Nuclear Quadrupole Spin Dynamics: How Weak RF Pulses and Double Resonance Cross-Relaxation Contribute to Explosives Detection.

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at George Mason University

By

David Prescott
Master of Science
George Mason University, 2005
Bachelor of Science
Northwestern University, 1983

Director: Dr. Karen L. Sauer, Professor
Department of Physics and Astronomy

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George Mason University
Fairfax, VA
Dedication

This is dedicated to; all my friends and family for their encouragement; my parents who provided me with the role models that I am still striving to emulate; and my loving wife, Julie—without her patience and support this would have just been a dream.
Acknowledgments

No race is truly solo and I must acknowledge all who provided support and encouragement to make this possible, starting from my earliest teachers and friends that encouraged me in this undertaking. A heartfelt recognition to the staff of the Physics and Astronomy department for the help over the years and to the faculty for the patience to respond to my questions. A special thanks to Orang and Michael for all the helpful and interesting discussions, and last minute editing! Thanks to Joel Miller for the construction of the probe for the experiments using glycine hemihydrochloride, and Scott Douglass and Michael Malone for additional data collection. A special acknowledgement to Mike Buess, the author of the excellent NMR Tools freeware software package. Finally, but most of all, I must acknowledge my advisor Dr. Karen L. Sauer—without her guidance and expertise this would not have been possible. I also must gratefully recognize the National Science Foundation for their support. To all those who lent me their time and equipment I deeply appreciated it.
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<tr>
<td>NQR</td>
<td>Nuclear Quadrupole Resonance</td>
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<td>SPE</td>
<td>Single-Pulse Echo</td>
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<tr>
<td>DPE</td>
<td>Double-Pulse Echo</td>
</tr>
<tr>
<td>rf</td>
<td>Radio-Frequency</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>EIB</td>
<td>Electric field gradient Inhomogeneously Broadened</td>
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<tr>
<td>SNR</td>
<td>Signal to Noise Ratio</td>
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<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<td>SLSE</td>
<td>Spin-Lock Spin-Echo</td>
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<tr>
<td>pPAPS</td>
<td>Preparatory pulse Phase Alternating Pulse Sequence</td>
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<td>DR</td>
<td>Double Resonance</td>
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<td>CR</td>
<td>Cross-Relaxation</td>
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Abstract

NUCLEAR QUADRUPOLE SPIN DYNAMICS: HOW WEAK RF PULSES AND DOUBLE RESONANCE CROSS-RELAXATION CONTRIBUTE TO EXPLOSIVES DETECTION.

David Prescott, Ph.D.
George Mason University, 2010
Dissertation Director: Dr. Karen L. Sauer

Nuclear quadrupole resonance (NQR) is a type of radio-frequency (rf) spectroscopy which can detect quadrupolar nuclei \((I > 1/2)\), such as nitrogen, in crystalline solids. NQR spectroscopy is useful for the detection of the many types of explosives containing \(^{14}\text{N}\), however it suffers from a low signal to noise ratio (SNR) particularly in samples with long spin-lattice relaxation times. To improve the SNR the nuclear quadrupole spin dynamics are exploited in two limiting cases: systems with long spin relaxation times and systems where the excitation power is limited. The former is addressed through double resonance effects and the latter through spin echoes created by weak rf pulses.

The double resonance effect occurs in samples that also contain a second faster relaxing nuclear species, such as \(^1\text{H}\) in ammonium nitrate. In this sample an \(^1\text{H}^{14}\text{N}\) double resonance can be created between the species that improves the SNR. While
the focus is on the common case of solids containing both nitrogen and hydrogen, the theory is generally applicable to solids containing spin-1 and spin-1/2 nuclei. A model of this system is developed that treats the motionally averaged secular dipolar Hamiltonian as a perturbation of the combined quadrupole and Zeeman Hamiltonians. This model reveals three types of double resonance conditions, involving static and rf fields, and predicts expressions for the cross-relaxation rate ($W_d$) between the two species. Using this cross-relaxation rate, in addition to the hydrogen and nitrogen autorelaxation rates, expressions governing the relaxation back to equilibrium in a spin-1/2 and spin-1 system are determined. The three different types of double resonance conditions are created experimentally; one of them for the first time in any system and another for the first time in a solid. Under these double resonance conditions, the increase in $W_d$ and improvements in SNR are explored both theoretically and experimentally using ammonium nitrate.

The second effect investigated is the NQR spin echo that forms after excitation of a powder sample by a single weak resonant radio-frequency pulse. This single-pulse echo is identified for the first time, and when applications are limited by a weak rf field, can be used effectively to increase the SNR over conventional detection techniques.
Chapter 1: Introduction

Nuclear quadrupole resonance (NQR) has become a popular option for the detection of explosives because of the ability to operate without a large magnetic field, its experimental simplicity, the abundance of nitrogen \((I = 1)\) in most explosives, and its unique frequency signatures. Unfortunately it suffers from a low signal-to-noise ratio (SNR) [1–4]. While an increase in SNR is possible through repeated measurements, for many substances of interest the time to return to thermal equilibrium, characterized by \(T_1\), and thus regain full signal can be relatively long. For instance, ammonium nitrate \((\text{NH}_4\text{NO}_3)\), the explosive material used in the Oklahoma City bombing, has a nitrogen \(T_1\) over 15 s, making its detection by NQR a lengthy process. For the large number of samples where the hydrogen \(T_1\) is much smaller than that of nitrogen, such as ammonium nitrate, the SNR can be increased by as much as 350 % [5] by creating a double resonance which effectively increases the \(^1\text{H}-^{14}\text{N}\) cross-relaxation rate [6–8]. Here, double resonance cross-relaxation is the process where two frequency matched spin systems exchange energy through mutual energy conserving spin-flips mediated by magnetic dipolar coupling. This work concentrates on exploring the nuclear quadrupole spin dynamics that contribute to the increased cross-relaxation rate in order to improve the NQR SNR.

Another experimental difficulty with NQR for explosives detection is the reduction in signal when trying to detect a powder. The powder form means that only a portion of the sample is excited where the rf is applied in any given direction (about 43% of the pure crystal signal is obtained from a powder [9]). Furthermore, there is the reduction in excitation strength due to the distance to the material of interest and in-the-field...
power limitations. The investigation, in this thesis, into the spin dynamics of the quadrupole single-pulse echo suggests that these weak rf pulses can be optimized to improve detectability. While one motivation for this research is explosives detection or even more broadly, illegal substance detection, such as cocaine and heroin, this work also focuses on ways to increase the sensitivity of low-field NQR experiments while exploring the information that can be gained about a sample based on the spin dynamics [10].

NQR is being actively pursued as explosives detection technology [11–14]. One advantage of the technology is that because of the unique NQR frequency signatures of illicit substances, detection sequences can be optimized for the substance of interest. Another advantage of NQR is its experimental simplicity compared to nuclear magnetic resonance (NMR) techniques, since there is no need for a superconducting magnet and its accompanying cryogenics. Additionally, in high-field NMR the quadrupole broadening can be significant, with broad linewidths obscuring all but the strongest lines, while in low-field NQR the broadening can be avoided altogether. Furthermore, NQR is a bulk detection technique that inspects volumes as long as the sample is not shielded from the rf pulses. These advantages are compelling, but the low SNR for in-the-field explosives detection is problematic.

For example, the NQR magnetic flux density from 100 g of TNT at a distance of 10 cm was calculated to be 1 fT, which drops off as $1/r^3$ [1,13]. For this sample, the NQR signal induces in a Faraday coil, with the geometry like a land mine detector, a rms voltage estimated to be $-160$ dBm. But, for a detector dominated solely by Johnson noise, at room temperature, the rms noise level is approximately $-140$ dBm [13]. While in this scenario the sample can be detected in the lab with current multipulse techniques, the need to increase the SNR for NQR explosives detection is apparent.
In an NQR or NMR experiment the voltage induced in a Faraday detector is given by three major factors \([13,15]\). The first is the nuclear polarization due to the population difference between the transition levels, which is proportional to the transition frequency \(\nu\). The second is the induced voltage, due to Faraday’s law, in the pickup coil, also proportional to \(\nu\). The third describes the detector geometry and is proportional to \(\nu^{-1/2}\). Combined, these factors estimate the signal size from both NQR and NMR Faraday detectors as proportional to \(\nu^{3/2}\). In NMR, \(\nu\) is proportional to the static field, \(B_0\). Hence the larger the external magnetic field the larger the SNR.

NQR has no such multiplicative factor, since \(\nu\) is fixed for one material and typically under 5 MHz. Therefore other techniques such as multi-pulse sequences \([14,16,17]\), composite pulses \([18]\), single-pulse echoes \([19]\), three-frequency \([20]\), and double resonance techniques \([7,8,21,22]\) are pursued to improve the sensitivity of NQR and to characterize these materials.\(^1\) While most research and applications in NMR focus on experiments that are performed at the highest magnetic field affordable, a number of experiments can be done at low fields (<200 G), which gather valuable scientific information and lend themselves to practical applications. Compared to traditional NMR research, very little work has been done in the low-field arena, due to the much lower sensitivity at these field strengths. As a reminder, in a high magnetic field the spin-1/2 particle has two Zeeman energy levels due to the quantization of the spin in a magnetic field and the populations of the levels are given by Boltzmann statistics. When a small rf pulse, of strength \(B_1\), is applied perpendicular to the static field the Zeeman Hamiltonian is

\[
H = \gamma \left( \frac{B_1}{2} \cos(\omega_0 t) + B_0 \right),
\]

where \(\gamma\) is the gyromagnetic ratio of the sample. For this pulse the Larmor frequency

\(^1\)Unfortunately, the term double resonance has many meanings in the NMR and NQR community, so comparisons to other work must be based on its experimental conditions. One of the most famous types of double resonance is Hartman-Hahn \([23]\), which is different from the work discussed in this thesis. It requires two rf fields at \(B_1\) and \(B_2\) and the resonance is \(\gamma_1 B_1 = \gamma_2 B_2\).
is defined as $\omega_0 K = \gamma B_0$ and the Rabi frequency is defined as $\omega_1 K = \gamma B_1$. When the rf is on resonance, the populations of the levels adjust and a signal can be detected. In this example, the signal is proportional to the population difference, and hence, the static magnetic field strength. In order to achieve low-field magnetic resonance, the population difference must be obtained from a source other than the magnetic field.

Nature handily provides this source for nuclei of spin $I > 1/2$ through the quantization of the energy levels of the electric quadrupole moment of the nucleus. These energy levels are created through the interaction of the electric quadrupole charge distribution with the electric field gradient (EFG) provided by the surrounding electronic structure of the nucleus [24]. This quantization leads to differences in populations which create a signal that can be detected independently of an external static magnetic field. This NQR signal reveals information about the nuclear environment such as the quadrupole moment, spin dynamics, and the 3D structure. It is well known that the sensitivity of these NQR experiments can be improved by double resonance techniques similar to NMR [23–25].

In particular, the use of NMR double resonance techniques to detect rare spins by monitoring the hydrogen atoms in a substance has a long successful history [26]. Most of the previous work on double resonance in NQR has focused on polarizing the hydrogen atoms at high field and then decreasing the field to resonantly transfer polarization to the nitrogen. This allows for the direct detection of the nitrogen or indirect detection through measurement of the hydrogen’s loss of polarization [27–30]. But this technique requires equipment to produce a large magnetic field, which presents engineering challenges that may be undesirable in a bomb detection application. These schemes mostly rely on the level crossing effect, reviewed by Edmonds [6], for a signal gain. The effect is explained with a spin-temperature model
Nitrogen Hydrogen

$E_{y}$ $E_{x}$ $E_{z}$ $E_{-1/2}$ $E_{+1/2}$

$W_{z}$ $W_{x}$ $W_{d}$ $\omega_{z}$ $\omega_{x}$ $\rho$

$\gamma_{H}B_{0}$

Figure 1.1: Energy level diagram of nitrogen and hydrogen in a small external magnetic field under the double resonance condition $\gamma_{H}B_{0} = \omega_{z}$, where $\gamma_{H}$ is the hydrogen’s gyromagnetic ratio. $E_{x}$, $E_{y}$, and $E_{z}$ are the energy levels of the nitrogen. $W_{d}$ is the dipole-dipole cross-relaxation rate. $W_{x}$, $W_{y}$, and $W_{z}$ are the $^{14}$N autorelaxation rates corresponding to the NQR transition frequencies $\omega_{x}$, $\omega_{y}$, and $\omega_{z}$, respectively, and $\rho$ is the $^{1}$H autorelaxation rate between the two levels.

of the different populations [31–34]. In this model, if the energy level splittings of the two different systems are matched then they will strongly couple by means of mutual spin-flips, exchange energy and establish a common equilibrium temperature. The model is not used to calculate the exchange rate, but does predict the final equilibrium values. More recently Thurber et al. [7] demonstrated the potential of using small magnetic fields ($\leq 260$ G), which are more easily implemented in the field, to increase the nitrogen SNR using $^{1}$H-$^{14}$N double resonance conditions. This work, as well as the majority of other double resonance work [6,35,36], concentrates on the final populations of the $^{1}$H and $^{14}$N atoms as predicted by a spin-temperature model. In contrast, this thesis concentrates on the rates of achieving these final populations by exploring the nuclear quadrupole spin dynamics.
In double resonance cross-relaxation two spin systems in close contact and frequency matched can exchange energy. The mechanism for this cross-relaxation is the magnetic dipole-dipole coupling between the nuclei [24, 25]. The energy from the polarized spin 1/2 system is transferred to the spin-1 system through mutual energy conserving spin-flips. During the double resonance created with a static magnetic field there is no emission (it is nonradiative), and the population levels can be brought back to thermal equilibrium faster [37]. The benefit of such double resonance techniques is two-fold: (1) the hydrogen can serve to manipulate the population differences between the three nitrogen levels to maximize the signal in the transition to be measured, and (2) the hydrogen, if it has a faster relaxation rate then the nitrogen, can effectively increase the relaxation rate of the nitrogen so that repeated measurements can be done rapidly. The larger signal is due to meeting multiple double resonance conditions and the faster relaxation rate is due to the increased cross-relaxation created by the double resonance. In samples with a short hydrogen $T_1$, the normally lengthy nitrogen $T_1$ is greatly reduced when the $^1$H-$^{14}$N cross-relaxation rate is increased during double resonance. The double resonance conditions studied use a combination of static and rf magnetic fields to create the resonance condition between the hydrogen and nitrogen and to increase the effective cross-relaxation rate.

The double resonance effect investigated occurs in samples that contain spin-$K$ and spin-$I$ nuclei, where $K = 1/2$ and $I > 1/2$. A model of this system is developed that combines, in a small static field, the $I$ quadrupole and the $I$ and $K$ Zeeman Hamiltonians, with a perpendicular rf field applied at, $\omega_{0K}$, of the $K$ spins, which is typically the Larmor frequency. The cross-relaxation is modeled as a perturbation due to the secular part of the dipolar Hamiltonian that is motionally averaged. The energy levels and their rates are shown in Fig. (1.1). In the absence of a double resonance the systems are independent and after a disturbance relax back to
their thermal equilibrium values at these rates. Under specific conditions during the double resonance, the $W_d$ rate is increased and the $^{14}$N can relax back to equilibrium faster than without the double resonance, leading to an increase in SNR. The model reveals that this occurs for three double resonance conditions, involving static and rf fields. From this model the cross-relaxation rate and the relaxation back to thermal equilibrium can be derived. It will be shown that $W_d$ is different for each of the conditions, due to the geometrical relationships among the moving nuclei, the electric field gradient, and the static and rf fields.

The first double resonance condition is created by matching the Larmor frequency of the $^1$H to one or more of the $^{14}$N NQR transition frequencies, $\omega_{0K} = \gamma_H B_0 = |\omega_{NQR}|$, where $\omega_{NQR}$ can be $\omega_x > |\omega_y| > |\omega_z|$ as shown in Fig. (1.1). An increase in SNR is predicted by matching to one or more frequencies and experiments show that the SNR is increased by 230 % using ammonium nitrate [8]. Additional signal can be gained by flipping the $^1$H polarization [7] by using a rf "π" pulse. The rf "π" pulse produces the spin-flip and experiments show an SNR improvement of 350 % for a fixed period of time [5]. Here, double resonance is created between the nitrogen in the NO$_3^-$ ions with the hydrogen in the NH$_4^+$ ions, as shown in Fig. (1.2), where each nitrogen couples with the hydrogens in the ammonium ion of a different molecule [38].

The second double resonance condition is created by matching the Rabi frequency to $\omega_{NQR}$ ($\omega_{1K} = \gamma_H B_1 = |\omega_{NQR}|$), where $B_1$ is applied perpendicular to $B_0$ at the $^1$H Larmor frequency. A similar resonance scheme, between the Rabi frequency of one species with the Larmor frequency of a second species, was first suggested by Kaplan and Hahn [39] and was first demonstrated with $^{129}$Xe and surface protons [40]. The third double resonance is created by matching the combination of the Rabi and Larmor frequencies to one of the $\omega_{NQR}$, i.e. $\gamma_H B_0 \pm \gamma_H B_1 = |\omega_{NQR}|$. To the best of the author’s knowledge this is the first time the Rabi double resonance condition
Figure 1.2: Chemical crystallographic structure of ammonium nitrate (NH₄NO₃), at room temperature, from Choi et al. [38]. A double resonance is created between nitrogen at the N(2) site of the NO₃ (red 5-point star) and the hydrogens at the H(2) and H(1) sites of the NH₄ (blue 4-point stars). The distances from the nitrogen to the hydrogens range from 2-3 Å. The other distances are in angstroms.

has been created and investigated in a solid. Additionally, this is the first time that the Rabi and Larmor double resonance has been created and investigated in any
sample. Both of these conditions are investigated to determine their different cross-relaxation rates. The detailed treatment of the theory in Chapter 2 will show that there are different $W_d$’s for each double resonance condition and for each of the three NQR transitions. For both of these double resonance conditions the experiments show that $W_d$ is increased and the improvement in SNR is similar to the first double resonance condition when $\gamma_H B_0 = |\omega_{NQR}|$. Therefore, the data indicate that similar improvements in SNR can be achieved by using any of the three resonance conditions. Experimentally, $W_d$ is characterized by measuring the effectiveness of the cross-relaxation as a function of the field sweep rate through the double resonance condition. Its measurement also provides insight into molecular motion and structure of solids. The experiments, together with the derived expressions, suggest that cross-relaxation during double resonance is dominated by the static dipolar coupling, in which the effective coupling is reduced, or averaged out, by molecular motion within the crystal.

