW ESR, the number of electron spins in the sample beaker is measured by doubly integrating the derivative spectra of the sample and comparing this to doubly integrated spectra of a ruby standard fixed to the bottom of the resonant cavity. Quantifying the spins in our samples by pulsed ESR is much more difficult because the strength of the spin echo depends strongly on the instantaneous diffusion of the sample, as described in chapter 4. In turn, the instantaneous diffusion is dependent on the concentration and distribution of spins within the sample. Consequently there is no simple relationship between echo amplitude and the number of spins in the sample. Even relative measurements are spoiled; if the number of spins in a sample decreases over time, the attenuation of the spin echoes by instantaneous diffusion also decreases, so the amplitude of a spin echo measured with a given interpulse time \( \tau > 0 \) may either decrease or increase. Only the echo amplitude in the limit where \( \tau \rightarrow 0 \) changes proportionally with the number of electron spins. Unfortunately we cannot approach this limit because of the dead-time imposed by our microwave resonator, which is 200 ns for strong samples (krypton clusters) and 300 ns for weak samples (molecular deuterium clusters). We also cannot extrapolate the echo amplitudes back to \( \tau \rightarrow 0 \) because our instantaneous diffusion varies from sample to sample, does not follow a simple form, and cannot be measured with our equipment for \( \tau < 200 \) ns.

One way to quantify the spins without the complication of instantaneous diffusion is to measure the longitudinal magnetization of the sample, the component parallel to
$\vec{B}_0$. This is commonly used in systems with short echo decay times $T_2$ and short spin thermalization times $T_1$ [42, 25]. In the usual LODESR scheme, the sample is exposed to microwaves that are amplitude modulated at a frequency $\Omega$, where $\Omega$ is much less than $1/T_1$. If the sample is resonant with the microwaves, the polarization of the spins along $B_0$ will be reduced in proportion to the power of the absorbed microwaves. Thus the longitudinal magnetization of the sample will oscillate at the modulation frequency of the microwaves. This changing magnetization induces a voltage in a coil surrounding the sample that is amplified using lock-in detection. This scheme is only effective if the $T_1$ of the samples is short, which allows $\Omega$ to be large ($\gtrsim 10$ kHz) and Faraday detection to be efficient.

Our krypton based samples thermalize with a $T_1$ of 20–40 ms, and atoms in the molecular deuterium samples have $T_1$ values of 100–200 ms, so neither system is a candidate for the above scheme. Instead, we surround the sample and microwave resonator with a pair of coils that form part of an LC circuit that resonates at 2.1 MHz. The coils contain 17 turns apiece and are connected in series with each other and a 1.3 m coaxial line that ends outside the top of the cryostat, as shown in figure 6.2. The wavelength of the resonant frequency in the coax is long enough (95 m $\approx$ 0.013 porankusemaa) that transmission line effects are negligible. An amplifier connected to the coaxial line outside the cryostat senses the voltage across the capacitor. The $Q$ of the resonant circuit is reduced to about 20 by the addition of a 9 k$\Omega$ load resistor in parallel to the connection with the amplifier. Loading the LC circuit to a low $Q$ makes it insensitive to temperature induced changes in the resistivity of the wire in the coils. The coils are positioned at the "magic angle" of 54.7° $\approx$ arccos$(3^{-1/2})$ with respect to $\vec{B}_0$ and are as close as possible to the sample. This maximizes the capture of the approximately dipolar longitudinal component of the magnetic flux produced by the spins in the sample. The microwave shield of the loop-gap resonator is constructed from a stack of Stycast bonded copper rings so
that it is transparent to the longitudinal field produced by the sample. The cylindrical wall of the cavity resonator is similarly made of a stack of insulated brass rings.

Two $\pi$ pulses were applied to the spins to excite the LODESR circuit. These caused two inversions of the sample magnetization, which induced corresponding voltage pulses in the coils. The Faraday voltage induced by the second pulse is of opposite sign to that of the first pulse, so the LC circuit is most effectively driven if the pulses are separated in time by half its resonant period. This is advantageous because any unwanted coupling of the microwave pulses to the resonant LC circuit will be identical for the first and second pulses. The timing of the pulses then causes the effects of the unwanted coupling to cancel. This is shown in figure 6.5 for pulses of 48 ns duration.

The transient oscillation of the LODESR circuit is amplified, sampled and stored in an oscilloscope. Then a background signal is obtained under identical conditions but with $B_0$ adjusted far away from resonance. The magnitude of the difference of these signals is proportional to the number of spins in the sample. Our LODESR scheme is very similar to the "pulse-train" longitudinal detection method developed by Granwehr et al. [43]. Their method continues the application of pulses until variations in $B_1$ within the microwave resonator and the effects of finite pulse time dephase the spins. This results in a larger signal but a much greater sensitivity to the length and power of the microwave pulses and the placement of the sample within the resonant cavity.