Another effect investigated is the spin dynamics which occur in samples irradiated by weak radio-frequency pulses. The use of NQR for the detection of contraband material has received significant attention because of its ease of implementation and ability to uniquely identify illicit substances. Practical considerations push NQR detection technology to operate at lower rf and magnetic fields for reduced power requirements, larger detection volumes, and safe operation around delicate instrumentation. Therefore, to improve the NQR detection capability it is important to understand the spin dynamics which occur in samples irradiated by weak rf pulses. NQR experiments conducted with a single resonant weak radio-frequency pulse show the creation of a spin-echo; in contrast to the usual spin-echo experiment that requires a refocusing pulse to create an echo.

This single-pulse echo can be used effectively to increase the SNR over
conventional techniques. These effects can be used to optimize the NQR detection of contraband containing quadrupole nuclei and they are demonstrated with glycine hemihydrochloride and the military explosive hexhydro-1,3,5-trinitro-1,3,5-triazine (RDX).

In the next chapter the general theory of the nuclear quadrupole double resonance spin dynamics is developed. In Chapter 3 this theory is applied to the specific condition where the double resonance is created with small static magnetic fields, using ammonium nitrate as a sample. Experimental results are presented that confirm the theoretical predictions. The two other double resonance conditions, the Rabi double resonance and the Rabi plus Larmor double resonance, require an additional rf field. Hence, these experiments require a more complicated experimental setup; the required hardware, pulse sequences, and experimental methods are described in Chapter 4. In Chapter 5 the results of the Rabi double resonance and the Rabi plus Larmor double resonance experiments and the measurement of the different cross-relaxation rates are discussed in relation to the general theory derived in Chapter 2. In the conclusion to Chapter 5 the theory, experimental methods and results regarding all double resonance conditions are summarized. In Chapter 6 the first detection of a nuclear quadrupole single-pulse echo is presented along with an analysis of the spin dynamics that leads to the creation of these echoes by weak rf pulses. The appendices provide experimental details such as the specific pulse parameters and the details of the sequences for the experiments.
Chapter 2: Nuclear Quadrupole Double Resonance  
Spin Dynamics

2.1 Theoretical Approach

Consider a spin system consisting of a lattice of spin-$K$ (spin-1/2) and spin-$I$ (spin-1) nuclei coupled through the dipolar interaction. The spin system is immersed in a small static magnetic field, $B_0$, and a rotating magnetic field, $B_1$ applied orthogonally to the static field such that the total field, $B$ is

$$B = B_1 (\cos(\omega_K t)\hat{x}' - \sin(\omega_K t)\hat{y}')} + B_0 \hat{z}' .$$  (2.1)

Here, $\omega_K$ is close to $\omega_{0K} = \gamma_K B_0$, the Larmor frequency, but not close to any $\omega_{NQR}$ and $B_0$ is externally applied and defines the $z'$ axis of the laboratory frame as shown in Fig. (2.1).

The Hamiltonian of the system is

$$\hbar H = \hbar H_Q + \hbar H_Z + \hbar H_D,$$  (2.2)

where the quadrupole $\hbar H_Q$, Zeeman $\hbar H_Z$, and the heterogeneous dipole $\hbar H_D$ Hamiltonians are described in detail below. The static field and the rotating magnetic field combine to create the different double resonance conditions. Near one of the double resonance conditions, where the spin-1/2 Larmor frequency is close to one of the spin-1 NQR frequencies, the heterogeneous dipolar coupling can greatly impact
Figure 2.1: The left figure shows the laboratory frame \((x', y', z')\) defined by the static magnetic field and the principal axis (PAS) frame of the electric field gradient \((x, y, z)\). On the right, the displacement vector from the spin-I to the spin-K nucleus is shown with respect to the PAS frame.

The cross-relaxation rates.

The system is studied by determining how the density operator \(\rho\) evolves under the Hamiltonian \(\hbar H\) according to the Liouville equation,

\[
\frac{d}{dt} \rho = i[\rho, H]. \tag{2.3}
\]

This set of differential equations is solved by a perturbation approach. The total Hamiltonian is divided into a main part, \(H_0\), and a perturbation, \(H_1\), that is the coupling between the spin system. The main part determines the energy levels for the system while the perturbation, \(H_1\), causes the transitions between the levels [24,25,41–43].
2.1.1 Quadrupole Hamiltonian

The quadrupole Hamiltonian results from the static electric field gradient at the spin-1 nucleus, \( V_{\alpha\beta} \), which is generated by the local molecular and crystalline environment. For these nuclei with a non-spherical charge density \( \rho(r) \) there is an interaction with the potential \( V(r) \) from the surrounding electronic structure. This interaction energy is given by \( E = \int \rho(r)V(r)d^3r \). The associated quadrupole Hamiltonian \( \hbar H_Q \) is \( [24] \)

\[
H_Q = \frac{\omega_Q}{3} \sum_{i=1}^{N_I} \left\{ 3I^{(i)2} - I(I+1) + \eta(I^{(i)2} - I_y^{(i)2}) \right\},
\]

(2.4)

defined with respect to \((x, y, z)\), the principal axes (PAS) of \( V_{\alpha\beta} \) and \( N_I \) is the number of spin-1 nuclei. Here the asymmetry parameter is \( \eta \equiv \frac{V_{xx} - V_{yy}}{V_{zz}} \), the coupling constant is \( \omega_Q \equiv \frac{3V_{zz}eQ}{4\hbar} \), \( Q \) is the spin-1 quadrupole moment, \( V_{zz} \) is the largest component of the electric field gradient tensor in the principal axes frame, and \( e \) is the elementary charge constant. Since this is a powder sample, the PAS frame is randomly oriented with respect to \( B_0 \). For spin-1 the eigenfunctions of \( I_z \) are \( |+1\rangle, |-1\rangle, \) and \( |0\rangle \).

The eigenstates of \( H_Q^{(i)} \) are expressed in terms of the spin states of \( I_z^{(i)} \), and have the corresponding eigenvalues \( E_x, E_y, \) and \( E_z \), as shown in Fig. (2.2). The NQR transition energies are then

\[
\begin{align*}
\hbar \omega_x &= E_y - E_z, \\
\hbar \omega_y &= E_z - E_x, \\
\hbar \omega_z &= E_x - E_y,
\end{align*}
\]

(2.5)
\[ E_y \mid y \rangle \equiv \frac{1}{\sqrt{2}} (\mid 1 \rangle + \mid -1 \rangle) \]

\[ E_x \mid x \rangle \equiv \frac{1}{\sqrt{2}} (\mid 1 \rangle - \mid -1 \rangle) \]

\[ E_z \mid z \rangle \equiv |0\rangle \]

Figure 2.2: Spin-1 \((\eta \neq 0)\) eigenenergy level diagram: \(E_x, E_y,\) and \(E_z\) are the energies corresponding to the eigenstates \(|x\rangle, |y\rangle,\) and \(|z\rangle\). The NQR transition frequencies are \(\omega_x, \omega_y,\) and \(\omega_z\).

\[
\begin{align*}
\omega_x &= \omega_Q \left(1 + \frac{\eta}{3}\right), \\
\omega_y &= -\omega_Q \left(1 - \frac{\eta}{3}\right), \\
\omega_z &= -\frac{2\omega_Q \eta}{3},
\end{align*}
\]

(2.6)

where \(\omega_x > |\omega_y| > |\omega_z|\).

For ease of calculation, the quadrupole Hamiltonian can also be defined with respect to fictitious spin-1/2 operators. This representation has the nice property that it simplifies the calculation of a three level spin-1 system. When two states of a system are linked by a rf pulse, \(\omega = (E_a - E_b)/\hbar\), where \(E_a\) and \(E_b\) are the
energy levels of the two states, then the system is modeled as equivalent to a spin-1/2 particle in a fictitious magnetic field and the other energy levels are ignored. The fictitious spin-1/2 reduces the multi-level system subject to a resonant rf field to a two-level system. The density matrix, energy levels, and expectation values all can be written in this fictitious spin 1/2 system, simplifying the problem [25,44]. Since there are three transitions in a spin-1 system there exist three sets of fictitious spin-1/2 vector operators [9,45]: $I_x$ corresponding to the $\omega_x$ transition; $I_y$ to $\omega_y$; and $I_z$ to $\omega_z$ transition. The definitions of the fictitious spin-1/2 operators, along with their commutation relations, are given in the Appendix A. The equivalent ways of representing $H_Q$ are

$$H_Q = \sum_{i=1}^{N_T} \left( \omega_x I_x^{(i)} + \frac{1}{3} (\omega_y - \omega_z) I_y^{(i)} \right),$$

$$= \sum_{i=1}^{N_T} \omega_y I_y^{(i)} + \frac{1}{3} (\omega_z - \omega_x) I_y^{(i)}, \quad (2.7)$$

$$= \sum_{i=1}^{N_T} \omega_z I_z^{(i)} + \frac{1}{3} (\omega_x - \omega_y) I_z^{(i)},$$

which can be further simplified

$$H_Q = \sum_{i=1}^{N_T} \omega_x I_x^{(i)} + \omega'_x I_x^{(i)},$$

$$= \sum_{i=1}^{N_T} \omega_y I_y^{(i)} + \omega'_y I_y^{(i)}, \quad (2.8)$$

$$= \sum_{i=1}^{N_T} \omega_z I_z^{(i)} + \omega'_z I_z^{(i)}.$$
In addition, the $I_p$ operators, where $p$ is one of $x, y, z$, are proportional to the corresponding population differences and hence the signal at each transition. The definitions of the operators in terms of level populations are:

$$\langle I_{x^3}(i) \rangle = \frac{N_y - N_z}{2N_I},$$

$$\langle I_{y^3}(i) \rangle = \frac{N_z - N_x}{2N_I},$$

$$\langle I_{z^3}(i) \rangle = \frac{N_x - N_y}{2N_I},$$

where the sum of the populations of the $|x\rangle$, $|y\rangle$, and $|z\rangle$ eigenstates equals the total number of spin-$I$ atoms, $N_x + N_y + N_z = N_I$.

### 2.1.2 Zeeman Hamiltonian

The Zeeman Hamiltonian $\hbar H_Z$ in the static and rf field is

$$H_Z = H_Z^K + H_Z^I$$

$$H_Z^K = -\gamma_K B \cdot \sum_{k=1}^{N_K} K^{(k)} = -N_K B \cdot K$$

$$H_Z^I = -\gamma_I B \cdot \sum_{i=1}^{N_I} I^{(i)} = -N_I B \cdot I,$$

where $K \equiv \frac{1}{N_K} \sum_{k=1}^{N_K} K^{(k)}$, $I \equiv \frac{1}{N_I} \sum_{i=1}^{N_I} I^{(i)}$, and $\gamma_K$ and $\gamma_I$ are the gyromagnetic ratios of the spin-$1/2$ and spin-$1$ nuclei, respectively. When $K$ corresponds to hydrogen and $I$ to nitrogen, $\gamma_K \approx 14\gamma_I$. For ease of later analysis, $K$ is expressed with respect to the lab frame, $K = K_x^x \hat{x} + K_y^y \hat{y} + K_z^z \hat{z}$, and $I$ with respect to the

16
PAS frame, $\mathbf{I} = I_x \hat{x} + I_y \hat{y} + I_z \hat{z}$. The $\mathbf{I}$ spins are converted to the lab frame by using direction cosines [46].

### 2.1.3 Dipolar Hamiltonian

The magnetic dipole coupling between nuclei is expressed as the dipole Hamiltonian $\hbar H_D$ [24,25],

$$
H_D = \kappa \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} \frac{1}{r_{ik}^3} \{ \mathbf{K}_k \cdot \mathbf{I}_i - 3(\mathbf{K}_k \cdot \hat{r}_{ik})(\mathbf{I}_i \cdot \hat{r}_{ik}) \}, \tag{2.13}
$$

where $\kappa = \frac{\mu_0}{4 \pi} \gamma_I \gamma_K \hbar$ and $\mathbf{r}_{ik} = r_{ik} \hat{r}_{ik}$, is the displacement vector between the $i$th spin-1 nuclei and the $k$th spin-1/2 nuclei as shown in Fig. (2.1). Equivalently this interaction can be written more compactly with a dipolar rank 2 tensor. In this representation

$$
H_D = \kappa \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} \frac{1}{r_{ik}^3} \mathbf{K}^{(k)} \cdot (\mathbf{1} - 3\hat{r}_{ik} \hat{r}_{ik}) \cdot \mathbf{I}^{(i)}. \tag{2.14}
$$

Here $H_D$ is the dyadic product of the spatial and the spin components and provides a simplified notation. [47].

### 2.1.4 Transformation to the Rotating Frame

The $K$ Zeeman Hamiltonian, Eq. (2.11), can be simplified by transforming to the rotating frame ([24] pg. 166),

$$
H^K_Z = -\omega_0 K_z - \frac{\omega_1 K}{2}(K_{z+} e^{i\omega_K t} + K_{z-} e^{-i\omega_K t}) \tag{2.15}
$$

$$
= U_1 (-\omega_0 K_{z'} - \omega_1 K_{z'}) U_1^{-1} \tag{2.16}
$$
where \( U_1 = e^{i\omega t K z'} \) is the rotation operator, \( \omega_{1K} = \gamma_K B_1 \) is the Rabi frequency, and \( K_{z\pm} = K_{x'} \pm iK_{y'} \) are the standard raising and lowering operators in the \( K_{z'} \) basis. In the rotating frame where

\[
\tilde{H} \equiv U_1^{-1} H U_1 \quad \text{(2.17)}
\]

\[
\tilde{\rho} \equiv U_1^{-1} \rho U_1 \quad \text{(2.18)}
\]

and the Liouville equation, Eq. (2.3), becomes

\[
\frac{d}{dt} \tilde{\rho} = i[\tilde{\rho}, \tilde{H} + \omega_K K_{z'}]. \quad \text{(2.19)}
\]

Since \( K_{z'} \) commutes with \( I \), which gives \( \tilde{H}_Q = H_Q \), and \( \tilde{H}_{Z}^{(f)} = H_Z^{I} \). The \( K \) Zeeman Hamiltonian in the rotating frame is

\[
\tilde{H}_{Z}^{(K)} = -\omega_{0K} K_{z'} - \omega_{1K} K_{x'}. \quad \text{(2.20)}
\]

and thus

\[
\frac{d}{dt} \tilde{\rho} = i[\tilde{\rho}, H_Q - \omega_{1K} K_{x'} - (\omega_{0K} - \omega_K) K_{z'} + H_Z^{I} + \tilde{H}_D]. \quad \text{(2.21)}
\]

Together the terms \(-\omega_{1K} K_{x'} - (\omega_{0K} - \omega_K) K_{z'}\), can be rewritten as \(-\gamma_K K \cdot B_{\text{eff}}\) where \( \gamma_K B_{\text{eff}} = \omega_{1K} \hat{x}' + (\omega_{0K} - \omega_K) \hat{z}' \) is the effective magnetic field in the rotating frame. Notice, only the last term \( \tilde{H}_D \) has an explicit time dependence. Both \( H_Z^{I} \) and \( \tilde{H}_D \) are assumed to be much smaller than the time-independent \( H_0 = H_Q - \omega_{1K} K_{x'} - (\omega_{0K} - \omega_K) K_{z'} \). In particular \( \tilde{H}_D \ll H_0 \) and \( H_Z^{I} \ll H_Q \), since
\( H^I_Z \) commutes with \( K \). This means that in the rotating frame \( \tilde{H} \) now has a static, or dominant part, \( H_0 \), and a small time-dependent perturbation, \( H^I_Z + \tilde{H}_D \).

### 2.1.5 Transformation to the Doubly-Rotating Frame

Treating \( H_1 = H^I_Z + \tilde{H}_D \) as a perturbation of \( H_0 \) and working in the interaction representation of \( H_0 \) results in

\[
\dot{\rho} \equiv U_0^{-1} \dot{\rho} U_0 = U_0^{-1} U_1^{-1} \rho U_1 U_0 \tag{2.22}
\]

\[
\tilde{H}_1 \equiv U_0^{-1} \left( H^I_Z + \tilde{H}_D \right) U_0 \tag{2.23}
\]

\[
\frac{d}{dt} \tilde{\rho} = i[\tilde{\rho}, \tilde{H}_1], \tag{2.24}
\]

where \( U_0 = e^{-iH_0t} \). This allows us to evaluate \( \tilde{H}_1 \), and make the approximation that the rapidly oscillating terms do not make a significant contribution to the evolution of the density matrix, an approximation known as the secular approximation.

Transforming the \( I \) Zeeman Hamiltonian part of Eq. (2.23) into the doubly rotating frame, denoted by the breve, reveals

\[
\tilde{H}_Z^{(i)} = U_0^{-1} H^I_Z U_0 \tag{2.25}
\]

\[
= -\gamma_I \sum_{i=1}^{N_I} B \cdot \tilde{I}^{(i)} \tag{2.26}
\]

\[
= -\gamma_I \sum_{i=1}^{N_I} \left\{ B_1 \left( e^{i\omega_K t} \hat{x}' + i\hat{y}' + c.c. \right) + B_0 \hat{z}' \right\} \cdot \tilde{I}^{(i)}, \tag{2.27}
\]

where \( c.c. \) stands for the complex conjugate of the term to the left of it. \( I \) transforms
\[
\mathbf{I}^{(i)} = \hat{x}I_x^{(i)} + \hat{y}I_y^{(i)} + \hat{z}I_z^{(i)}
\]
\[= \hat{x}I_{x+}^{(i)} + \hat{y}I_{y+}^{(i)} + \hat{z}I_{z+}^{(i)} + h.c.
\]
\[
\tilde{\mathbf{I}}^{(i)} = \mathbf{I},
\]

where \(h.c.\) stands for the Hermitian conjugate, and \(I^{(i)}_{x+} = I^{(i)}_{x1} + iI^{(i)}_{x2}\) and similarly for \(I^{(i)}_{y+}\) and \(I^{(i)}_{z+}\). In the doubly rotating frame

\[
\tilde{\mathbf{I}}^{(i)} = \hat{x}I_{x+}^{(i)}e^{i\omega_x t} + \hat{y}I_{y+}^{(i)}e^{i\omega_y t} + \hat{z}I_{z+}^{(i)}e^{i\omega_z t} + h.c.
\]

Therefore, it is easy to see that as long as \(\omega_K\) is not close to one of the three NQR frequencies, there are no secular terms and the contribution of \(H_{IZ}^{(i)}\) to the evolution of the density matrix can be neglected. It will however, play a role in defining the width in field of the resonance condition.

Transforming the dipolar Hamiltonian part of Eq. (2.14) into the doubly rotating frame results in

\[
\tilde{H}_D = \kappa \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} \frac{1}{r_{ik}^3} \mathbf{K}^{(k)} \cdot (\mathbf{1} - 3\mathbf{r}_{ik}\mathbf{r}_{ik}) \cdot \tilde{\mathbf{I}}^{(i)}
\]

\[
\tilde{H}_D = \kappa \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} \frac{1}{r_{ik}^3} \mathbf{K}^{(k)} \cdot (\mathbf{1} - 3\mathbf{r}_{ik}\mathbf{r}_{ik}) \cdot \tilde{\mathbf{I}}^{(i)},
\]

since \(\mathbf{K}\) and \(\mathbf{I}\) commute with \(\tilde{\mathbf{r}}\).

\(\tilde{\mathbf{I}}^{(i)}\), Eq. (2.31), has already been transformed. \(\mathbf{K}^{(k)}\) is transformed first to the
rotating frame

\[
\mathbf{K}^{(k)} = \hat{z}' \mathbf{K}_z^{(k)} + \left( \frac{\hat{x}' - i\hat{y}'}{2} \mathbf{K}_x^{(k)} + h.c. \right) \tag{2.34}
\]

\[
\tilde{\mathbf{K}}^{(k)} = \hat{z}' \mathbf{K}_z^{(k)} + \left( \frac{\hat{x}' - i\hat{y}'}{2} \mathbf{K}_x^{(k)} e^{-i\omega_K t} + h.c. \right) \tag{2.35}
\]

\[
\tilde{\mathbf{K}}^{(k)} = -\frac{i\hat{z}'}{2} \mathbf{K}_x^{(k)} + \frac{\hat{x}' - i\hat{y}'}{2} \left( \mathbf{K}_x^{(k)} + i \frac{\mathbf{K}_x^{(k)} + \mathbf{K}_x^{(k)}}{2} \right) e^{-i\omega_K t} + h.c.
\]

For simplicity, assume that \( \omega_K = \omega_0 K \), \( \tilde{\mathbf{K}}^{(k)} \) can be written as

\[
\tilde{\mathbf{K}}^{(k)} = -\frac{i\hat{z}'}{2} \mathbf{K}_x^{(k)} e^{-i\omega_1 K t} \tag{2.36}
\]

\[
+ \frac{\hat{x}' - i\hat{y}'}{2} \left( \mathbf{K}_x^{(k)} e^{-i\omega_0 K t} + \frac{i}{2} \mathbf{K}_x^{(k)} e^{-i(\omega_0 K + \omega_1 K) t} + \frac{i}{2} \mathbf{K}_x^{(k)} e^{-i(\omega_0 K - \omega_1 K) t} \right) + h.c.
\]

where \( \mathbf{K}_x^{(k)} \equiv \mathbf{K}_y^{(k)} \pm i \mathbf{K}_z^{(k)} \) are the raising and lowering operators in the \( K_z' \) basis.

### 2.1.6 Double Resonance Conditions

As seen in Eq. (2.32), the dyadic \( (\mathbf{1} - 3\hat{r}_{ik} \hat{r}_{ik}) \) serves to make bilinear terms from \( \mathbf{I} \) and \( \mathbf{K} \), and we invoke the secular approximation to get rid of the highly oscillatory terms. Using this criteria the different resonant conditions emerge, which are summarized in the Table (2.1), along with the truncated \( \tilde{H}_D \) corresponding to that particular resonance condition. For the resonance condition given in the first column the secular piece of the dipole Hamiltonian is \( \tilde{H}_D^S = \sum_{i=1}^{N_t} \sum_{k=1}^{N_K} (F_{ik} A_{ik} + h.c.) \); where \( F_{ik} \) and \( A_{ik} \) are given in Table (2.1). Note that \( F_{ik} \) corresponds to the geometric term and \( A_{ik} \) to the spin operator.
The $A_{ik}$ term can be made more transparent by recognizing that it consists of the two raising/lowering operators; one for $K$ and one for $I$. Looking at the static double resonance condition $\omega_x = \omega_{0K}$, are the standard raising operator $K_x' + iK_y'$ and the analogous raising operator in the fictitious spin-1/2 operator space $(I_{x1}, I_{x2}, I_{x3})$, corresponding to the $\omega_x$ transition. The “flip-flop” nature of the operator $A_{ik}$ can be emphasized by equivalently writing $A_{ik}$ as $|i = y; k = 1/2 \rangle \langle i = z; k = -1/2 |$, where the first term in the ket-bra corresponds to the eigenstate of the $i$th spin-1 nucleus and the second to the $k$th spin-1/2 nucleus. Equivalent energy-conserving “flip-flop” terms corresponding to the double resonance conditions for the other transitions and conditions can easily be found in a similar manner.

### 2.1.7 Constants of Motion

To find the cross-relaxation rate, the rate equations for each of the double resonance conditions are calculated. The rate equations are partially based on the constraints on the system such as the conservation of the number of spins and can be facilitated by identifying the constants of motion. The constants of motion are found by working in the doubly rotating frame. With the secular approximation and the assumption of $\omega_{0K} = \omega_K$, Eq. (2.21) simplifies to

$$\frac{d}{dt} \tilde{\rho} = i[\tilde{\rho}, H_Q - \omega_{1K}K_x' + \tilde{H}_D^S],$$

(2.37)

where $\tilde{H}_D^S \equiv U_0\tilde{H}_D^S U_0^{-1}$ for a given resonance condition. Equivalently,

$$\frac{d\tilde{\rho}}{dt} = i[\tilde{\rho}, \tilde{H}_D^S],$$

(2.38)
Table 2.1: Resonance conditions for static fields and fields rotating at the Larmor frequency. The secular piece of the dipole Hamiltonian, for the resonance condition $\Delta \omega = 0$, with $\Delta \omega$ given in the first column, is given by the two middle columns through $\hat{H}_D^S = \sum_{i=1}^{N_f} \sum_{k=1}^{N_K} (F_{ik} A_{ik} + h.c.)$; $F_{ik}$ corresponds to the geometric term and $A_{ik}$ to the spin operator.

<table>
<thead>
<tr>
<th>$\Delta \omega$</th>
<th>$F_{ik} = \frac{\kappa}{\tau_{ik}} \times$</th>
<th>$A_{ik}$</th>
<th>Rate relationships between expectation values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static $\omega_{1K} = 0$</td>
<td>$\frac{1}{2} (\hat{x}' - i \hat{y}') \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{x}$</td>
<td>$K_{x+}^{(k)} I_{x+}^{(i)}$</td>
<td>$\hat{I}<em>{x3} = R \hat{K}</em>{x'} = 2 \hat{I}<em>{y3} = 2 \hat{I}</em>{z3}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2} (\hat{x}' - i \hat{y}') \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{y}$</td>
<td>$K_{y+}^{(k)} I_{y+}^{(i)}$</td>
<td>$\hat{I}<em>{y3} = -R \hat{K}</em>{x'} = 2 \hat{I}<em>{z3} = 2 \hat{I}</em>{x3}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2} (\hat{x}' - i \hat{y}') \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{z}$</td>
<td>$K_{z+}^{(k)} I_{z+}^{(i)}$</td>
<td>$\hat{I}<em>{z3} = -R \hat{K}</em>{x'} = 2 \hat{I}<em>{x3} = 2 \hat{I}</em>{y3}$</td>
</tr>
<tr>
<td>Rotational $\omega_{x} - \omega_{1K}$</td>
<td>$-\frac{i}{2} \hat{z}' \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{x}$</td>
<td>$K_{x+}^{(k)} I_{x+}^{(i)}$</td>
<td>$\hat{I}<em>{x3} = R \hat{K}</em>{x'} = 2 \hat{I}<em>{y3} = 2 \hat{I}</em>{z3}$</td>
</tr>
<tr>
<td></td>
<td>$-\frac{i}{2} \hat{z}' \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{y}$</td>
<td>$K_{y+}^{(k)} I_{y+}^{(i)}$</td>
<td>$\hat{I}<em>{y3} = -R \hat{K}</em>{x'} = 2 \hat{I}<em>{z3} = 2 \hat{I}</em>{x3}$</td>
</tr>
<tr>
<td></td>
<td>$-\frac{i}{2} \hat{z}' \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{z}$</td>
<td>$K_{z+}^{(k)} I_{z+}^{(i)}$</td>
<td>$\hat{I}<em>{z3} = -R \hat{K}</em>{x'} = 2 \hat{I}<em>{x3} = 2 \hat{I}</em>{y3}$</td>
</tr>
<tr>
<td>Combination $\omega_{x} - \omega_{0K} \mp \omega_{1K}$</td>
<td>$\frac{i}{4} (\hat{x}' - i \hat{y}') \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{x}$</td>
<td>$K_{x+}^{(k)} I_{x+}^{(i)}$</td>
<td>$\hat{I}<em>{x3} = \pm R \hat{K}</em>{x'} = 2 \hat{I}<em>{y3} = 2 \hat{I}</em>{z3}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{i}{4} (\hat{x}' - i \hat{y}') \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{y}$</td>
<td>$K_{y+}^{(k)} I_{y+}^{(i)}$</td>
<td>$\hat{I}<em>{y3} = \mp R \hat{K}</em>{x'} = 2 \hat{I}<em>{z3} = 2 \hat{I}</em>{x3}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{i}{4} (\hat{x}' - i \hat{y}') \cdot (1 - 3 \hat{f}<em>{ik} \hat{f}</em>{ik}) \cdot \hat{z}$</td>
<td>$K_{z+}^{(k)} I_{z+}^{(i)}$</td>
<td>$\hat{I}<em>{z3} = \mp R \hat{K}</em>{x'} = 2 \hat{I}<em>{x3} = 2 \hat{I}</em>{y3}$</td>
</tr>
</tbody>
</table>
is an expression which reveals the constants of motion under a certain double
resonance condition.

In general, for an operator $Q$ with no explicit time dependence,

$$\frac{d\langle \hat{Q} \rangle}{dt} = \frac{dTr(\hat{\rho}Q)}{dt} = Tr(\frac{d\hat{\rho}}{dt}Q) = iTr(\hat{\rho}\hat{H}_D^S Q - \hat{H}_D^S \hat{\rho}Q) = iTr(\hat{\rho}[\hat{H}_D^S, Q]).$$  (2.39)

When $\frac{d\langle \hat{Q} \rangle}{dt}$ is zero the constraints on the spin system’s rate equations can be found.

One example, from the list of possible double resonance conditions in Table (2.1),
is a resonance created using both the rf and the static fields. This resonance condition
is created by matching the Larmor frequency, $\omega_0K$, plus the Rabi frequency, $\omega_1K$, with
a $\omega_{NQR}$. For example, for $\hat{H}_D^S$ for $\omega_x = \omega_0K + \omega_1K$,

$$\left[\hat{H}_D^S, N_I I_{x3} - N_K K_{x'} \right] = 0$$  (2.40)

$$\left[\hat{H}_D^S, I_{x4} \right] = \left[\hat{H}_D^S, (I_{y3} - I_{z3}) \right] = 0.$$  (2.41)

Therefore, the expectation value of $N_I \hat{I}_{x3} - N_K \hat{K}_{x'}$ and $I_{x4}$ are constants of motion.

The former corresponds to conservation of energy, the latter to the conservation of
the spin-$I$ population not involved in the cross-relaxation.

In addition, corresponding to the conservation of the number of spin-$I$ atoms,
$I_{x3} + I_{y3} + I_{z3} = 0$, requires the following relation between the physical observables

$$\frac{d\langle I_{x3} \rangle}{dt} = R \frac{d\langle \hat{I}_{x3} \rangle}{dt} = 2\frac{d\langle I_{y3} \rangle}{dt} = 2\frac{d\langle I_{z3} \rangle}{dt},$$  (2.42)
where \( R = \frac{N_K}{N_I} \). Similarly each resonance condition has a set of relationships, summarized in the last column of Table (2.1). The relationship that ties the rate of change of \( I_{x3} \) to \( \tilde{K}_{x'} \) is discussed below.

### 2.1.8 Cross-Relaxation Rates

To find that relationship involving \( I_{x3} \), the cross-relaxation between the \( i \)th spin-\( I \) nucleus and the \( k \)th spin-\( K \) nucleus under a particular resonance condition is examined. The rate of this cross-relaxation, \( W_{ik} \), is determined using Fermi’s golden rule [48,49], applied near one of the nine resonant conditions listed in Table (2.1). Below, the \( W_{ik} \) of the three different resonance conditions, static, rotating, and a combination of the two, are analyzed separately.

First consider the last set of resonance conditions. In this case Fermi’s golden rule for a periodic perturbation is used,

\[
\hbar H' = A e^{i\omega t} + A^\dagger e^{-i\omega t},
\]

(2.43)

where \( A \) is the non-time dependent part of the perturbation depending on the resonance condition and is identified in Table (2.1). The emission and absorption rates are [50]

\[
W(\varphi_i, \alpha_f) = 2\pi\hbar|\langle \alpha_f|A|\varphi_i \rangle|^2 \rho(E_f = E_i - \hbar \omega) \quad \text{(emission)}
\]

(2.44)

\[
W(\varphi_i, \alpha_f) = 2\pi\hbar|\langle \alpha_f|A^\dagger|\varphi_i \rangle|^2 \rho(E_f = E_i + \hbar \omega) \quad \text{(absorption)},
\]

(2.45)

where \( E_f \) denotes the energy for the final state \( \alpha_f \) and \( E_i \) for the initial state \( \varphi_i \). \( \rho \) is the density of the final states which conserves energy. This rate is established after a few cycles \( \omega t \gg 2\pi \) and Fermi’s golden rule expresses the average transition rate.
after a long time. For example, close to the resonance condition \( \omega_x = \omega_{0K} + \omega_{1K} \), the contributing part of the dipolar Hamiltonian in the rotating frame is

\[
\hbar H' = A e^{i \omega t} + A^\dagger e^{-i \omega t}
\]

\[
= F_{ik} K_x^{(k)} I_x^{(i)} e^{-i \omega K t} + h.c.
\]

For absorption, the initial and final states in the rotating frame are \( |\bar{\phi}_i \rangle = |i = z, m_z^{(k)} = -\frac{1}{2} \rangle \) and \( |\bar{\alpha}_f \rangle = |i = y, m_z^{(k)} = \frac{1}{2} \rangle \) and for emission the states are reversed. Therefore, the cross-relaxation rate is the same for emission and absorption and is given by

\[
W_{ik} = 2\pi \hbar |\langle \bar{\alpha}_f | F_{ik} A_{ik} | \bar{\phi}_i \rangle|^2 \rho(|E_f - E_i| = \hbar \omega_K).
\]

In calculating the initial and final energy the full Hamiltonian minus the heterogenous dipolar coupling creating the cross-relaxation is included,

\[
E_f = \hbar \langle \alpha_f | H_Q + H_D^I + H_Z^K + H_D^K | \alpha_f \rangle
\]

\[
= \hbar \langle \alpha_f | U_1 \{ U_1^{-1} (H_Q + H_D^I + H_Z^K + H_D^K) U_1 \} U_1^{-1} | \alpha_f \rangle
\]

\[
= \hbar \langle \tilde{\alpha}_f | H_Q + H_D^I + H_Z^K + H_D^K | \tilde{\alpha}_f \rangle
\]

where the \( I \) spin homogenous dipolar Hamiltonian is \( \hbar H_D^I \) and the \( K \) spin homogenous dipolar Hamiltonian is \( \hbar H_D^K \).