The timescale over which the spins in a sample will precess coherently in the transverse plane can either be measured directly from the duration of the spin echo or calculated from the breadth of the CW ESR spectrum. As an example of the second method, we consider the high-field line of the featured sample of chapter 5, which is about half a Gauss peak to peak, with almost all of the line contained within 5 Gauss from the line center. Using $f = \Delta B \gamma \epsilon$ we estimate that the spins will precess coherently for about
Figure 6.6: Theoretical prediction of the LODES R circuit response to a pair of 48 ns microwave pulses. Upper pane: Impulses from the Faraday voltage induced by the reorienting magnetic moment of the sample. Middle pane: Impulses induced by unwanted coupling of the microwave pulses to the LODES R circuit. Lower pane: Response of the LODES R circuit to the impulses.
70 ns. The LODESR scheme described above avoids the problem of spin dephasing by keeping the spins aligned parallel or antiparallel to $B_0$, except for the brief periods when the microwave pulses are applied. The "B" term of the dipolar broadening (equation 5.3) operates on the transverse components of the spin angular momenta, which are absent when the spins are parallel or antiparallel to $B_0$. The "A" term is still active but cannot affect the spins while they are in an eigenstate of the unperturbed Hamiltonian $H_u$ established by $B_0$. Consequently, the spins are immune to dephasing while they are aligned antiparallel to $B_0$ for the half-period (240 ns) between the microwave pulses, though they are exposed during the two microwave pulses. Based on the 70 ns timescale estimated for the dephasing of the spins of the featured sample, an appropriate choice of pulse length would be 32 ns. Shorter pulses could be used at the cost of LODESR signal strength, which scales linearly with the length of the pulses in the limit where the pulse duration is much shorter than the resonant period of the LC circuit.

Our LODESR circuit produced 70% of the signal strength predicted theoretically, and we were able to measure to an uncertainty of $3 \cdot 10^{15}$ spins by using 100 cycles of averaging for each of the signal and background traces. This uncertainty corresponded to a voltage of 4.4 μV at the amplifier input. The process of signal averaging, field shifting, background averaging and finally subtracting required four minutes. The timing of the pulses influenced the proportions of the ESR and unwanted microwave coupling signals in the LODESR circuit as expected, resulting in an eightfold reduction in the amplitude of the unwanted signal.

Unfortunately, our LC LODESR circuit was beset with a powerful and unpredictably intermittent noise signal that limited its successful use to the measurement of only two samples. Though disappointing, this established for molecular deuterium samples that spin-echo amplitudes can be used as a proxy for the number of spins in the sample.
despite the complications of instantaneous diffusion. We never attempted LODESR measurements of the hydrogen-krypton samples. The noise was independent of $B_0$ and therefore not a magnetic resonance phenomenon. It was dependent on the setting of the attenuator following the traveling-wave tube amplifier, suggesting that the amplifier was sometimes producing microwaves when it should not have been. We excluded the microwaves from anything that might plausibly have a rectifying effect that would couple them to the low frequency of the LC circuit, but were unable to reduce the strength of the noise.
APPENDIX A

CALCULATING ESEEM SIGNALS

"Whatever in creation exists without my knowledge exists without my consent."

—Judge Holden (Blood Meridian [44], Cormac McCarthy)

A.1 The density matrix

The density matrix provides a convenient way of tracking the populations and quantum coherences among an ensemble of \( N \) identical systems. Descriptions more thorough than this one are given in Slichter, Levitt, and Schweiger & Jeschke.[30][45][25]

The systems composing the ensemble are assumed to be identical and non-interacting. Each system \( n = 1 \ldots N \) is described by a wavefunction that can be decomposed into a set of \( M \) static normalized orthogonal basis functions:

\[
|\psi_n\rangle = \sum_{i=1}^{M} c_{ni}(t) |\varphi_i\rangle.
\]  \hspace{1cm} (A.1)

The weights \( c_{ni}(t) \) of the basis functions provide a complete but impractically large \( (N \times M) \) terms) microscopic description of the ensemble at time \( t \). The weights change to allow the wavefunction of the system to evolve in time (Schrödinger picture) under the action of Hamiltonian \( H \):

\[
\frac{d}{dt} |\psi_n\rangle = \sum_{i'=1}^{M} |\varphi_{i'}\rangle \frac{d}{dt} c_{ni'}(t) = -\frac{i}{\hbar} \sum_{i'=1}^{M} |\varphi_{i'}\rangle \sum_{i=1}^{M} \langle \varphi_{i'} | H(t) | \varphi_i \rangle c_{ni}(t) = -\frac{i}{\hbar} H(t) |\psi_n\rangle.
\]  \hspace{1cm} (A.2)
A measurement of the ensemble average of the quantity $\mathcal{G}$ is found by adding the contributions of the expectation values $< \mathcal{G}_n >$ of each microscopic system $n$.

$$< \mathcal{G} > = N^{-1} \sum_{n=1}^{N} < \mathcal{G}_n > = N^{-1} \sum_{n=1}^{N} \sum_{i,r} \langle \varphi_i | \mathcal{G} | \varphi_r \rangle c_{ni}^* c_{nr} $$

(A.3)