The rotating resonance condition, in which the spin-\( K \) Rabi frequency is matched to the spin-\( I \) NQR frequency, is also governed by Fermi’s golden rule, but for a constant perturbation turned on suddenly. As above, the relevant final and initial
states are in the rotating frame, and the cross-relaxation rate becomes

\[ W_{ik} = 2\pi\hbar |\langle \alpha_f | F_{ik} A_{ik} | \tilde{\varphi}_i \rangle|^2 \rho(|E_f - E_i| = 0), \quad (2.51) \]

where the energies are defined in Eq. (2.48) and the appropriate \( F_{ik} \) can be found in Table (2.1). Therefore, the same broadening mechanisms exist for both resonance conditions involving a radio-frequency field applied near the spin-\( K \) Larmor frequency.

The static resonance condition, in which the spin-\( K \) Rabi frequency is matched to the spin-\( I \) NQR frequency, is also governed by Fermi’s golden rule for a static perturbation turned on suddenly. The difference here being that the initial and final states are in the laboratory frame:

\[ W_{ik} = 2\pi\hbar |\langle \alpha_f | F_{ik} A_{ik} | \varphi_i \rangle|^2 \rho(|E_f - E_i| = 0), \quad (2.52) \]

where the energy is given by

\[ E_f = \hbar \langle \alpha_f | H_Q + H^I_D + H^I_Z + H^K_D | \alpha_f \rangle. \quad (2.53) \]

**Double Resonance Broadening**

The major difference in the broadening mechanisms between static and non-static resonance condition comes through the spin-\( K \)’s contribution. Broadening due to the spin-\( K \) Zeeman Hamiltonian arises through magnetic field inhomogeneity. For the static case this is the inhomogeneity in the static magnetic field across the sample. For the non-static case, this is the inhomogeneity of the effective field in the rotating frame, namely \( B_{eff} = \sqrt{B^2 + (B_0 - \omega_K/\gamma_K)^2} \). Estimates of the broadening due to field inhomogeneities in our experiments, expressed as a second moment \( \Delta^2_B \), are given
in Table (2.2).

Table 2.2: Combining both nitrogen and hydrogen broadening mechanisms to get a prediction for the width in field of various resonance conditions for ammonium nitrate. The second moments $\Delta^2$ are in terms of squared Gauss. A field inhomogeneity across the sample of 2% is assumed for all fields. It is also assumed that various contributions to the broadening are not correlated. The sum of the second moments is in the $\Delta^2_{tot}$ column.

<table>
<thead>
<tr>
<th>Double resonance condition</th>
<th>$\Delta^2_H$ (G$^2$)</th>
<th>$\Delta^2_N$ (G$^2$)</th>
<th>$\Delta^2_B$ (G$^2$)</th>
<th>$\Delta^2_{tot}$ (G$^2$)</th>
<th>FWHM (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_z + \omega_{0K} = 0$</td>
<td>2.7 &lt; 0.1 &lt; 0.1 2.7</td>
<td>3.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_z + \omega_{1K} = 0$</td>
<td>$\frac{27}{4}$ 1.0</td>
<td>1.7 3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_y + \omega_{0K} = 0$</td>
<td>2.7 0.71 0.7</td>
<td>4.1 4.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_y + \omega_{0K} + \omega_{1K} = 0$</td>
<td>$\frac{27}{4}$ 0.4 &lt; 0.1 1.1 2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The broadening due to the hydrogen atoms, in the form of $\tilde{H}_D^K$ or $H_D^K$, tends to dominate over the broadening mechanisms due to the nitrogen, predominantly because of its much larger gyromagnetic ratio. Slichter [24] finds, for large effective fields in the rotating frame, that the homogenous dipolar Hamiltonian in the rotating frame can be truncated to

$$\tilde{H}_Z^K \simeq \frac{1}{2} \left( 3 \cos^2 \beta - 1 \right) \sum_{m>n} \frac{\gamma^2_k \mathcal{H}_\mu}{r^3_{mn} 4\pi} \left\{ 1 - 3(\hat{r}_{mn} \cdot \hat{z}')^2 \right\} \{ 3I^{(m)}_Z I^{(n)}_Z - \mathbf{I}^{(m)} \cdot \mathbf{I}^{(n)} \}, (2.54)$$

where the angle $\beta$ between $z'$ of the laboratory and the quantization axis $Z$ of the rotating coordinate system is defined by

$$\tan \beta = \frac{\omega_{1K}}{\omega_{0K} - \omega_K}. \quad (2.55)$$

28
This permits the modification of the standard calculation of the second moment \[24\] by the factor \( C = \frac{1}{2} (3 \cos^2 \beta - 1) \) to be

\[
\langle \Delta^2_{H_K} \rangle = C^2 \frac{3}{4^4 \pi^2} \gamma_H^2 \hbar^2 K (K + 1) \sum_n \{1 - 3(\hat{r}_{mn} \cdot \hat{z}')^2\}.
\] (2.56)

Here a particular representative spin \((m)\) is chosen to calculate around, and the width is calculated in terms of the field. When close to resonance, \(C^2 \approx \frac{1}{4}\). Therefore, the resonance width due to homogenous dipolar coupling is reduced by a factor of 2 over the static case. In ammonium nitrate the hydrogen second moment has been measured \[51\] in terms of static field to be \(\Delta^2_{H} = 2.7\ G^2\). Under the rotating double resonance conditions this would correspond to a reduction in broadening to \(\frac{27}{4}\ G^2\), as shown in Table (2.2).

Resonance broadening due to the nitrogen comes from three mechanisms; electric field gradient inhomogeneity, homogenous dipolar coupling, and the Zeeman perturbation. The broadening due to electric field gradient inhomogeneities (spread in \(H_Q\)) combined with the broadening due to the combined term, \(H_Q + H^I_D\), can be estimated by the width of the NQR signal at zero field. For ammonium nitrate these widths are quite narrow — on the order of 100 Hz — so the corresponding width in field would be less than 0.03 G. This is much smaller than the hydrogen broadening effects, and is therefore not included in Table (2.2). The broadening due to the spin-\(I\) Zeeman Hamiltonian is only a second order effect \[52\], but still has a noticeable contribution to some of the double resonance conditions. The nitrogen eigenenergies and transition frequencies due to the quadrupole and Zeeman Hamiltonians have been calculated exactly through numerical means, Table (2.3).
Table 2.3: Zeeman broadening and the shift of the NQR frequencies are calculated as a function of experimentally relevant static fields. Zero field frequencies were measured experimentally, at a temperature of about 10°C, and were used in the calculations at a nonzero $B$ field.

<table>
<thead>
<tr>
<th>$B_0$ (G)</th>
<th>$\nu_x \pm \sigma_x$ (kHz)</th>
<th>$\nu_y \pm \sigma_y$ (kHz)</th>
<th>$\nu_z \pm \sigma_z$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>501.3</td>
<td>421.8</td>
<td>79.5</td>
</tr>
<tr>
<td>$\omega_z / \gamma_H = 18.7$</td>
<td>501.6 \pm 0.1</td>
<td>421.6 \pm 0.1</td>
<td>79.9 \pm 0.2</td>
</tr>
<tr>
<td>85</td>
<td>506.6 \pm 1.5</td>
<td>418.6 \pm 2.7</td>
<td>88.0 \pm 4.2</td>
</tr>
<tr>
<td>$\omega_y / \gamma_H = 99.0$</td>
<td>508.4 \pm 1.9</td>
<td>417.5 \pm 3.6</td>
<td>90.9 \pm 5.5</td>
</tr>
</tbody>
</table>

Net Cross-Relaxation Rate and Nitrogen Signal

To find the net cross-relaxation rate for a specific double resonance condition expression for $I_{x3}$ is needed. This is found by examining the cross-relaxation between the $i$th spin-$I$ nucleus and the $k$th spin-$K$ nucleus under a particular resonance condition.\footnote{As a reminder, this specific double resonance case involves $I_{x3}$, but this analysis can be applied to any of the nine case listed in Table (2.1). Which means that when $I_{x3}$ is mentioned it can easily be generalized to $I_{p3}$, where $p$ is one of $x, y,$ or $z$ depending on the NQR transition of interest.} Initial and final states of interest can easily be determined by looking at $\hat{H}_D^S$ in Table (2.1). For resonant conditions involving a rotating field these states are in the rotating frame, otherwise they are in the laboratory frame. Using these states the following projection operator is defined

$$\Delta P = |\varphi_i\rangle\langle\varphi_i| - |\alpha_f\rangle\langle\alpha_f|.$$  \hspace{1cm} (2.57)

The expectation value of $\Delta P$, gives the probability of finding the $i$th spin-$I$ nucleus and the $k$th spin-$K$ nucleus in the initial state minus the probability of finding them in the final state. For instance, when close to the condition $\omega_x = \omega_{0K} + \omega_{1K}$, the
corresponding $\tilde{H}_D^S$, specified in Table (2.1), contains the “flip-flop” term $K_x^{(k)} I_x^{(i)}$, and the relevant pair of initial and final states are $|i = z, m_x^{(k)} = -\frac{1}{2}\rangle$ and $|i = y, m_x^{(k)} = \frac{1}{2}\rangle$ in the rotating frame. In this instance Eq. (2.57) becomes

$$\Delta P = |\tilde{\phi}_i\rangle\langle\tilde{\phi}_i| - |\tilde{\alpha}_f\rangle\langle\tilde{\alpha}_f|$$

(2.58)

$$= |i = z, m_x^{(k)} = -1/2\rangle\langle i = z, m_x^{(k)} = -1/2|$$

(2.59)

$$- |i = y, m_x^{(k)} = 1/2\rangle\langle i = y, m_x^{(k)} = 1/2|.$$  

(2.60)

For the same resonance condition, $\tilde{H}_D^S$ also contains the “flip-flop” term $K_{x^+}^{(k)} I_{x^+}^{(i)}$, and therefore the transition probability is the same if the initial and final states are reversed.

In general, the transition rate is the same if the initial and final states are reversed. Therefore, the rate for the expectation value of $\Delta P$ is

$$\langle \Delta \hat{P} \rangle = -2W_{ik} \langle \Delta P \rangle.$$ 

(2.61)

The projection operator $\Delta P$ can always be rewritten in terms of $I$ and $K$ operators. For instance, for the same resonance condition as above, $\omega_x = \omega_{0K} + \omega_{1K}$, and

$$\Delta P = I_{x^+}^{(i)} + \frac{2}{3} K_{x^+}^{(k)} + \frac{2}{3} I_{x^+}^{(i)} K_{x^+}^{(k)}.$$  

(2.62)

The expectation value of this operator expression, in the rotating frame, becomes

$$\langle \Delta P \rangle = \langle I_{x^+}^{(i)} \rangle + \frac{2}{3} \langle K_{x^+}^{(k)} \rangle + \frac{2}{3} \langle I_{x^+}^{(i)} K_{x^+}^{(k)} \rangle.$$ 

(2.63)
Making the approximation that

$$\langle \Delta P \rangle \approx \langle I_x^{(i)} \rangle + \frac{2}{3} \langle \tilde{K}^{(k)}_{x'} \rangle.$$  \hspace{1cm} (2.64)

is equivalent to invoking the high temperature limit and that the intra-species interactions are strong enough to maintain a common spin-temperature within each species, the prevalent spin-temperature model for cross-relaxation. Therefore,

$$\langle \hat{I}_x^{(i)} \rangle + \frac{2}{3} \langle \hat{\tilde{K}}^{(k)}_{x} \rangle = -2W_{ik} \left( \langle I_x^{(i)} \rangle + \frac{2}{3} \langle \tilde{K}^{(k)}_{x'} \rangle \right).$$  \hspace{1cm} (2.65)

For a simple pair interaction, conservation of energy dictates $\langle \hat{I}_x^{(i)} \rangle - \langle \hat{\tilde{K}}^{(k)}_{x} \rangle = 0$. Combining this with the Eq. (2.65) reveals

$$\langle \hat{I}_x^{(i)} \rangle = \langle \hat{\tilde{K}}^{(k)}_{x} \rangle = -\frac{6}{5} W_{ik} \left( \langle I_x^{(i)} \rangle + \frac{2}{3} \langle \tilde{K}^{(k)}_{x'} \rangle \right).$$  \hspace{1cm} (2.66)

Adding to the relaxation $I_x^{(i)}$ the contribution from all spin-$K$ particles and then averaging over all of the spin-$I$ particles results in

$$\langle \hat{I}_x^{(i)} \rangle = -\frac{6}{5} \sum_{k=1}^{N_K} W_{ik} \left( \langle I_x^{(i)} \rangle + \frac{2}{3} \langle \tilde{K}^{(k)}_{x'} \rangle \right).$$  \hspace{1cm} (2.67)

$$\langle \dot{I}_x^{(i)} \rangle = -\frac{6}{5} \frac{1}{N_I} \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} W_{ik} \left( \langle I_x^{(i)} \rangle + \frac{2}{3} \langle \tilde{K}^{(k)}_{x} \rangle \right)$$  \hspace{1cm} (2.68)

$$\approx -2W_d \left( \langle I_x^{(i)} \rangle + \frac{2}{3} \langle \tilde{K}_x \rangle \right).$$  \hspace{1cm} (2.69)
The net cross-relaxation rate $W_d$ is

$$W_d \equiv \frac{3}{5} \frac{1}{N_f} \sum_{i=1}^{N_f} \sum_{k=1}^{N_K} W_{ik}$$

$$= 2\pi g(\Delta \omega) \frac{3}{5} \frac{1}{N_f} \sum_{i=1}^{N_f} \sum_{k=1}^{N_K} |F_{ik}|^2. \tag{2.71}$$

where $g(\Delta \omega) = \frac{\hbar}{\rho}(\Delta E)$ is the spectral density function and is the density of final states per unit of frequency. The terms for $F_{ik}$ can be found in Table (2.1). This rate is close to that given by Stokes and Ailion [53] for a generalized Zeeman-quadrupole cross-relaxation rate, but is derived using a different method and adapted for spin-1 nuclei in an asymmetric electric field gradient ($\eta \neq 0$) under the combination of static and rotating magnetic field. Following Pershan’s treatment [48], an expression for the spectral density function can be approximated by convoluting the spectral distribution of the spin-$I$ atoms, characterized by the second moment $\Delta^2_I$, with that of the spin-$K$ atoms, characterized by $\Delta^2_K$. The convolution of the two Gaussian distributions is a Gaussian, whose width in frequency is

$$\gamma^2_K \Delta^2 = \gamma^2_K \Delta^2_I + \gamma^2_K \Delta^2_K,$$

where $\Delta \omega$ is defined in Table (2.1), and estimates of $\Delta^2$ are given in Table (2.2). In using this spectral density function the broadening of the spin-1/2 and spin-1 levels are assumed independent of one another and that $H_D$ is static [37]. In order to obtain the static $H_D$, the dipolar coupling is averaged over a timescale long with respect to the fluctuations caused by rapid relative motion between spins [25]. The time averaging can be represented by replacing $F_{ik}$ with the average value $\bar{F}_{ik}$ in
Eq. (2.71), which results in a reduced cross-relaxation, much as the rapid motion in a solid results in a narrowed NMR linewidth [25].

### 2.1.9 Dipolar Coupling Strength

The cross-relaxation rate is composed of two terms in Eq. (2.71): the spectral density $g(\Delta \omega)$, and another term, defined as the dipolar coupling strength $\omega_D^2$. The dipolar coupling strength is

$$\omega_D^2 = \frac{6\pi}{5} \frac{1}{N_I} \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} |F_{ik}|^2,$$

and contains the geometric spin-$I$ spin-$K$ dipolar coupling terms. The cross-relaxation rate for a given resonance condition is measured by sweeping the magnetic field through the peak resonant field $B_{\text{resonant}}$. The rate varies as a function of $\Delta \omega$, or $\gamma_K (B - B_{\text{resonant}})$, given by $W_d(\Delta \omega)$. Note that $\omega_D^2$ can also be expressed as

$$\omega_D^2 = \int_{\text{full spectrum}} W_d(\Delta \omega) d\Delta \omega = W_d^0 (\sqrt{2\pi} \gamma_K \Delta)$$

where $W_d^0 = W_d(\Delta \omega = 0)$ is the maximum value of the cross-relaxation rate. It is clear from this that the maximum rate depends on the various broadening mechanisms including field inhomogeneity, but the net integration of $W_d$ over the full spectral width does not. In principle then, to find the dipolar coupling strength it is not strictly necessary to characterize the width of the transition but only to ensure that you have swept entirely through it. In our experiments however, the widths of the resonance conditions are separately measured and then only the central portion of each is swept through.
The measured effective cross-relaxation rate $W_{\text{exp}}$ for a given experiment swept from $B_{\text{low}}$ to $B_{\text{high}}$ is given by

$$W_{\text{exp}} (B_{\text{high}} - B_{\text{low}}) = \int_{B_{\text{low}}}^{B_{\text{high}}} W_d dB$$

(2.75)

$$= W_0^d \int_{B_{\text{low}}}^{B_{\text{high}}} \exp\left(-\frac{\Delta B^2}{2\Delta^2}\right) dB$$

(2.76)

$$= hW_0^d (\sqrt{2\pi}\Delta)$$

(2.77)

$$= h\omega_D^2 / \gamma_K$$

(2.78)

where $h$ is the fraction of the overall spectral distribution covered by the field sweep, and $\Delta B = B - B_{\text{resonant}}$. The fraction covered is

$$h = \frac{\int_{B_{\text{low}}}^{B_{\text{high}}} \exp\left(-\frac{\Delta B^2}{2\Delta^2}\right) dB}{(\sqrt{2\pi}\Delta)}.$$ 

(2.79)

The maximum cross-relaxation rate is then given by

$$W_0^d = \frac{W_{\text{exp}} (B_{\text{high}} - B_{\text{low}})}{\int_{B_{\text{low}}}^{B_{\text{high}}} \exp\left(-\frac{\Delta B^2}{2\Delta^2}\right) dB}$$

(2.80)

$$= \frac{W_{\text{exp}} (B_{\text{high}} - B_{\text{low}})}{h\sqrt{2\pi}\Delta},$$

(2.81)

with the strength of the nitrogen-hydrogen coupling given by

$$\omega_D^2 = \frac{\gamma_K W_{\text{exp}} (B_{\text{high}} - B_{\text{low}})}{h}.$$ 

(2.82)
Therefore, the measure of the effective cross-relaxation rate over a given field range \( W_{\text{exp}} \), combined with the fraction of the resonance condition met by our sweep, \( h \), permits us to measure the nitrogen-hydrogen dipolar coupling strength.