Most magnetic resonance experiments involving large ensembles of identical quantum systems, including ours, are only able to measure macroscopic expectation values $< \mathcal{G} >$ that average across the entire ensemble. These measurements cannot distinguish between microscopic systems; they are blind to the expectation values $< \mathcal{G}_n >$ of individual microscopic systems. The Hamiltonian $\mathcal{H}$ also acts without distinguishing between microscopic systems. The symmetries with respect to $n$ of the operators $\mathcal{G}$ and $\mathcal{H}$ allow for a great simplification: It is sufficient to track only the average properties of the microscopic systems to predict the macroscopic expectation values $< \mathcal{G} >$. This information is contained in the density matrix $\rho$, which is an average of the outer products of the spinors that represent the wavefunctions $|\psi_n\rangle$ of the microscopic systems.

$$\rho = N^{-1} \sum_{n}^{N} |\psi_n\rangle \langle \psi_n | = \sum_{i,r}^{M} c_{r}^* c_{i} |\varphi_i\rangle \langle \varphi_r |$$

(A.4)

$$\rho_{fi} = c_{r}^* c_{i} = N^{-1} \sum_{n}^{N} c_{ni}^* c_{nr}$$

(A.5)

Combining and manipulating the above equations gives a compact expression for the macroscopic expectation value

$$< \mathcal{G} > = \text{tr}(\mathcal{G} \rho)$$

(A.6)

and a similarly compact form (the Liouville-von Neumann equation) for the time evolution of the density matrix.

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [\mathcal{H}(t), \rho(t)]$$

(A.7)
The $M^2$ elements of the density matrix are not independent of each other. The main diagonal elements $\rho_{ii}$ represent the fractional occupation of quantum state $i$ in the ensemble; these populations are nonnegative, real, and always sum to one. Thus $M - 1$ numbers are needed to describe the populations. The off-diagonal elements $\rho_{ij}$ are complex and represent the average phase coherence between the states $i$ and $j$. The density matrix is Hermitian, so $(M^2 - M)/2$ complex numbers are needed to describe the coherences.

Consider the example of an ensemble of three $M = 2$ systems. The spinors are

$$\left| \psi_1 \right> = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \left| \psi_2 \right> = \begin{pmatrix} \sqrt{2}/2 \\ \sqrt{2}/2 \end{pmatrix} \quad \left| \psi_3 \right> = \begin{pmatrix} 1/2 \\ -\sqrt{3}/2 \end{pmatrix}$$

and these have outer products $\langle \psi_4 | \psi_4 \rangle$ of

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}, \quad \begin{pmatrix} 1/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & 3/4 \end{pmatrix}.$$ System $|\psi_1\rangle$ is in a pure state and does not contribute to the off-diagonal coherence terms. System $|\psi_2\rangle$ has equally populated states in a coherent superposition, giving the off-diagonal term in the outer product. System $|\psi_3\rangle$ contains a superposition of unequally populated states, and these states are out of phase by an angle $\pi$, giving a factor of $\exp(i\pi) = -1$ in the coherences. The density matrix of this system is

$$\rho = \begin{pmatrix} 7/12 & (2 - \sqrt{3})/12 \\ (2 - \sqrt{3})/12 & 5/12 \end{pmatrix}.$$  

Suppose the states evolve in time under a diagonalized Hamiltonian

$$\mathcal{H} = |\phi_1\rangle E_1 \langle \phi_1 | + |\phi_2\rangle E_2 \langle \phi_2 |$$

The density matrix then evolves as

$$\rho(t) = \begin{pmatrix} 7/12 & \frac{(2 - \sqrt{3})\exp(-i(2E_2 - E_1)t/\hbar)}{12} \\ \frac{(2 - \sqrt{3})\exp(-i(2E_2 - E_1)t/\hbar)}{12} & 5/12 \end{pmatrix}.$$  

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The populations are unchanged in time because $\mathcal{H}$ is diagonal in the basis $|\varphi_i\rangle$ that $\rho$ is written. Note the small magnitude of the coherences in $\rho$ relative to the coherences in the outer products $|\psi_2\rangle\langle\psi_2|$ and $|\psi_3\rangle\langle\psi_3|$. This is because the coherences due to systems 2 and 3 nearly cancel. Many other sets of microscopic wavefunctions $|\psi_n\rangle$ could be written that averaged to the density matrix shown above. The differences between these sets could not be discerned through ensemble averaged measurements $<\mathcal{G}>$. In this way, the density matrix hides most of the microscopic detail of the system.

### A.2 The spin 1/2 rotation matrices

The spin 1/2 rotation matrices are equal to half of the Pauli spin matrices:

\[
I_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}, \quad I_x = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}, \quad I_y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix}.
\]

They have many algebraic properties:

\[
I^2_\alpha = 1/4 \quad ; \quad e^{i\theta I_\alpha}e^{-i\theta I_\alpha} = I_\alpha \quad \text{for } \alpha = x, y, z
\]

\[
I_xI_y = \frac{i}{2}I_z \quad ; \quad I_yI_x = -\frac{i}{2}I_z \quad \text{and cyclic permutations.}
\]

For a vector $\vec{I} = \alpha I_x + \beta I_y + \gamma I_z$ with $\alpha^2 + \beta^2 + \gamma^2 = 1$:

\[
\vec{I}^2 = 1/4 \quad e^{i\theta \vec{I}} = 1 \cos(\theta/2) + 2i \vec{I} \sin(\theta/2)
\]

\[
e^{i\theta I_x}e^{-i\theta I_z} = \alpha I_x + \beta (I_y \cos(\theta) - I_z \sin(\theta)) + \gamma (I_y \sin(\theta) + I_z \cos(\theta))
\]

and cyclic permutations.