### 2.1.10 Determining Distances

The cross-relaxation rates that emerge from the secular dipolar Hamiltonian that was calculated for the different double resonance conditions, Table (2.1), can be utilized to factor out the effects of a powder. By using combinations of the cross-relaxation rates one can in principle determine the orientations and distances between the spin-\( I \) and spin-\( K \) nuclei that are cross relaxing. To make this more transparent, define the geometrical quantity 

\[ \frac{1-\hat{z}_{\text{ik}} \hat{r}_{ik}}{r_{ik}} \cdot \hat{p} \]

by \( \vec{V}_{ik}^p \) to emphasize that it is a vector and \( p \) can be \( \hat{x} \), \( \hat{y} \) or \( \hat{z} \). By examining the \( F_{ik} \) terms from Table (2.1), it becomes apparent that each cross-relaxation rate can be written as a combination of \( \vec{V}_{ik}^p \cdot V_{ik}^p \) and \( |\hat{z} \cdot \vec{V}_{ik}^z|^2 \). Thus, for certain combinations of the terms the result is completely in the PAS frame. This property occurs when one of the Rabi cross-relaxation geometrical terms is combined with the equivalent term from one of the other conditions, but they both must be along the same directions.

For example, if the \( \hat{z} \) axis is important then the Rabi cross relaxation \( \omega_z + \omega_{1K} = 0 \), combined with either the Larmor \( \omega_z + \omega_{0K} = 0 \) or the Rabi plus Larmor condition \( \omega_z + \omega_{0K} + \omega_{1K} = 0 \) can be utilized. For this example the \( \omega_z + \omega_{1K} = 0 \) and the \( \omega_z + \omega_{0K} = 0 \) double resonance \( F_{ik} \) terms are added to form

\[ \frac{1}{4} |(\hat{x}' - i\hat{y}') \cdot V_{ik}^z|^2 - \frac{1}{4} |\hat{z}' \cdot V_{ik}^z|^2. \quad (2.83) \]
This is expanded to

\[
= \frac{1}{4} \left[ (\hat{x}' \cdot \vec{V}^i_{z})^2 + (\hat{y}' \cdot \vec{V}^i_{z})^2 + (\hat{z}' \cdot \vec{V}^i_{z})^2 \right] \tag{2.84}
\]

\[
= \frac{1}{4} \vec{V}^i_{z} \cdot \vec{V}^i_{z} \tag{2.85}
\]

\[
= \frac{1}{4r^6_{ik}} [(1 - 3\hat{r}_{ik} \hat{r}_{ik}) \cdot \hat{z}] \cdot [(1 - 3\hat{r}_{ik} \hat{r}_{ik}) \cdot \hat{z}] \tag{2.86}
\]

\[
= \frac{1}{4r^6_{ik}} (1 + 3(\hat{r}_{ik} \cdot \hat{z})^2). \tag{2.87}
\]

With corresponding definitions for \( \vec{V}^i_{y} \) and \( \vec{V}^i_{x} \), result in

\[
\vec{V}^i_{y} \cdot \vec{V}^i_{y} = \frac{1}{r^6_{ik}} (1 + 3(\hat{r}_{ik} \cdot \hat{y})^2) \tag{2.88}
\]

\[
\vec{V}^i_{z} \cdot \vec{V}^i_{x} = \frac{1}{r^6_{ik}} (1 + 3(\hat{r}_{ik} \cdot \hat{x})^2). \tag{2.89}
\]

Notice, that these expressions do not depend in any way on the unprimed coordinate system and therefore would not change for a powder. Therefore if the dipolar coupling strengths \( \omega_D^2 \) are added from the two experiments \( \omega_z + \omega_{0K} = 0 \) and \( \omega_z + \omega_{1K} = 0 \), using Eqs. 2.87 & 2.73, the sum is

\[
\frac{6\pi}{5} \frac{1}{4} \frac{1}{N_I} \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} \frac{1}{r^6_{ik}} (1 + 3(\hat{r}_{ik} \cdot \hat{z})^2), \tag{2.90}
\]

which is independent of the powder average, and reveals the underlying structure of the sample.
2.1.11 Rate Equations

The last column in Table (2.1) is expanded to get the full set of rate equations for the nine different double resonance conditions. The rate equations are derived according to detailed-balance of the populations at a finite lattice temperature and the constants of the motion are derived for each condition [25,41,48,52,54,55]. The rate equations are written in terms of the expectation values since they are proportional to population differences relative to the thermal equilibrium values. The rate equations for an isolated spin-1 system are:

\[
\begin{align*}
\delta \dot{I}_{x3} &= -2W_x \delta I_{x3} + W_y \delta I_{y3} + W_z \delta I_{z3}, \\
\delta \dot{I}_{y3} &= W_x \delta I_{x3} - 2W_y \delta I_{y3} + W_z \delta I_{z3}, \\
\delta \dot{I}_{z3} &= W_x \delta I_{x3} + W_y \delta I_{y3} - 2W_z \delta I_{z3}.
\end{align*}
\]

(2.91)

where \( \delta I_{p3} = \langle I_{p3} \rangle - \langle I_{p3}^0 \rangle \) and \( \langle I_{p3}^0 \rangle \) are the thermal equilibrium values. As shown in Fig. (1.1), \( W_x, W_y, \) and \( W_z \) are, respectively, the autorelaxation rates between the \( I \)-eigenstates, where the three nitrogen autorelaxation rates are determined from the measurement of two of the \( T_1 \)'s for a spin-1 sample. Petersen calculated them as a function of \( T_1s \) and \( T_1l \) [56], for ammonium nitrate \( T_1l \) is the \( T_1 = 16.9 \pm 1.0 \) s at \( \omega_y \) and \( T_1s \) is the \( T_1 = 11.6 \pm 0.5 \) s at \( \omega_x \) [8]. The corresponding nitrogen autorelaxation rates are calculated to be \( W_x = 0.033 \) s\(^{-1} \), \( W_y = 0.015 \) s\(^{-1} \), and \( W_z = 0.024 \) s\(^{-1} \).

The rate equation for the isolated spin 1/2 is:

\[
\delta \dot{K}_{z'} = -\rho \delta K_{z'},
\]

(2.92)

where \( \delta K_{z'} = \langle K_{z'} \rangle - \langle K_{z'}^0 \rangle \), and \( \langle K_{z'}^0 \rangle \) is the thermal equilibrium value.

\(^2\text{See Appendix B}\)
The rate equations for the different double resonance conditions combine Eq. (2.91) and Eq. (2.92) since both systems are no longer isolated and incorporate the cross-relaxation rate. While the rate equations for the different double resonance conditions have similar derivations, the major difference between the static double resonance and the other double resonance conditions is the treatment of the hydrogen in the rf field. In the static only double resonance condition the hydrogen is aligned with the static field and in the following equations
\[ \langle K_q' \rangle = \langle K_z' \rangle \quad \text{and} \quad \delta K_q' = \delta K_z' = \langle K_{0z}' \rangle - \langle K_{0z}' \rangle \]. While for the rotating and the combined conditions \(^1\text{H}\) is treated in the rotating frame so \[ \langle K_q' \rangle = \langle \tilde{K}_{x} \rangle \quad \text{and} \quad \delta K_q' = \delta \tilde{K}_{x} = \langle \tilde{K}_{x} \rangle - \langle \tilde{K}_{0x} \rangle \], but in the rotating frame, exactly on resonance, \[ \langle \tilde{K}_{0x} \rangle = 0 \] (page 243).

The rate equations for the three conditions at the three transition frequencies, including the \( K \) and \( I \) autorelaxation rates, become

\[
\begin{align*}
\delta \dot{I}_{x3} &= -2W_x \delta I_{x3} + W_y \delta I_{y3} + W_z \delta I_{z3} + (1 - 3\delta x_p)W_d \left( \frac{2}{3} K_{q'} + I_{p3} \right), \\
\delta \dot{I}_{y3} &= W_x \delta I_{x3} - 2W_y \delta I_{y3} + W_z \delta I_{z3} + (1 - 3\delta y_p)W_d \left( \frac{2}{3} K_{q'} + I_{p3} \right), \\
\delta \dot{I}_{z3} &= W_x \delta I_{x3} + W_y \delta I_{y3} - 2W_z \delta I_{z3} + (1 - 3\delta z_p)W_d \left( \frac{2}{3} K_{q'} + I_{p3} \right), \\
\delta \dot{K}_{q'} &= -(\rho \delta K_{q'}) - 2\frac{W_d}{R} \left( \frac{2}{3} \tilde{K}_{q'} + I_{p3} \right),
\end{align*}
\] (2.93)

where \( \delta_{ij} \) is the Kronecker delta. The values of \( p \) and \( q \) depend on resonance conditions (static, rotating, and combination as in Table (2.1):

1. Corresponding to the static resonance condition: \( \delta K_{q'} = \delta K_{z'} \)
   (a) \( \omega_{nqr} = \omega_x, p = x, I_{p3} = \delta I_{x3}, \) and \( K_{q'} = \delta K_{z'} \)
   (b) \( \omega_{nqr} = |\omega_y|, p = y, I_{p3} = \delta I_{y3}, \) and \( K_{q'} = -\delta K_{z'} \)
(c) $\omega_{nqr} = |\omega_z|, p = z, I_{p3} = \delta I_{z3}, \text{ and } K_{q'} = -\delta K_{x'}$

2. Corresponding to the rotating or Rabi double resonance condition: $\delta K_{q'} = \delta \tilde{K}_{x'}$

(a) $\omega_{nqr} = \omega_x, p = x, I_{p3} = I_{x3}, \text{ and } K_{q'} = \tilde{K}_{x'}$

(b) $\omega_{nqr} = |\omega_y|, p = y, I_{p3} = I_{y3}, \text{ and } K_{q'} = -\tilde{K}_{x'}$

(c) $\omega_{nqr} = |\omega_z|, p = z, I_{p3} = I_{z3}, \text{ and } K_{q'} = -\tilde{K}_{x'}$

3. Corresponding to the combination or the Rabi plus Larmor double resonance condition for $+\omega_1K$: $\delta K_{q'} = \delta \tilde{K}_{x'}$

(a) $\omega_{nqr} = \omega_x, p = x, I_{p3} = I_{x3}, \text{ and } K_{q'} = \tilde{K}_{x'}$

(b) $\omega_{nqr} = |\omega_y|, p = y, I_{p3} = I_{y3}, \text{ and } K_{q'} = -\tilde{K}_{x'}$

(c) $\omega_{nqr} = |\omega_z|, p = z, I_{p3} = I_{z3}, \text{ and } K_{q'} = -\tilde{K}_{x'}$

where $R = N_K/N_I$. The $^1\text{H}$ autorelaxation rate, $\rho$, has two meanings depending on the type of double resonance. If there is no rf then $\rho$ is the $K$ autorelaxation rate $(1/T_{1H})$. If there is an applied rf then $\rho$ is the $K$ autorelaxation rate in the rotating frame or $(1/T_{1H\rho})$. As will be seen later both $(1/T_{1H\rho})$ and $(1/T_{1H})$ can be measured for ammonium nitrate. Note, that the four equations of Eqs. (2.1) can be reduced to three using the identity $\delta I_{x3} + \delta I_{y3} + \delta I_{z3} = 0$.

In the next chapter the static double resonance conditions will be treated in detail including experimental results. In Chapter 5 the rotating and combined double resonance conditions will be addressed.
Chapter 3: Low-Field Static Double Resonance

3.1 Rate Equations for $\gamma_H B_0 = \omega_x$

This chapter investigates the double resonance created with a small static field, $B_0$, applied such that the hydrogen Zeeman frequency, $\gamma_H B_0$, matches one of the three NQR frequencies of nitrogen, $\omega_{NQR}$. This chapter is a specific application of the general theory developed in the previous chapter focused on the $\gamma_H B_0 = \omega_x$ double resonance condition. The theory allows us to model the spin dynamics of this system, and predicts both the evolution of the spins and the resulting spin populations and therefore the signal during the experiments. Table (2.1) provides the secular dipole Hamiltonian mediating the cross-relaxation, but the constants of motion and $W_{ik}$ for this condition need to be calculated, and the rate equations still need to be solved to provide the time evolution of the system. Experiments were conducted to investigate the cross-relaxation rates and the improvement in SNR and these were compared with the theoretical predictions. The experiments showed additional gains in SNR were achievable by successively matching to multiple NQR frequencies. Using ammonium nitrate, gains in SNR of 230% have been observed with this double resonance technique.

Near the double resonance condition, $\gamma_H B_0 = \omega_x$, the Hamiltonian is $H = H_Q + H_Z + H_D^S$. For small fields the nitrogen Zeeman Hamiltonian is much smaller than the nitrogen quadrupole Hamiltonian and can be considered a perturbation. 

\footnote{Parts of this chapter were published as: D. Prescott, O. Olmedo, S. Soon, K. Sauer, Low-field approach to double resonance in nuclear quadrupole resonance of spin-1 nuclei, Journal of Chemical Physics 126 (2007) 204504.}
of it. Since the nitrogen quadrupole and Zeeman Hamiltonians do not commute, this perturbation is zero to first order and the nitrogen Zeeman contribution is negligible [52]. The Hamiltonian is thus $H = H_Q + H^Z_N + H^S$ and following section (2.1.7) in the previous chapter provides the constants of motion.\(^2\) Using Eq. (2.39) the expectation values of the following observables are constants of motion:

\[ I_{x3} - RK_{z'}, \quad (3.1) \]
\[ I_{x4} = I_{y3} - I_{z3}, \quad (3.2) \]

where $R = N_K/N_I$,

\[ I_{x3} = \frac{1}{N_I} \sum_{i=1}^{N_I} I_{x3}^{(i)}, \quad \text{and} \quad K_{z'} = \frac{1}{N_K} \sum_{k=1}^{N_K} K_{z'}^{(k)}. \quad (3.3) \]

The invariance of $\langle I_{x3} - RK_{z'} \rangle$ with time is equivalent to global conservation of energy, with

\[ \langle K_{z'} \rangle = \frac{1}{2} \frac{N_I - N_\downarrow}{N_K}, \quad (3.4) \]

which is proportional to the population difference between the $K$-nuclear spin pointing with the field, $N_\uparrow$ (or $|m_z = +1/2\rangle$), and against the field, $N_\downarrow$ (or $|m_z = -1/2\rangle$). The constant of motion, $I_{x4}$, is directly proportional to the population of the undisturbed nitrogen eigenstate. Further, using conservation of the number of nitrogen atoms, or

\(^2\)The constant of motion are needed to find the relationships among the populations and formulate the rate equations.
\[ \langle I_{x3} \rangle + \langle I_{y3} \rangle + \langle I_{z3} \rangle = 0, \]

the following rates are found:

\[ \langle \dot{I}_{y3} \rangle = \langle \dot{I}_{z3} \rangle = -\langle \dot{I}_{x3} \rangle / 2. \quad (3.5) \]

Therefore, in determining the evolution of \( I_{x3} \), all of the other population differences of interest, \( I_{y3}, I_{z3}, K_z' \), are determined.

To determine the evolution of \( I_{x3} \) the cross-relaxation between the \( k \)th spin-1/2 and the \( i \)th spin-1 nucleus is investigated. In particular, the transition rate between

an initial state \( \varphi_i = |i = z; m_z^{(k)} = -1/2 \rangle \) and a final state \( \alpha_f = |i = y; m_z^{(k)} = +1/2 \rangle \)

is calculated using Fermi’s golden rule,

\[ W_{ik} = 2\pi \hbar |\langle \alpha_f | H_D | \varphi_i \rangle|^2 \rho(E_f = E_i, \Delta E), \quad (3.6) \]

where \( H_D^S \) is from Table (2.1). In the equation above, \( \rho(E_f = E_i, \Delta E) \) is the density of final states with the energy difference \( \Delta E \) between the final state and the resonance as determined by the dominant Hamiltonian \( H_Q + H_Z \), which also conserves energy due to the broadening in energies of the final state from the pair’s interaction with other nuclei [48,49].

To find an expression for \( I_{x3} \) for this static double resonance case the same procedure as in Chapter 2 is followed, except that we are not in the rotating frame. The following projection operator was defined previously, Eq. (2.57),

\[ \Delta P = |\varphi_i \rangle \langle \varphi_i | - |\alpha_f \rangle \langle \alpha_f |, \quad (3.7) \]

where \( \Delta P \) is the probability of a pair being found in the \( |i = y; m_z^{(k)} = +1/2 \rangle \) state minus the probability of a pair being found in the \( |i = z; m_z^{(k)} = -1/2 \rangle \) state. For
this static double resonance condition Eq. (2.57) becomes

\[ \Delta P = \frac{2}{3} \langle K_{z'}^{(k)} \rangle + \langle I_{x3}^{(i)} \rangle + \frac{2}{3} \langle I_{x4}^{(i)} K_{z'}^{(k)} \rangle. \]  

(3.8)

Because the transition rate is the same if the initial and final states are reversed, the following rate is found

\[ \Delta \dot{P} = -2W_{ik} \Delta P. \]  

(3.9)

In the high temperature limit \( \Delta P \) can be approximated as \( \langle I_{x3}^{(i)} + \frac{2}{3} K_{z'}^{(k)} \rangle \). Therefore, Eq. (3.9) can be written as

\[ \langle \dot{I}_{x3}^{(i)} + \frac{2}{3} \dot{K}_{z'}^{(k)} \rangle = -2W_{ik} \langle I_{x3}^{(i)} + \frac{2}{3} K_{z'}^{(k)} \rangle. \]  

(3.10)

With a single “flip-flop” transition conservation of energy dictates \( \langle \dot{I}_{x3}^{(i)} - \dot{K}_{z'}^{(k)} \rangle = 0 \). Combining this with Eq. (3.10) shows \( \langle \dot{I}_{x3}^{(i)} \rangle = -\frac{6}{5} W_{ik} \langle I_{x3}^{(i)} + \frac{2}{3} K_{z'}^{(k)} \rangle \). Adding in the relaxation from all the spin-1/2 nuclei, as well as averaging \( \langle I_{x3}^{(i)} \rangle \), then

\[ \langle \dot{I}_{x3} \rangle = -\frac{6}{5} \frac{1}{N_I} \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} W_{ik} \langle I_{x3}^{(i)} + \frac{2}{3} K_{z'}^{(k)} \rangle \approx -2W_d \langle I_{x3} + \frac{2}{3} K_{z'} \rangle, \]  

(3.11)

where the net cross-relaxation rate is

\[ W_d = \frac{3}{5} \frac{1}{N_I} \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} W_{ik}. \]  

(3.12)
Using Eq. (3.1), then

\[ \langle \dot{K}_z \rangle \approx -2 \frac{W_d}{R} \langle I_{x_3} + \frac{2}{3} K_{z'} \rangle. \]  

(3.13)

In the limit when the time spent at the double resonance condition is much longer than \(1/W_d\), Eqs. 3.5, together with Eqs. 3.11 and 3.13, yield final populations of the \(K\) and \(I\) eigenstates equivalent to the common spin-temperature model \([6]\), as expected.

Considering the expression for Fermi’s golden rule, Eq. (3.6), the only term of the dipolar Hamiltonian that contributes to the matrix element is \(A_{ik} F_{ik}\) from Table (2.1). For the resonance condition, \(\omega_x = \omega_{0K}\), the \(F_{ik}\) and \(A_{ik}\) terms are given in the table. Note that \(F_{ik}\) corresponds to the geometric term and \(A_{ik}\) to the spin operator of the two raising operators: one for \(K\) and one for \(I\). In this case, \(K_{x+}^{(k)}\) is the standard raising operator \(K_{x'} + iK_{y'}\), and \(I_{x+}^{(i)}\) is the analogous raising operator in the fictitious spin-1/2 operator space \((I_{x_1}, I_{x_2}, I_{x_3})\), corresponding to the \(\omega_x\) transition. The “flip-flop” nature of \(A_{ik}\) can be emphasized by equivalently writing \(A_{ik}\) as \(|i = y; k = 1/2\rangle \langle i = z; k = -1/2|\), where the first term in the ket-bra corresponds to the eigenstate of the \(i\)th spin-1 and the second to the \(k\)th spin-1/2 nucleus. Expressions for the other static double resonance conditions are constructed in a similar manner.

Here, the cross-relaxation rate is

\[ W_d = 2\pi g(\Delta \omega) \frac{3}{5} \frac{1}{N_I} \sum_{i=1}^{N_I} \sum_{k=1}^{N_K} |F_{ik}|^2, \]  

(3.14)

where \(g(\Delta \omega) = h\rho(\Delta E)\) is the density of final states per unit frequency \(\omega\), and the
geometric operator $F_{ik}$ is in Table (2.1):

$$F_{ik} = \frac{\kappa}{2r_{ik}^2} \{(1 - 3(\hat{x} \cdot \hat{r}_{ik})^2)\hat{x} + (\hat{x} \cdot \hat{r}_{ik})(\hat{y} \cdot \hat{r}_{ik})\hat{y} +$$

$$(\hat{x} \cdot \hat{r}_{ik})(\hat{z} \cdot \hat{r}_{ik})\hat{z}\} \cdot \{\hat{x}' - i\hat{y}'\}.$$  \hspace{2cm} (3.15)

In general, the cross-relaxation depends on the relative orientation of the PAS frame $(x, y, z)$ with respect to the laboratory frame $(x', y', z')$, and therefore varies from one crystallite of the powder to another. When observing the signal after the excitation of the powder sample with a rf pulse, not all crystallites contribute equally, but a certain subset is monitored preferentially as determined by the orientation and strength of the rf field. For example, the weighting of the crystals observed with $\omega_x$ irradiation of strength $B_1$ and duration $t_p$ is $\epsilon_{x-rf} \sin(\gamma f B_1 t_p \epsilon_{x-rf})$, where $\epsilon_{x-rf}$ is the direction cosine between the PAS $x$-axis and the direction of the rf excitation field. Therefore, the powder cross-relaxation can be written as

$$W_{dpowder} = \frac{\int W_d \epsilon_{x-rf} \sin(\gamma f B_1 t_p \epsilon_{x-rf})d\Omega}{\int \epsilon_{x-rf} \sin(\gamma f B_1 t_p \epsilon_{x-rf})d\Omega},$$

where the integration is over all the possible orientations of the PAS frame with respect to the laboratory frame.

Using Eq. (2.93), when $B_0$ is near $\omega_x/\gamma K$, the rate equations, including the $K$ and
\[ I \text{ autorelaxation rates, become} \]

\[
\begin{align*}
\delta \dot{I}_{x3} & = -2W_x \delta I_{x3} + W_y \delta I_{y3} + W_z \delta I_{z3} - 2W_d \left( \frac{2}{3} \delta \hat{K}_{x'} + \delta I_{x3} \right), \\
\delta \dot{I}_{y3} & = W_x \delta I_{x3} - 2W_y \delta I_{y3} + W_z \delta I_{z3} + W_d \left( \frac{2}{3} \delta \hat{K}_{x'} + \delta I_{x3} \right), \\
\delta \dot{I}_{z3} & = W_x \delta I_{x3} + W_y \delta I_{y3} - 2W_z \delta I_{z3} + W_d \left( \frac{2}{3} \delta \hat{K}_{x'} + \delta I_{x3} \right), \\
\delta \dot{\hat{K}}_{x'} & = -\rho \delta \hat{K}_{x'} - 2 \frac{W_d}{R} \left( \frac{2}{3} \delta \hat{K}_{x'} + \delta I_{x3} \right),
\end{align*}
\]

where, according to detailed-balance and the finite temperature of the lattice [25,41], $\delta I_{x3} \equiv \langle I_{x3} \rangle - \langle I_{x3}^0 \rangle$ is defined with respect to the equilibrium value of the observable $\langle I_{x3}^0 \rangle$. The other observables in Eq. (3.17) are similarly defined with respect to their equilibrium values. As shown in Fig. (1.1), $W_x$, $W_y$, and $W_z$ are, respectively, the autorelaxation rates between the $I$-eigenstates $|y\rangle$ and $|z\rangle$, $|x\rangle$ and $|z\rangle$, and $|y\rangle$ and $|x\rangle$.

The rate equations above are similar in form to those found in Ref. [52], but include the $K$ autorelaxation $\rho$. Note again, that the previous four equations, Eqs. (3.17), can be reduced to three using $\delta I_{x3} + \delta I_{y3} + \delta I_{z3} = 0$.

Solving Eqs. (3.17) in the limit that $W_d \gg \rho \gg W_x, W_y, W_z$, then the relaxation rates ($\lambda_D, \lambda_K, \lambda_I$) and the corresponding eigenvectors ($V_D, V_K, V_I$) for the case when $B_0$ is close to $\omega_x/\gamma_K$ are in Table (3.1). Using the same procedure as outlined above, the appropriate rates and eigenvectors for the other two resonance conditions, $B_0 = |\omega_x|/\gamma_K$ and $B_0 = |\omega_y|/\gamma_K$, were found and are summarized in Table (3.1).

Therefore, $T_1$ relaxation under any double resonance condition is characterized by

\footnote{These solutions are in the limit that $W_d \gg \rho \gg W_x, W_y, W_z$ and the equations have the concise analytic solution as shown in the table. When the subsequent experimental data are compared to the model the numerical solution to Eq. (3.17) is used.}
three rates: one rate dominated by cross-relaxation ($\lambda_D$), a second proportional to $K$ autorelaxation ($\lambda_K$), and a third characterized by the $I$ autorelaxation ($\lambda_I$). The return to thermal equilibrium is then governed by

$$\begin{align*}
(\delta I_{x3}, \delta I_{y3}, \delta I_{z3}, \delta K_x) = a_D V_D e^{-\lambda_D t} + a_K V_K e^{-\lambda_K t} + a_I V_I e^{-\lambda_I t},
\end{align*}$$

(3.18)

where $a_D$, $a_K$, and $a_I$ depend on the initial conditions of the system.

This equation predicts the spin populations and therefore the signal that is detected after the double resonance, as the populations return to equilibrium. This master signal equation, Eq. (3.18), along with Table (3.1), can be used for any of the static double resonance conditions. These will be referred to in Chapter 5 when the other double resonance conditions are investigated.

Since the experimental conditions are controlled, the initial state of the system, e.g. after saturation, is known. For example, a simple experiment would be to saturate the $\omega_x$ transition, create the double resonance, $B_0 = |\omega_x|/\gamma_K$, and then let the spins evolve according to Eq. (3.18). One common experimental condition is to saturate a particular transition which provides an experimental zero condition, i.e. an immediate measurement of the saturated transition should result in zero signal. The calculation of these initial conditions due to saturation is thus important to the modeling of the spin dynamics.

### 3.1.1 Saturation and Initial Conditions

Typical initial conditions correspond to the case where the transition under observation has been saturated and the static field has just been ramped rapidly to $B_0$. If, for example, the observed transition is $\omega_x$, this corresponds to $\langle I_{x3} \rangle = 0$, $\langle I_{y3} \rangle = -\langle I_{z3} \rangle = (I^0_{y3})/2 - (I^0_{z3})/2$. 

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Table 3.1: The relaxation rates and the corresponding (non-normalized) eigenvectors \((\delta I_x, \delta I_y, \delta I_z, \delta K')\) for all three double resonance conditions under the condition \(W_d \gg \rho \gg W_x, W_y, W_z\).

<table>
<thead>
<tr>
<th></th>
<th>(\omega_x)</th>
<th>(\omega_y)</th>
<th>(\omega_z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_D)</td>
<td>({2 + 4/(3R)}W_d)</td>
<td>({2 + 4/(3R)}W_d)</td>
<td>({2 + 4/(3R)}W_d)</td>
</tr>
<tr>
<td>(\lambda_K)</td>
<td>(\rho R/(R + 2/3))</td>
<td>(\rho R/(R + 2/3))</td>
<td>(\rho R/(R + 2/3))</td>
</tr>
<tr>
<td>(\lambda_I)</td>
<td>(2W_y + W_z)</td>
<td>(2W_z + W_x)</td>
<td>(2W_x + W_y)</td>
</tr>
</tbody>
</table>

\(V_D\):
\[
\begin{pmatrix}
1 & -1/2 & -1/2 \\
-1/2 & 1 & 1 \\
-1/2 & -1/2 & 1 \\
1/R & -1/R & -1/R \\
\end{pmatrix}
\]

\(V_K\):
\[
\begin{pmatrix}
1 & -1/2 & -1/2 \\
-1/2 & 1 & 1 \\
-1/2 & -1/2 & 1 \\
-3/2 & 3/2 & 3/2 \\
\end{pmatrix}
\]

\(V_I\):
\[
\begin{pmatrix}
0 & 1 & 1 \\
1 & 0 & 1 \\
-1 & -1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\]
Saturation consists of repeatedly applying an rf at the transition of interest. The effect of an rf pulse, at $\omega_x$, given by the Hamiltonian

$$H_{rf} = -\gamma_N I \cdot B_{rf} \cos(\omega_x t),$$

(3.19)
on the density matrix must be evaluated. First, $H_{rf}$ is converted from the lab frame to the PAS and since only $I_x$ connects the levels between the two systems, the Hamiltonian is

$$H_{rf} = -\gamma_N I_x \cos(\phi) B_{rf} \cos(\omega_x t),$$

(3.20)

where $\phi$ is an angle between the PAS frame and the rf direction. $H_{rf}$ is treated as a perturbation of $H_Q$ and

$$\tilde{H}_{rf} = e^{-iH_Q t} H_{rf} e^{iH_Q t} = \theta I_{x1},$$

(3.21)

where $\theta = -\gamma_N B_{rf} \cos(\phi)$ in the interaction representation. The initial density matrix is $\rho^0 \approx 1/3 - \hbar H_Q/(3KT)$, but since only the deviation is important the focus is on the reduced density matrix $\sigma^0 \approx \hbar H_Q/(3KT)$. The effect of the pulse at the $\omega_x$ transition frequency is

$$\rho(t) = e^{-iH_Q t} e^{-iI_{x1} \sigma^0} e^{iI_{x1} \sigma} e^{iH_Q t}$$

(3.22)

$$= e^{-iH_Q t}[\omega_x \cos \theta I_{x3} - \omega_x \sin \theta I_{x2} + \omega_x' I_{x4}] e^{iH_Q t}$$

(3.23)

$$= \omega_x \cos \theta I_{x3} - \omega_x \sin \theta (I_{x1} \cos \omega_x t + I_{x2} \sin \omega_x t) + \omega_x' I_{x4},$$

(3.24)

where $\omega_x'$ is defined by Eq. (2.8). Using $\langle Q \rangle = Tr \{Q \rho \}$ gives the following expectation.
values:

\[
\langle I_{x3} \rangle - \langle I_{x3}^0 \rangle = (\cos \theta - 1) \frac{\hbar \omega_x}{6kT},
\]

\[
\langle I_{y3} \rangle - \langle I_{y3}^0 \rangle = -\frac{1}{2} (\cos \theta - 1) \frac{\hbar \omega_x}{6kT},
\]

\[
\langle I_{z3} \rangle - \langle I_{z3}^0 \rangle = -\frac{1}{2} (\cos \theta - 1) \frac{\hbar \omega_x}{6kT},
\]

Saturation only on \( \omega_x \) corresponds to the condition that \( \theta = \pi/2 \). Similar solutions result if the saturation rf is at \( \omega_y \) or \( \omega_z \).

The equilibrium values, \( \langle I_{x3}^0 \rangle \), \( \langle I_{y3}^0 \rangle \), and \( \langle I_{z3}^0 \rangle \), are easily found using the equilibrium density matrix \( \sigma^0 \):

\[
\langle I_{x3}^0 \rangle \approx -\frac{\hbar \omega_x}{6kT}, \quad \langle I_{y3}^0 \rangle \approx -\frac{\hbar \omega_y}{6kT}, \quad \langle I_{z3}^0 \rangle \approx -\frac{\hbar \omega_z}{6kT},
\]

where \( k \) is the Boltzmann constant and \( T \) is the temperature. For the spin-1/2 nuclei, the magnetization from resting in Earth’s field is negligible and therefore \( \langle K_z'(t = 0) \rangle = 0 \). The thermal equilibrium value of \( \langle K_z' \rangle \) is \( \langle K_z' \rangle = \hbar \gamma_K B_0 / (4kT) \).

From the above equations, the complete initial conditions can then be described as

\[
(\delta I_{x3}, \delta I_{y3}, \delta I_{z3}, \delta K_z') = \frac{\hbar \omega_x}{6kT} \left( 1, -0.5, -0.5, -\frac{3 \gamma_K B_0}{2 \omega_x} \right).
\]

When \( \gamma_K B_0 = \omega_x \), this initial condition corresponds to the \( V_K \) eigenvector of the \( \omega_x \) double resonance condition. Therefore, the return-to-equilibrium conditions are governed by \( \lambda_K = \rho R / (R + 2/3) \). The higher the ratio of spin-1/2 to spin-1 nuclei the closer \( \lambda_K \) comes to the \( K \) autorelaxation rate. For ammonium nitrate, \( R = 4 \).
The above example shows how, through double resonance, the spin-1 nuclei can take on the relaxation rate of the spin-1/2 nuclei. In addition, by using the other spin-1 transitions, the spin-1 signal size from a given transition can also be increased. For instance, consider the above example after a time greater than $1/\lambda_K$ when the population differences have reached equilibrium and $(\delta I_{x3}, \delta I_{y3}, \delta I_{z3}, \delta K_z') = (0, 0, 0, 0)$. If the field is now ramped down to $B_0 = |\omega_z|/\gamma_K$, the equilibrium value $\langle K_z^0 \rangle$ changes with the field so $(\delta I_{x3}, \delta I_{y3}, \delta I_{z3}, \delta K_z') = (0, 0, 0, \hbar|\omega_y|/(4kT))$.

Examining the eigenvectors for the $\omega_z$ double resonance condition, after a time long compared to $1/\lambda_D$, but short compared to $1/\lambda_K$,

$$\langle I_{x3} \rangle = \langle I_{x3}^0 \rangle \left(1 + \frac{|\omega_y|}{\omega_x(2 + 4/(3R))}\right). \quad (3.30)$$

For ammonium nitrate this value corresponds to 136% of the equilibrium signal for the $\omega_x$ transition. Further, if the field is also paused at the $\omega_y$ transition, additional magnetization is pushed into the $\omega_x$ transition, creating a total predicted gain of 142%.