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A.3 The two-pulse ESEEM signal of an $S = 1/2$, $I = 1/2$ system

The system composed of a single $S = 1/2$ electron coupled to an $I = 1/2$ nucleus gives the simplest nontrivial ESEEM signal, first calculated by Rowan [27]. The signals of $S = 1/2$ systems containing multiple nuclei, and nuclei of higher spin, are calculated from this basic signal. This derivation uses the density matrix formalism and is loosely based on those in Slichter and Dikanov & Tsvetkov.[30][26]

Consider an ensemble of identical systems, each containing one electron, $S$, and two nuclei, $I_a$ and $I$. The electron occupies a spherical (S) orbital and is centered on nucleus $I_a$, forming an atom. Nucleus $I$ is located within a nearby molecule. This is shown in figure A.1. Both $S$ and $I$ are spin 1/2 particles. An external field $\vec{B}_0$ is applied at an angle $\theta_v$ with respect to the vector $\vec{r}$ pointing from the electron to the nucleus $I$. We will calculate using coordinates with the z-axis aligned with $\vec{B}_0$ and the x-z plane containing $\vec{r}$.

Each system has four quantum states. In the case where the electron and the nucleus $I$ are uncoupled, the external field provides the only terms in the Hamiltonian and the eigenstates corresponding to $S$ and $I$ point parallel or antiparallel to $\vec{B}_0$. (We ignore the states of $I_a$, which are unchanging during the ESEEM experiment and only act to shift the precession frequency of the electron. We also assume an isotropic electronic $g$-factor.) Using $\uparrow$ and $\downarrow$ to indicate spin states with positive and negative angular momentum along the z-axis, the four states are written as $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$. The first arrow in each ket indicates the direction of the electron spin $S$ and the second indicates the direction of the nuclear spin $I$. This choice of basis will not correspond to the eigenstates of the system once electron-nuclear coupling is included; however, the ESR spectrometer applies and senses fields $\vec{B}_1$ that are perpendicular to the z-axis, so
Figure A.1: The geometry of the electron spin $S$, atomic nucleus $I_a$, and neighboring nucleus $I$.

the interaction of $\vec{B}_1$ with $\rho$ is most easily calculated in the uncoupled basis.

In the two-pulse experiment, the spectrometer applies two microwave pulses along the $y$-axis of the rotating frame. Prior to the first pulse, the nuclear eigenstates align with the sum of the electronic and external fields. The first pulse, at time $t = 0$, lasts for a duration sufficient to rotate the electron spin through an angle of $\pi/2$ radians. For simplicity of calculation, the pulses are assumed to act instantaneously relative to the precession of the nucleus. After the first pulse, the direction of the electronic field at the nucleus has changed, and the nucleus precesses about the new direction of the sum of the electronic and external fields until the second microwave pulse is applied. At time $t = \tau$ the second pulse is applied; it rotates the electron spin through an angle $\psi$. The nucleus again evolves under the influence of the electronic and the external fields until the time $t = 2\tau$. At this time, the electron spins are refocused by the static magnetic
field inhomogeneity $\Delta \vec{B}_0$, forming a spin echo that is measured by the spectrometer.

The calculation proceeds by beginning with the density matrix of the thermally relaxed ensemble. The density matrix is then exposed to four rotations. The first and third rotations are due to the microwave pulses applied by the spectrometer at times $t = 0$ and $t = \tau$. The second and fourth rotations are due to the evolution of the system during the times of length $\tau$ between the two pulses and after the second pulse. Finally, the density matrix is used to calculate the electronic magnetization when the echo forms at time $t = 2\tau$.

The rotations due to the first and second microwave pulses are indicated by operators $\sigma_{M1}$ and $\sigma_{M2}$, while $\sigma_E$ indicates the nuclear rotation during the evolution periods. The expectation value of the $x$-axis magnetization at time $2\tau$ is

$$< \mathcal{M}_x(2\tau) > = \text{tr}(-\hbar \gamma_S S_x \rho(2\tau)) = \text{tr}(-\hbar \gamma_S S_x \sigma_E \sigma_{M2} \sigma_E \sigma_{M1} \rho_{\text{h}} \sigma_{M1}^{-1} \sigma_{E}^{-1} \sigma_{M2}^{-1} \sigma_{E}^{-1})$$

(A.8)