A detailed derivation of Eq.(3.30) is illustrative. After a long time in the field $B_0 = |\omega_x|/\gamma_K$, then $\delta K_z' = 0$, which gives $\langle K_z' \rangle = 3/2$ in units of $\hbar\omega_x/6kT$. As the field is ramped to $B_0 = |\omega_z|/\gamma_K$, the equilibrium value becomes $\langle K_z^0 \rangle = 3|\omega_z|/(2\omega_x)$ and therefore

$$\delta K_z' = \langle K_z' \rangle - \langle K_z^0 \rangle \quad (3.31)$$

$$= 3\omega_x/(2\omega_x) - 3|\omega_z|/(2\omega_x) \quad (3.32)$$

$$= 3|\omega_y|/(2\omega_x). \quad (3.33)$$

\footnote{For simplicity in this derivation the expectation values will be in these units.}
Using Eq.(3.18) and Table (3.1) constants $a_D$, $a_K$, and $a_I$ can be found from the initial conditions. Looking at the $\omega_z$ column in Table (3.1) the three equations at $t = 0$ are

\begin{align*}
\delta I_{x3} &= -a_D/2 - a_K/2 + a_I/2 = 0 \quad (3.34) \\
\delta I_{z3} &= a_d + a_K = 0 \quad (3.35) \\
\delta K' &= -a_D/R + 3a_K/2 = 3|\omega_y|/(2\omega_x). \quad (3.36)
\end{align*}

Therefore, $a_D = -a_K$, $a_I = 0$ and $a_K = \frac{|\omega_y|}{(\omega_x(1+2/(3R)))}$. The complete $\delta I_{x3}$ solution is

\begin{equation*}
\delta I_{x3} = a_K e^{-\lambda_D t}/2 - a_K e^{-\lambda_K t}/2. \quad (3.37)
\end{equation*}

For a time short compared to $1/\lambda_K$ only the first term survives, $\delta I_{x3} = I_{x3} - I^0_{x3} = a_K/2 = \frac{|\omega_y|}{(\omega_x(2 + 4/(3R)))}$, and therefore

\begin{equation*}
\langle I_{x3} \rangle = \langle I^0_{x3} \rangle \left(1 + \frac{|\omega_y|}{\omega_x(2 + 4/(3R))} \right). \quad (3.38)
\end{equation*}

### 3.2 Experimental Conditions

The sample used is 99.5% pure ammonium nitrate, whose characteristic NQR frequencies are $|\nu_z| = 74$ kHz, $|\nu_y| = 423$ kHz, and $\nu_x = 497$ kHz at room temperature. Temperature of the powder sample, and hence the NQR frequencies, was well controlled during an experiment using water cooling to minimize drifting off-resonance. Since, the sample temperature slowly varied between 20 °C and 25 °C, following variations in the water temperature, it was always in a phase IV orthorhombic crystalline state stable between -18 °C and 32 °C [38].
For the majority of the experiments the static field was created using a notch type solenoid [57,58] to provide a homogeneous field (±1%) at the sample. For these experiments, the rf excitation was parallel to the static field and a 180 g sample was used. To explore the impact of the orientation of the static field, with respect to the rf, on the measured relaxation rates another probe was constructed. This probe uses a Helmholtz coil for the static field, to easily accommodate the two orientations of a sample. In these experiments a larger sample of 812 g and a high-Q tuned circuit, to speed the accumulation of data, were used. In this configuration the inhomogeneity over the sample was larger, approximately ±6%, but still smaller than the measured width in field strength of the double resonance effect. In particular, the relaxation rates, as a function of field around the \( \omega_z \) double resonance condition, corresponding to the lower fields available with the Helmholtz coil (< 24 G), were studied.

To measure the \( T_1 \) relaxation time of the powder sample under various double resonance conditions the sequence began by saturating the transition under observation with numerous rf pulses of varying strength. The pulses were spaced far enough apart so that the transverse isochromats had dephased, but close enough so that relaxation back to equilibrium would be negligible. Following saturation, the static field was ramped to the appropriate field. After a prescribed wait time, the field was returned to Earth’s field for monitoring of the population difference in the observed transition using a spin-lock spin-echo (SLSE) sequence [59]. This monitoring was done in Earth’s field, in order to avoid the second-order broadening of the signal from the magnetic field [52].

In order to obtain a measure of the width of the resonance, the decay of the echoes in a multipulse SLSE sequence (characterized by the time constant \( T_{2e} \)) for various field strengths was studied. Since these measurements were done at field, there were no ramp times to potentially skew the relaxation measurements. As the field increases,
the NQR transitions become increasingly broadened for a powder sample [52], leading to a decrease in $T_{2e}$. Therefore, $T_{2e}$ was measured around the $\omega_z$ double resonance condition where the broadening of the NQR transitions due to the static field was negligible.

Data were collected using a Tecmag Apollo spectrometer with a home-built probe with a resonant circuit tuned to the NQR frequencies of interest, Fig. (4.1). The rf pulses were created by a Kalmus power amplifier linear between 500 kHz and 65 MHz. The static magnetic field was powered by a wide band Kepco power supply controlled by the Apollo.

3.3 Experimental Results

Two different types of double resonance conditions were studied. In the first type, a NQR transition was saturated, then for a given period of time a static field was applied that satisfied the double resonance condition corresponding to the saturated transition. Afterward, the field was ramped down to measure the NQR signal from that same transition. In ramping the field up and down the other double resonance conditions were purposely avoided and were not slowly swept through. This allowed us to focus on the increase in nitrogen $T_1$ relaxation under a single double resonance condition. In the second type, the field was slowly swept through, or paused at, the other double resonance conditions, as a means for increasing the signal in the transition chosen for observation.

Before beginning the double resonance experiments the “zero-field” relaxation of the $\omega_x$ transition, $T_1 = 11.6 \pm 0.5$ s, and the $\omega_y$ transition, $T_1 = 16.9 \pm 1.0$ s, were measured. As mentioned in Chapter 2, using the expressions derived in Ref. [56], the corresponding nitrogen autorelaxation rates are $W_x = 0.033$ s$^{-1}$, $W_y = 0.015$ s$^{-1}$, and
$W_z = 0.024 \text{ s}^{-1}$. The hydrogen autorelaxation rate was indirectly measured through the double resonance experiments, as described in detail in the next section.

### 3.3.1 Matching at the Observed Transition Frequency

According to Table (3.1), if the $\omega_x$ transition is saturated in zero-field, and the field is ramped to $B_0 = \omega_x / \gamma_K$, the relaxation rate of the resulting signal at $\omega_x$ should be given by $\frac{8}{\tau} \rho$ for $R = 4$. The same relaxation rate is predicted if the $\omega_y$ transition is saturated, and the field is ramped to $B_0 = |\omega_y| / \gamma_K$, and observed at $\omega_y$. As shown in Fig. (3.1), the measured double resonance relaxation rate for $\omega_x$ is $3.4 \pm 0.6 \text{ s}$, and that for $\omega_y$ is $3.8 \pm 0.5 \text{ s}$, the same value to within experimental errors. The corresponding hydrogen autorelaxation time is therefore $1/\rho = 3.1 \pm 0.4 \text{ s}$. There is no previously reported value in the literature of the hydrogen $T_1$ in ammonium nitrate at such low magnetic fields (99 G for $\omega_y$, 117 G for $\omega_x$). Riggin et al. [51], however, did measure a hydrogen $T_1 = 5 \text{ s}$ in a static field of 6.6 kG, and a spin-lock relaxation time in a resonant rf field with $B_1 = 3.4 \text{ G}$ of $T_{1\rho} = 3.5 \text{ s}$. These values give credence to our indirect measurement of the hydrogen autorelaxation time. Riggin concluded, through the measurement of relaxation as a function of temperature, that fast reorientations of the ammonium ion ($\tau_{\text{reorient}} \approx 10^{-11} \text{ s at room temperature}$) are responsible for this hydrogen autorelaxation rate.

Therefore, given the nitrogen $T_1$’s at zero field, there is a 3.4-fold increase in relaxation for the $\omega_x$ transition and a 4.4-fold increase in relaxation for the $\omega_y$ transition. For repeated measurements this corresponds to faster accumulation of data, or for a fixed time, an increase in SNR by a factor of $1.8 \pm 0.2$ for the $\omega_x$ transition and an increase in SNR by a factor of $2.1 \pm 0.2$ for the $\omega_y$ transition.
Figure 3.1: Under the double resonance condition $B_0 = \omega_x / \gamma K$ the signals at $\omega_x$ (■) relax 3.4 times faster than $\omega_x$ signals at no field (▼). Similarly, under $B_0 = |\omega_y| / \gamma K$, $\omega_y$ signals (□) relax 4.4 times faster than at no field (△). Fits to experimental data are shown as lines.

3.3.2 Matching at the Unobserved Transition Frequencies

In addition to increasing nitrogen relaxation through double resonance, it is also possible to increase the nitrogen signal size. For instance, if after decaying to equilibrium at the resonance condition $B_0 = \omega_x / \gamma K, B_0$ is swept so as to slowly match the double resonance conditions corresponding to $\omega_y$ and $\omega_z$, the population difference in the $\omega_x$ transition will increase. See Fig. (3.2). This increase comes at a slight expense; since the hydrogen’s magnetization is being used in this scheme to interact with all three transitions, it takes slightly longer to reach the maximum possible signal than when matching only to the $\omega_x$ transition. Using the value of $\rho$ obtained
Figure 3.2: Predicted (dashed line) and experimental $T_1$ curves (○) for a double resonance scheme which shows both increase in relaxation and signal. After saturating the $\omega_x$ transition, the field is ramped to $B_0 = \omega_x/\gamma_K$ for the wait time shown on the horizontal axis. While returning to Earth’s field for observation of the $\omega_x$ NQR signal, $B_0$ was slowly swept through $B_0 = |\omega_y|/\gamma_K$ and then $B_0 = |\omega_z|/\gamma_K$. The resulting signal shows a gain of 149% in amplitude and an increase of 2.4 times in relaxation over the $\omega_x$ signal at zero field (solid line).

in the previously described experiments, both the maximum signal ($1.42 \langle t_{x,0}^0 \rangle$) and the time constant associated with the rise of this signal (4.4 ± 0.5 s) are predicted. This prediction is shown as a dotted line in Fig. (3.2), along with the experimental data. An exponential fit to the experimental data (not shown) reveals a signal gain of 149 ± 4% and a time constant of 4.8 ± 0.2 s, in fair agreement with predictions. The corresponding increase in SNR is then 2.3 ± 0.1.

While the slow sweep through lower-field double resonance conditions has a beneficial effect for the $\omega_x$ transition, it has a detrimental effect for the $\omega_y$ transition,
as shown in Fig. (3.3) (open circles). Using the values in Table (3.1), it can be shown that the signal is reduced to

$$
\langle I_{y3} \rangle = \langle I_{y3}^0 \rangle \left( 1 - \frac{1}{2 + 4/(3R)} \frac{|\omega_y| - |\omega_z|}{|\omega_y|} \right),
$$

(3.39)

or $\langle I_{y3} \rangle = 0.65 \langle I_{y3}^0 \rangle$ for ammonium nitrate. In the experiment the signal in Fig. (3.3) is not reduced to 65%, but to 71 ± 3%. This discrepancy arises from not sweeping slowly enough through $B_0 = |\omega_z|/\gamma K$, as explored in more detail below. One possibility to
reverse this loss of signal, as suggested in Ref. [7], would be to flip the polarization of the hydrogen atoms before sweeping through \(B_0 = |\omega_z|/\gamma_K\). The gain in signal would then be dictated by

\[
\langle I_{y3} \rangle = \langle I_{y3}^0 \rangle \left( 1 + \frac{1}{2 + 4/(3R)} \frac{\omega_x}{|\omega_y|} \right),
\]

or \(\langle I_{y3} \rangle = 1.50\langle I_{y3}^0 \rangle\) for ammonium nitrate. This experiment was conducted with another probe capable of applying rf at the hydrogen Larmor frequency and is discussed in Chapter 5.

In addition to the reduction in \(\omega_y\) signal after a long wait time (greater than \(4T_1\)’s), there is also observed a very fast rise time in the \(\omega_y\) signal for wait times much shorter than the hydrogen \(T_1\). Theoretically, this behavior should be the same if the field is ramped only to \(B_0 = |\omega_z|/\gamma_K\), instead of to \(B_0 = |\omega_y|/\gamma_K\) with a sweep through \(B_0 = |\omega_z|/\gamma_K\), since the rapid transfer of polarization occurs at the lower double resonance condition. Experimentally, as shown in Fig. (3.3), the fast rise time is seen whether passing through both \(B_0 = |\omega_y|/\gamma_K\) and \(B_0 = |\omega_z|/\gamma_K\) (open circles) or only through \(B_0 = |\omega_z|/\gamma_K\) (filled squares). This immediate gain in signal is predicted to be

\[
\langle I_{y3} \rangle = \langle I_{y3}^0 \rangle \left( \frac{1 + 2|\omega_z|/|\omega_y|}{4 + 8/(3R)} \right)
\]

(29% for ammonium nitrate) with a rise time of \(\lambda_D = \{2 + 4/(3R)\}W_d\). Therefore, in principle, this fast rise time could be used to measure \(W_d\). In practice, the time to ramp the fields up and down interferes with the ability to get reliable data for short time periods. Instead, \(W_d\) was measured by sweeping through the resonance.
condition $B_0 = |\omega_z|/\gamma_K$ at varying rates. This cross-relaxation rate was measured again using a different probe and a higher resolution experiment and is discussed in Chapter 5.

### 3.3.3 Characterizing the Cross-Relaxation

![Figure 3.4](image_url)

Figure 3.4: Measurement of $W_d$ is achieved by sweeping down through $B_0 = |\omega_z|/\gamma_K$ at various rates. The ramp-down is started from $B_0 = |\omega_y|/\gamma_K$, after the sample has come into equilibrium at this field, and is only slowed down during the 3.6 G surrounding $B_0 = |\omega_z|/\gamma_K$. Fitting the data finds $W_d(\Delta \omega = 0) = 103 \pm 22$ s$^{-1}$ is measured.

In sweeping through $B_0 = |\omega_z|/\gamma_K$ to measure the cross-relaxation rate, it was necessary to begin from an equilibrium condition at a higher field. $B_{\text{initial}} = |\omega_y|/\gamma_K$ was chosen because the nitrogen relaxation is dominated by $\rho$, to speed data acquisition. As seen in Fig. (3.4), when the time spent on resonance is not long
enough for the nuclei to interact, the reduction in signal is small. The largest cross-
relaxation corresponds to a reduction in signal of 0.65, as mentioned above. As the
time on resonance becomes longer, eventually the hydrogen atoms begin to relax to
equilibrium at the lower field, thereby negating the reduction effect. By taking into
account the shape of the relaxation rate with static field, as shown in Eq. (2.72), the
maximum cross-relaxation rate, or $W_d(\Delta \omega = 0)$, can be determined from the data of
Fig. (3.4), and from the variance $\Delta^2$. Here, the broadening under this static double
resonance condition is the main focus.

The second moment $\Delta$ is dominated by that of the hydrogen, $\Delta_H$, which has been
measured to be $2.7 \text{ G}^2$ [51] or $\Delta_H = (4.4 \times 10^4 \text{ s}^{-1})^2$. The linewidth of hydrogen under
the double resonance condition would be further broadened by the static field from
the nitrogen nuclei; this broadening would, however, be negligible because of the small
gyromagnetic ratio of nitrogen compared to hydrogen. In comparison, the linewidth
of nitrogen for both the $\omega_x$ and $\omega_y$ transitions at zero field is about $3.5 \times 10^2$ rad
s$^{-1}$, Appendix B. These linewidths only broaden two to three times under the lowest
double resonance condition and confirm that the hydrogen linewidth dominates $\Delta$.
For comparison, $T_{2e}$ was measured as a function of field strength. $T_{2e}$ is the time
constant of the decay of the echoes in a SLSE sequence. As shown in the inset of
Fig. (3.5), $T_{2e}$ was measured as a function of field both for the field parallel to the
rf irradiation, as in the previous experiments (solid circles), and perpendicular to the
irradiation (open circles). While the rates are somewhat different due to geometrical
dependencies, the fastest $T_{2e}$ relaxation was observed for both orientations when
$B_0 = |\omega_z|/\gamma_K = 17.4 \text{ G}$, and Gaussian fits to the data, shown in the inset of Fig. (3.5),
reveal a common variance of about $3.6 \text{ G}^2$. This second moment is somewhat larger
than Riggin’s value, most likely due to inhomogeneities in the applied field.

Using the appropriate second moment, 3.6 G$^2$, and the data of Fig. (3.4) a cross-relaxation rate of $W_d(\Delta\omega = 0) = 103 \pm 22 \text{ s}^{-1}$ was obtained. Using Eqs. (3.14–3.16), the positions of the atoms in ammonium nitrate from Ref. [38], and the proposed PAS frame from Ref. [60], a theoretical cross-relaxation rate of 650 s$^{-1}$ without any averaging due to motion was calculated.$^6$ After including the rapid reorientation of the ammonium ion, which was observed by Ref. [51], this rate reduced to 400 s$^{-1}$. The discrepancy in these rates will be explained in Chapter 5 upon comparison to a higher resolution experiment.

Also shown in Fig. (3.5) is the normalized amplitude of the $\omega_y$ signal (rf $\perp B_0$), after only a short time spent at $B_0$. This amplitude is another indicator of increased cross-relaxation, but the finite ramps up and down to $B_0$ clearly skew this metric. The observed peak amplitude is also quite a bit larger than the expected value, 0.29, and bears further investigation, particularly into the populations of all levels under saturation conditions.