The Hamiltonian of the system is used to construct the evolution operator $\sigma_E$ is written in the the non-rotating lab frame and the uncoupled basis as

$$\mathcal{H}_{\text{Lab}} = \mathcal{H}_{3-B_0} + \mathcal{H}_{3-\Delta B_0} + \mathcal{H}_{1-B_0} + \mathcal{H}_{1-\Delta B_0} + \mathcal{H}_{\text{HFC}} + \mathcal{H}_{A}$$

where

$$\mathcal{H}_{3-B_0} = \hbar \gamma_S B_0 S_z \quad \text{and} \quad \mathcal{H}_{1-B_0} = -\hbar \gamma B_0 I_z$$

are the electron and nuclear interactions with $\vec{B}_0$. The interactions with the field inhomogeneity $\Delta \vec{B}_0$ are analogous. Spin matrices $\vec{S}$, $\vec{I}$, and $\vec{I}_a$ (and their components, such as $S_z$ and $I_z$) operate on the spinors of the electron, atomic nucleus, and neighboring nucleus respectively. The sign difference of the coupling to the field is due to the negative $g$-factor of electron. (I am assuming a positive $g$-factor for the nucleus, as is the case for protons and deuterons. The sign of the $g$-factor of the nucleus does not affect the
ESEEM spectra.) The electron and nuclear gyromagnetic ratios are $\gamma_e$ and $\gamma_n$. In these experiments the electron spin occupies an $S$ orbital around $I_e$, so the hyperfine coupling $\mathcal{H}_{\text{HFC}}$ is given by the Fermi contact interaction

$$\mathcal{H}_{\text{HFC}} = \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \mathbf{I}_e \cdot \mathbf{S} |\Psi(0)|^2$$

where $\mathbf{I}_e$ measures the spin of the atomic nucleus, which has Larmor frequency $\gamma_n$, and $|\Psi(0)|^2$ is the spatial probability density of the electron spin at the atomic nucleus.

Finally, the interaction of the electron with the neighboring nucleus is

$$\mathcal{H}_a = \frac{\hbar^2 \gamma_e \gamma_n}{r^3} \left[ 3(\mathbf{I} \cdot \mathbf{r}) \cdot (\mathbf{S} \cdot \mathbf{r}) - \mathbf{I} \cdot \mathbf{S} \right] + \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \mathbf{I} \cdot \mathbf{S} |\Psi(\mathbf{r})|^2.$$  

The first term is due to the magnetic dipolar coupling of the electron and the nucleus. The second term is due to the direct contact of the electron spin and the neighboring nucleus, and is called the isotropic superhyperfine interaction.

For interaction distances of $r > 3 \text{ Å}$ and external fields $B_0 > 0.3 \text{ T}$, the magnetic field at the electron due to the nucleus ($< 50 \mu \text{T}$) has a negligible effect on the direction of the total field at the electron. This allows the assumption that the eigenstates of the electron spin are the eigenstates of $S_z$ and are parallel or antiparallel to $\mathbf{B}_0$ and the $z$-axis. We are not assuming that the nuclear fields have a negligible effect on the eigenvalues of the electron spins—these effects are central to the ESEEM phenomenon because they allow the motions of the nuclei to dephase the electron spin echoes. The timescale of the nuclear precession is much larger than the timescale of the electronic precession because $B_0 \gamma_e >> B_0 \gamma_n$. This means that the slowly precessing nucleus effectively reacts to an average of the much faster precession of the electron. The terms in $\mathcal{H}_a$ containing $S_x$ and $S_y$ oscillate with the fast precession of the electron and average to zero over the nuclear precession timescale, allowing replacement of the operator $\mathbf{S}$ by $S_z$. The secular
(time-averaged over the electron precession) interaction Hamiltonian is then

\[ \mathcal{H}_A = I_x S_z \left[ \frac{\hbar^2 \gamma_e}{3} 3 \cos^2(\theta_t) - 1 \right] + \frac{8 \pi}{3} \gamma_s \gamma_e \hbar^2 |\Psi(\vec{r})|^2 \] + I_x S_z \frac{\hbar^2 \gamma_e}{3} \sin(\theta_t) \cos(\theta_t) \\
= I_z S_z A_\parallel + I_z S_z A_\perp. \]

A final approximation is that the field inhomogeneity \( \Delta \vec{B}_0 \) dephases the nuclear spins over a timescale much longer than the \( \sim 20 \mu s \) of the longest two-pulse ESEEM experiments. Thus we drop the \( \mathcal{H}_{\Delta \vec{B}_0} \) term.

At times \( t = 0 \) and \( t = \tau \), the spectrometer applies the transverse field \( \vec{B}_1 \) to the samples in the form of microwave pulses at a frequency \( \omega_{\text{Spec}} \). Transverse magnetizations \( \langle \mathcal{M}_x \rangle \) and \( \langle \mathcal{M}_y \rangle \) are measured through a mixer referenced to the same frequency. The standing microwave field \( \vec{B}_1 \) is equivalent to a sum of two circularly polarized fields counter-rotating at frequencies \( \pm \omega_{\text{Spec}} \). The spectrometer is tuned to

\[ S_z \omega_{\text{Spec}} / \hbar = \mathcal{H}_{\Delta \vec{B}_0} + \mathcal{H}_{\text{HFC}}, \]

so that one of the counter-rotating fields satisfies the resonance condition of the electron spin. (The non-resonant component of the microwave field has a negligible effect on the electron spin.) With the microwave pulses both applied and sensed at frequency \( \omega_{\text{Spec}} \), it is convenient to calculate in a correspondingly rotating frame of reference. The rotating frame Hamiltonian is given by

\( \mathcal{H}_{\text{Rot}} = \mathcal{H}_{\text{Lab}} - (\mathcal{H}_{\Delta \vec{B}_0} + \mathcal{H}_{\text{HFC}}). \) The subtracted terms correspond to the part of \( \mathcal{H}_{\text{Lab}} \) that has been separated by the rotation \( \omega_{\text{Spec}} t \). In the rotating frame the transverse electron spin rotation operators become

\[ S_{x,\text{Rot}} = e^{-i\omega_{\text{Spec}} t S_z} S_x e^{i\omega_{\text{Spec}} t S_z}, \quad S_{y,\text{Rot}} = e^{-i\omega_{\text{Spec}} t S_z} S_y e^{i\omega_{\text{Spec}} t S_z}, \]

with the corresponding magnetization operators \( \mathcal{M}_x \) and \( \mathcal{M}_y \) similarly transformed, so that they now correspond to measurements of perpendicular components of the electron spin magnetization oscillating at \( \omega_{\text{Spec}} \). In these transformations there is a degree of freedom that we fix by defining \( t = 0 \) so that the microwave pulses cause rotations of
the electron spins about the y-axis. From this point on we drop the "Lab" and "Rot" suffixes and work only in the rotating frame.

The thermalized density matrix $\rho_{th}$ assumes an electronic polarization $P$ along the z-axis due to $B_0$. The nuclei are assumed to be completely unpolarized. Then

$$\rho_{th} = \begin{bmatrix}
|\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \\
(1-P)/4 & 0 & 0 & 0 \\
0 & (1-P)/4 & 0 & 0 \\
0 & 0 & (1+P)/4 & 0 \\
0 & 0 & 0 & (1+P)/4 \\
\end{bmatrix} |\uparrow\uparrow\rangle \quad \text{(A.9)}$$

with the polarization given by

$$P = \tanh\left( \frac{\hbar \omega_{\text{spec}}}{2K_bT} \right) \simeq 0.16 \text{ at } 1.35 \text{K and } 9 \text{GHz.} \quad \text{(A.10)}$$

The unpolarized portion of $\rho_{th}$, corresponding to exactly 1/4 of the population in each state, is ignored beyond this point because it can never contribute to a measurable signal.

Now we finally begin working through equation A.8 to find $\langle M_x(2\tau) \rangle$. The first microwave pulse rotates the electron spins through an angle of $\frac{\pi}{2}$. This rotation is accomplished algebraically by application of $\mathcal{O}_{M1} = \exp(i\frac{\pi}{2}S_y)$ to $\rho$. The effect of the first microwave pulse is to rotate the initial z-magnetization to point along the x-axis, giving

$$\rho(0^+) = \mathcal{O}_{M1}\rho_{th}\mathcal{O}_{M1}^{-1} = \frac{P}{2}S_x = \frac{P}{4} \begin{bmatrix}
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
\end{bmatrix}$$

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for the density matrix immediately following the first microwave pulse. (The \(0^+\) notation is analogous to that of limits and refers to the time immediately after the first microwave pulse, which is assumed to be of zero length.) The evolution of the nuclei over the following period \(\tau\) is not as simple, because their rotation is not about the lab axes and because they act differently in the \(S^+ = 1/2 + S_z\) and \(S^- = 1/2 - S_z\) subspaces ("manifolds"), corresponding to the upper and lower halves of \(\rho\). The time evolution operator is constructed from the Hamiltonian as

\[
\mathcal{O}_E = \exp \left[ i \mathcal{S}^+ (I_{\parallel} T_{\parallel}^+ + I_{\perp} T_{\perp}^+) + i \mathcal{S}^- (I_{\parallel} T_{\parallel}^- + I_{\perp} T_{\perp}^-) + GS_z \right]
\]  

(A.11)

\[
T_{\parallel}^\pm = \frac{\hbar}{\gamma} (I_{\parallel} A_{\parallel} / 2) \quad T_{\perp}^\pm = \frac{\hbar}{\gamma} (I_{\perp} A_{\perp} / 2)
\]

where \(G = \tau \gamma B_0\) accounts for the randomly distributed external field inhomogeneity and \(T_{\parallel}^\pm\) and \(T_{\perp}^\pm\) are the angles through which the nucleus precesses about the \(z\) and \(x\) axes due to coupling to the electron and the external field. The \(I_z\) and \(I_x\) rotation operators can be combined to define normalized rotation operators \(I_D^\pm\) about axes that are tilted by angles \(\theta^\pm\) from the \(z\)-axis in the \(x\)-\(z\) plane. Defining

\[
I_D^\pm \Phi^\pm = I_z T_{\parallel}^\pm + I_x T_{\perp}^\pm = (I_z \cos(\theta^\pm) + I_x \sin(\theta^\pm)) \Phi^\pm
\]

\[
\Phi^\pm = \sqrt{(T_{\parallel}^\pm)^2 + (T_{\perp}^\pm)^2} \quad \theta^\pm = \tan^{-1} (T_{\perp}^\pm / T_{\parallel}^\pm)
\]

gives the compact form

\[
\mathcal{O}_E = \exp \left[ i \mathcal{S}^+ (I_D^+ \Phi^+ + G/2) + i \mathcal{S}^- (I_D^- \Phi^- - G/2) \right].
\]

The new rotation operators are illustrated in figure A.2. We continue to work through equation A.8 by applying the innermost pair of time evolution operators to the density matrix, giving

\[
\rho(\tau^-) =
\]

\[
= \frac{\rho}{2} \exp[i \mathcal{S}^+(I_D^+ \Phi^+ + G/2)] \exp[i \mathcal{S}^-(I_D^- \Phi^- - G/2)] \exp[-i(\cdots) - i(\cdots)] =
\]

\[
= \frac{\rho}{4} S L \exp(i G) \exp(i I_D^+ \Phi^+) \exp(-i I_D^- \Phi^-) +
\]

\[
= \frac{\rho}{4} S L \exp(-i G) \exp(i I_D^- \Phi^-) \exp(-i I_D^+ \Phi^+).\]
Figure A.2: The geometry of the evolution period Hamiltonian. Nuclear spins in the positive and negative subspaces rotate though angles $\Phi^\pm$ about vectors $I_D^\pm$. The magnitude and direction of these rotations results from adding the rotations $T_{\parallel}^\pm$ about the z-axis to the rotations $T_{\perp}^\pm$ about x-axis.

where $S^1 = S_x + iS_y$ and $S^\dagger = S_x - iS_y$ indicate the upper right and lower left quadrants of the density matrix. The second microwave pulse is applied with operator $\Theta_{M2} = \exp(i\psi S_y)$. This mixes the quadrants of $\rho$, giving

$$
\rho(\tau^+) = \\
\frac{\rho}{4} \left( S_z \sin(\psi) + S^\dagger \cos^2(\frac{\psi}{2}) - S^\dagger \sin^2(\frac{\psi}{2}) \right) \exp(iG) \exp(iI_D^+ \Phi^+) \exp(-iI_D^- \Phi^-) + \\
\frac{\rho}{4} \left( S_z \sin(\psi) - S^\dagger \sin^2(\frac{\psi}{2}) + S^\dagger \cos^2(\frac{\psi}{2}) \right) \exp(-iG) \exp(iI_D^- \Phi^-) \exp(-iI_D^+ \Phi^+) 
$$

(A.12)

After the second pulse there will be no further mixing of the electronic populations ($S^+$ and $S^-$) with the electronic coherences ($S^\dagger$ and $S^\dagger$). That is, there will only be mixing within the four quadrants of $\rho$, but not between them. The Hermitian property
of $\rho$ produces the equality

$$\text{tr}(S_+ \rho) = \text{tr}(\text{Re}[S^1 \ast \rho]) = \text{Re}[\rho_{13} + \rho_{24}] = \text{tr}(\text{Re}[S_+ \rho S_-]).$$

The term $S_+ \rho S_-$ equals $\rho$ in the upper right quadrant and is otherwise zero. The real part of this term contains only factors of $S_+$. This allows us to save work by neglecting the calculation of the $S_+$ and $S^1$ terms in A.12 when calculating $\langle \mathcal{M}_x(2\tau) \rangle$. Keeping only the $S^1$ terms and applying the outermost pair of time evolution operators gives

$$S_+ S_\downarrow \rho(2\tau) S_- =$$
$$\frac{P}{4} S^1 \cos^2\left(\frac{\pi}{2}\right) \exp(i2G) \exp(iU^+ \Phi^+) \exp(iU^- \Phi^-) \exp(-iU^+ \Phi^-) \exp(-iU^- \Phi^-) +$$
$$-\frac{P}{4} S^1 \sin^2\left(\frac{\pi}{2}\right) \exp(i(G - G)) \exp(iU^+ \Phi^+) \exp(iU^- \Phi^-) \exp(-iU^+ \Phi^-) \exp(-iU^- \Phi^-)$$

(A.13)

The phase angle $G$ in these terms is due to the static magnetic field inhomogeneity, and is dependent on the position of the atom in the sample. For the general case of $t \gg 2\pi(\gamma_0 \Delta B_0)^{-1}$, the individual electron spins are dephased and no magnetization is detectable in the transverse plane. However, at $t = 2\tau$ the lower line of equation A.13 is independent of $G$ because the effects of the static field inhomogeneity on the electron cancel at this time. This causes the sudden appearance of measurable macroscopic magnetization in the transverse plane, the “spin echo”. Since only the lower line contributes to a measurable magnetization, we neglect the upper line. To reconcile the four non-commuting rotation operators, we begin by evaluating the rotation of the second operator $I_D^-$ by the first and third operators $I_D^+$.  

A clockwise rotation of a unit vector $\hat{A}$ about a unit vector $\hat{B}$ by an angle $\phi$ results in a new unit vector $\hat{A}_{\text{rot}}$:

$$\hat{A}_{\text{rot}} = \hat{B}\cos(\theta^S) + \sin(\theta^S)(\sin(\phi)(\hat{A} \times \hat{B}) + \cos(\phi)(\hat{B} \times (\hat{A} \times \hat{B})))$$

where $\theta^S$ is the angle between the unit vectors. The definitions in section A.2 necessitate the clockwise sign convention. Within equation A.13 the vector $I_D^-$ is similarly rotated.
about $I_{D}^{+}$ by an angle $\Phi^{+}$, giving

$$
\exp(iI_{D}^{+}\Phi^{+})I_{D}^{-}\exp(-iI_{D}^{+}\Phi^{+}) =
\cos(\theta^{S})I_{D}^{-} + \sin(\theta^{S}) \left[ \sin(\Phi^{+})I_{D}^{-} \times I_{D}^{+} + \cos(\Phi^{+})(I_{D}^{+} \times (I_{D}^{-} \times I_{D}^{+})) \right] =
\cos(\theta^{S})I_{D}^{-} + \sin(\theta^{S}) \left[ \sin(\Phi^{+})I_{y} + \cos(\Phi^{+})(I_{D}^{+} \times I_{y}) \right]
$$

where $\theta^{S} = \theta^{+} - \theta^{-}$.

Writing

$$
\exp(iI_{D}^{-}\Phi^{-}) = \cos(\frac{\Phi^{-}}{2}) + 2iI_{D}^{-}\sin(\frac{\Phi^{-}}{2})
$$

and combining with the above leads to

$$
\exp(iI_{D}^{+}\Phi^{+})\exp(iI_{D}^{-}\Phi^{-})\exp(-iI_{D}^{+}\Phi^{+}) =
\cos(\frac{\Phi^{-}}{2}) + 2i\sin(\frac{\Phi^{-}}{2}) \left[ \cos(\theta^{S})I_{D}^{+} + \sin(\theta^{S}) \left[ \sin(\Phi^{+})I_{y} + \cos(\Phi^{+})(I_{D}^{+} \times I_{y}) \right] \right].
$$

(A.14)

Similarly, the fourth term in A.13 can be written as

$$
\exp(-iI_{D}^{-}\Phi^{-}) = \cos\left(\frac{\Phi^{-}}{2}\right) - 2iI_{D}^{-}\sin\left(\frac{\Phi^{-}}{2}\right).
$$

(A.15)

Multiplying this term to the right of A.14 gives a large expression equal to the last four terms in A.13. The terms in this expression contain products of zero, one or two rotation operators. The trace of this expression is found by resolving products of rotation operators into single rotation operators and pure numbers. Terms containing single rotation operators are then dropped because they are traceless. After some algebra we find an expression for the trace of the last four terms of equation A.13:

$$
\text{tr} \left( \text{Re} \left[ \exp(iI_{D}^{+}\Phi^{+})\exp(iI_{D}^{-}\Phi^{-})\exp(-iI_{D}^{+}\Phi^{+})\exp(-iI_{D}^{-}\Phi^{-}) \right] \right) =
\cos^{2}\left(\frac{\Phi^{-}}{2}\right) + 4\sin^{2}\left(\frac{\Phi^{-}}{2}\right) \left[ \cos(\Phi^{+})\sin^{2}(\theta^{S}) + \cos^{2}(\theta^{S}) \right] =
1 - \frac{1}{2}\sin^{2}(\theta^{S})(\cos(\Phi^{+}) - 1)(\cos(\Phi^{-}) - 1) =
1 - 2\sin^{2}(\theta^{S})\sin^{2}\left(\frac{\Phi^{-}}{2}\right)\sin^{2}\left(\frac{\Phi^{+}}{2}\right).
$$

With this result and equations A.8 and A.13 we reach the final result:

$$
< \mathcal{M}_{h}(2\tau) > = \frac{NPh_{\gamma}s}{2}\sin^{2}\left(\frac{\psi}{2}\right) \left[ 1 - 2\sin^{2}(\theta^{S})\sin^{2}\left(\frac{\Phi^{-}}{2}\right)\sin^{2}\left(\frac{\Phi^{+}}{2}\right) \right].
$$

(A.16)
or

\[ <M_x(2\tau) > = \frac{NP\Phi\gamma_0}{2} \sin^2 \left( \frac{\Psi}{2} \right) M(\tau). \hspace{1cm} (A.17) \]

The modulation function is compactly expressed as

\[ M(\tau) = 1 - 2K \sin^2 \left( \frac{\Phi^-}{2} \right) \sin^2 \left( \frac{\Phi^+}{2} \right) \]

\[ K = \left( 3 \sin(\theta_r) \cos(\theta_r) \frac{h^2\gamma_0\gamma_L}{r^3} \cdot \frac{\gamma B_0\tau}{\Phi^+\Phi^-} \right)^2 \]
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