Utilizing double resonance cross-relaxation the relaxation rate of the nitrogen as well as the nitrogen signal size has been increased. The best gains can be achieved for systems in which the ratio of hydrogen to nitrogen atoms is large and the hydrogen autorelaxation rate is much faster than the nitrogen autorelaxation rates. With static fields less than 120 G an increase in SNR of 2.3 for $\omega_x$ signals in ammonium nitrate has been shown. Under double resonance conditions a significant cross-relaxation rate ($W_d = 103 \pm 22 \text{ s}^{-1}$) in ammonium nitrate between the nitrogen of NO$_3^-$ and the hydrogen of NH$_4^+$ has been measured.

In the next chapter, the investigation of the cross-relaxation rate is continued by building a probe that can create both the static and the rf fields for the other double

$^6$ using all hydrogen nuclei within a 10 Å radius from the chosen nitrogen atom
Figure 3.5: The relaxation rate of the SLSE echoes (1/T_{2e}) is shown as a function of B_0 when the rf irradiation is parallel to B_0 (●, inset) and when it is perpendicular to B_0 (red ○, inset and main). Corresponding Gaussian fits to the data are shown in the inset. Also shown (stars) is the normalized amplitude of the ω_y signal (rf ⊥ B_0), after only a short time spent at B_0. In addition to the expected resonance at B_0 = |ω_z|/γ_K = 17.4 G, a subsidiary resonance is observed at half this field (arrow), corresponding to two hydrogen nuclei flipping simultaneously.

resonance conditions.
Chapter 4: Rabi and Larmor Double Resonance Probe and Experimental Methods

4.1 Introduction

The measurement of the cross-relaxation rate, $W_{dd}$, and investigation of the $^{1}$H-$^{14}$N Rabi and Larmor double resonance conditions required a probe that could produce the static and rf fields for the various double resonance conditions. To produce three necessary magnetic fields the probe required three coils. The static field, $B_0$, was produced by the static coil. The RF1 or pickup coil was designed to excite the nitrogen and operated at the nitrogen’s NQR frequency, $|\nu_y| = 0.4218 \text{ MHz}$. This coil both excited the nitrogen nuclei and detected the resulting NQR signal. The RF2 coil, designed to operate at $\nu_H = 0.362 \text{ MHz}$, corresponding to the hydrogen’s Larmor frequency at $B_0 = 85.5 \text{ G}$, was needed to create the double resonance conditions. The design of this probe and the physics behind its operation will be discussed in this chapter.

This probe detects an NQR signal of 2.3 nG rms (230 fT rms) emanating from a small sample of ammonium nitrate at the nitrogen’s $|\nu_y|$ frequency. The signal is detected just after a resonant 10.7 G excitation pulse is applied, where the same coil is used for both excitation and detection. Note that the excitation rf is ten orders of magnitude larger than the NQR signal. As explained later, this $B$ field induces a 140 nV rms signal in the pickup coil with Johnson noise of 6 nV rms. To improve the SNR, we use a multi-pulse sequence which continually refocuses the
signal, thus creating a series of echoes and increasing the SNR by a factor of 26, Appendix C. This is particularly important since the sample has a relatively long $T_1$ of 16.9 s, making single pulse detection a prohibitively lengthy process. Further complicating the detection is the application of static fields approaching 110 G and an RF2 field up to nearly 30 G in order to create the double resonance conditions. All the
while the temperature is maintained to within 0.45 K for accurate data comparison. Under these circumstances, double resonance cross-relaxation rates were accurately characterized, and double resonance sequences were created that show improvements in SNR using ammonium nitrate.

Figure 4.2: Schematic for a NQR double resonance detection experiment. Three circuits are controlled by the Tecmag spectrometer: 1) the RF1 or pickup coil is used to excite the nitrogen and detect the NQR signal, 2) the RF2 circuit generates rf pulses at the hydrogen’s Larmor frequency, and 3) the static coil circuit controls the static magnetic field. The RF2 circuit and the static coil circuit are needed to create the various double resonance conditions.

The standard NQR detection probe [1,13], as described in Fig. (4.1), was modified
to produce the required fields. Modeling and simulation of the magnetic fields created by different coil designs \cite{15, 62, 63} were compared before a design was finalized. In Fig. (4.2) is the schematic for the rf double resonance NQR probe. Three mutually perpendicular solenoids were used to create the static and rf magnetic fields for the various double resonance conditions and to detect the signal from the $^{14}\text{N}$ nuclei in the sample. The Tecmag single channel spectrometer controls the generation of the rf and static fields with a built-in rf pulse generator that is programmed to execute the desired sequences.$^{1}$ The Tecmag controls three circuits to create the desired rf and static magnetic fields. Since the Tecmag is a single channel spectrometer, a switch was needed between the two rf amplifiers for the RF1 and RF2 circuits, as shown in Fig. (4.2).$^{2}$ The layout of these coils is described in Fig. (4.3), with the parameters of each coil listed in Table (4.1). By aligning all three coils perpendicular to each other mutual inductance and cross-talk among the coils were minimized. Additionally, a copper screen grounded to the Faraday cage was placed inside the static coil to further reduce cross-talk. Due to the high voltages produced in the coils the layout of the circuit elements were designed to minimize arcing. Teflon, Q-Dope, Kapton, and other high dielectric materials were introduced to further isolate the three circuits from arcing dangerously. The components, surrounded by the dashed line in Fig. (4.2), are enclosed in a insulated 40 cm $\times$ 40 cm $\times$ 20 cm covered aluminium box that acts as a Faraday cage for the probe.

All experiments were carried out using $>99.5\%$ pure ammonium nitrate, (NH$_4$NO$_3$). The powder sample, occupying 17 mL, consisted of 29 g of ammonium nitrate in its phase IV crystalline state \cite{38}. The $|\nu_y|$ frequency of ammonium nitrate, in Earth’s field, has a linewidth of $53 \pm 20$ Hz (Appendix B) and the temperature

$^{1}$Tecmag, Houston TX. Other similar products can be used, but the help of these manufacturers is acknowledged.

$^{2}$The switch is a Mini-Circuits ZASWA-2-500R
Figure 4.3: Scaled top view of the three orthogonal coils that create the fields used in the various double resonance experiments. The solenoid that creates the $B_0$ static field has diameter of 20.3 cm and defines the $z'$-axis. The RF2 coil is aligned along the $y'$-axis. The pickup coil or RF1 coil, with the sample inside, is aligned along the $x'$-axis and is inside the RF2 coil. Temperature controlled air flows inside the RF2 coil over the pickup coil and sample. The dotted circle is the location of the copper screen and the shaded arc is the Teflon shield. The blue outer circle represents the hose for the chilled water to cool the static coil. The current in the static coil flows counterclockwise and the $B$ field created is out-of-the-page along the $+z'$-axis.

coefficient at $|\nu_y|$, in the temperature range of the experiment, of approximately 120 Hz/K [16,64,65]. This temperature related expansion and contraction of the crystalline environment changes the EFG across the nitrogen nuclei, as well as the energy levels and transition frequencies [16,38]. Therefore, control of the temperature was essential to minimize drifting off-resonance due to rf heating of the sample and thermal heating of the probe. The narrow linewidth, high temperature coefficient,
and long spin-lattice relaxation time, $T_1$, created experimental challenges for the repeatable detection of the NQR signal. The narrow linewidth and high temperature coefficient mean that the data collected must be within 60 Hz of the NQR frequency, or 0.45 K, for accurate data comparison. To minimize temperature changes the static coil was cooled with a recirculating chiller to remove heat generated by the current and the sample temperature was controlled by air cooling, Fig. (4.2). Most experiments were conducted at $|\nu_y| = 421.8$ kHz approximately $9.5 \pm 1 \, ^\circ C$. At $24.2 \, ^\circ C$ the measured NQR frequencies are $|\nu_y| = 423.6$ kHz and $\nu_x = 495.5$ kHz from which $|\nu_z| = 71.9$ kHz was calculated.

In the pickup coil the rms thermal or Johnson noise is given by

$$V_n = \sqrt{4kT R \Delta \nu},$$

where $R$ is the circuit resistance, $\Delta \nu$ is the bandwidth, $k$ is Boltzman’s constant, and $T$ is the ambient temperature. Therefore the noise estimate for this detector at room temperature with a bandwidth of 40 Hz is 6 nV rms.

The magnetization created by the nuclei after excitation with an optimum rf pulse is [1]

$$M = 0.43 \left( \frac{\gamma \hbar}{V} \right) \frac{N}{V} \left( \frac{h \nu}{3kT} \right),$$

where $\gamma$ is the gyromagnetic ratio, $V$ is the sample volume, $\hbar$ is Plank’s constant,
and \( N \) is the number of nuclei involved in the transition. The number of nuclei is

\[
N = \frac{N_A m P}{AW}
\]  

(4.3)

where \( N_A \) is Avogadro’s number, \( m \) is the mass of the sample, \( P \) is the mass percent of active nuclei and \( AW \) is the atomic weight of the nuclei being observed. The \( B \) field created by this magnetized sample is \( B = \mu_0 M \), where \( \mu_0 \) is the permittivity of free space.

The voltage induced in the detector was calculated from a modified version of Faraday’s law [13]

\[
v = -n \frac{d(B(t)A)}{dt} Q_{\text{mod}},
\]

(4.4)

where \( B(t) \) is the oscillating field created by the magnetized sample, \( Q_{\text{mod}} \) is a modified quality factor, \( Q \), incorporating the effects of the detector geometry, \( A \) is the detector area, and \( n \) is the number of turns in the coil. For this detector

\[
Q_{\text{mod}} = \eta \sqrt{\frac{QR}{2\pi \nu L}},
\]

(4.5)

where \( L \) is the inductance, and \( \eta \) is the “filling factor”: the amount of the detector volume filled by the sample. The voltage detected is therefore

\[
v = B \omega A n Q_{\text{mod}}.
\]

(4.6)

Since the \( B \) field is about 2.3 nG rms for this sample, the voltage induced in the coil is 140 nV rms.
Modeling the sample as an array of small current loops, given by the magnetization already calculated, the $B$ field components at any point in the sample were calculated. Further by summing the contribution of each loop of the actual coil, the axial and radial $B$ fields components at each point were calculated [62]. This calculation gave a measure of the homogeneity of the field over the sample and was performed for each coil: Table (4.1).

The optimal rf pulse to excite the nuclei in this sample is 10.7 G when using 100 $\mu$s pulses. The difference between the rf pulse strength, 10.7 G, and the signal to be detected, 2.3 nG rms, is ten orders of magnitude, but they are both at the same frequency and in the same coil. This highlights one of the chief engineering challenges of NQR detection. This detector, with a $Q = 58$, must dissipate its energy rapidly after every pulse. While the energy dissipates, the signals are obscured. The time it takes to dissipate this energy, or “deadtime,” is [13]

$$t_{\text{dead}} = C \frac{Q}{(\pi \nu)},$$  

(4.7)

where $C \approx \ln (B_{in}/B_{out})$, $B_{in}$ is the excitation pulse strength, and $B_{out}$ is the signal to be detected. $C$ just expresses the decay time of the input pulse. For this probe $C = 22$ which corresponds to $\sim 800 \mu$s of deadtime.

One method to increase SNR is to use a multi-pulse sequence such as spin-lock, spin-echo (SLSE) [13,59]. A multi-pulse sequence effectively stretches the signal out so that more signal can be accumulated. In a standard one-pulse NQR detection sequence the free-induction decay (FID) occurs after the pulse [34]. The FID decays exponentially and is described by $T_2^*$, which is 8 ms, Appendix B. The first and strongest part of the FID is obscured by the deadtime. One benefit of the SLSE sequence is that by refocusing the spins to create an echo the echo occurs after
Table 4.1: Dimensions and other parameters of each solenoid including the $Q$, or quality factor. $\Delta B$ is the calculated homogeneity of the magnetic field over the sample for each of the coils. All wire used was non-magnetic.

<table>
<thead>
<tr>
<th>Coil</th>
<th>Turns</th>
<th>Diameter (cm)</th>
<th>Length (cm)</th>
<th>Wire size (AWG)</th>
<th>Inductance (mH)</th>
<th>$Q$</th>
<th>$\Delta B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>140</td>
<td>20.32</td>
<td>22.86</td>
<td>16</td>
<td>2.836</td>
<td>–</td>
<td>1.5</td>
</tr>
<tr>
<td>RF2</td>
<td>130</td>
<td>7.62</td>
<td>16.0</td>
<td>22</td>
<td>1.388</td>
<td>50</td>
<td>1.5</td>
</tr>
<tr>
<td>RF1</td>
<td>132</td>
<td>3.6</td>
<td>6.0</td>
<td>28</td>
<td>0.344</td>
<td>68</td>
<td>0.2</td>
</tr>
</tbody>
</table>

the deadtime. A parameter that characterizes the SLSE sequence is $T_{2e}$ [34]. This is the decay of the spin echoes and is $4.1 \text{ s}$ for ammonium nitrate, with a pulse spacing of $\sim 1 \text{ ms}$, Appendix B. The SNR increase of this technique is therefore

$$SNR = \sqrt{\frac{T_{2e}}{T^*_{2e}}} = 26,$$  

Appendix C [13,34,59,66]. Additionally, the above sequence, and the general concept of phase cycling, removes coherent noise by taking advantage of the difference in phase between the noise and the NQR signal [1,13,67]. Utilizing these techniques the probe could successfully detect the weak NQR signal, create the double resonance conditions and measure their cross-relaxation rates.

### 4.2 Production of Fields and Calibration

#### 4.2.1 Static Field

This static field was generated by two 400 W master-slave cascaded bipolar operational power supplies in series-current mode\(^6\) connected to the static coil. Two Kepco power supplies were cascaded to deliver the desired current to this highly

\(^6\text{Kepco BOP 2020M, Flushing, NY.}\)
inductive load. Twinax cables were used to connect the components to minimize paths of noise entry and one 1 µF capacitor was connected in parallel with the inductor for noise suppression. A 0.1 ohm resistor on the ground side of the circuit was used to monitor the current. Ground loops were minimized by connecting the grounds of all components to the best Earth ground available.

The static coil was calibrated by measuring the field produced by a given current in the coil with a magnetometer positioned at the center of the sample. The Earth’s field measured at this location, with no current in the coils, was $-0.6$ G. The amplifiers were adjusted to cause a current to flow through the static coil creating a $B_0$ field opposite to the Earth’s field. The current through the resistor and the magnetic field were measured to calculate a calibration factor of $1.214 \pm 0.018$ G/V. But, to provide a check, this calibration was verified by letting the spins’ behavior reveal the magnetic field that they experience during a particular double resonance experiment.

Three experiments were conducted for verification of this calibration with the magnetometer. In the first experiment, the static field was varied to find $B_z = |\omega_z| / \gamma_H$, as described in Fig. (4.11) and Table (E.1). The signal was measured as the field was varied with a peak indicating the double resonance. The data was fit to a Gaussian to measure the width of the double resonance. This was repeated for the $B_y = |\omega_y| / \gamma_H$ condition. The third experiment measured $B_{rf}$, which was the static field corresponding to the hydrogen’s Larmor frequency, $B_{rf} = \omega_0 K / \gamma_H$. This measurement used the sequence described in Fig. (5.1). The results of the measurements are shown in Table (4.2) and the experiments are described in detail in the last section of this chapter. These three measurements confirmed the calibration with the magnetometer.

A nonlinear effect was noticed: at high currents of long duration the current would...
eventually decrease and the wires would warm up. The amount of time before this occurred varied with the applied current. Water cooling was added to extend the operating range but these operating conditions were identified and avoided in the experiments.

The static field homogeneity of the coil was also measured. The same experiment with the magnetometer was performed but with the probe positioned just outside the volume of the sample. The magnetic field was measured at different positions leaving the current constant. The measured homogeneity in the static field across the sample was 2 % while the calculated homogeneity was 1.5 %.

### 4.2.2 Nitrogen Excitation Field

The RF1 circuit created the rf pulses that excited the nitrogen nuclei and detected the resulting NQR signal. The RF1 coil and LC circuit, tuned to the NQR frequency of interest, are impedance matched to a T&C 400 W RF amplifier.\(^8\) There are 20 sets of crossed diodes in diode boxes between the amplifier and the LC circuit for noise reduction [68,69]. A diode box, consisting of a number of sets of eight crossed pairs of

---

\(^8\)T&RC Power Conversions, Rochester, NY
IN4151 diodes in parallel, allowed high-voltage rf pulses to pass through to the load. When the signal was detected, the noise from the amplifier was reduced. The more sets of diodes the more noise reduction, but also the higher the rf voltage required to drive the load.

![Circuit diagram of a π-box with clipping diodes. The circuit elements are selected to create a π-network and the diodes prevent voltages from exceeding the input specifications of the preamps connected to this circuit.](image)

After the excitation pulses, the nuclei generated a signal 90° out of phase with the excitation pulse, but along the same axis. The pickup coil detected the signal created by the oscillating nuclei and the signal was passed through a π-network [61], Fig. (4.4). The π-network matched the impedance when the low-voltage NQR signal was present, but then provided a high-impedance load when the high-voltage excitation pulses were present. There were 16 crossed diodes in parallel with this filter, which clipped the voltage to ±1.4 V. An additional 40 crossed pairs of diodes were added, in parallel, as further protection for the preamps, which have a maximum allowed input of +5 dBm. The signal was amplified by two Mini-Circuits low noise preamps, ZFL-500LN, each with a gain of 30 db. A Mini-Circuits low-pass filter, with a 2 MHz cutoff, was connected to the outputs of the preamps to remove more high frequency noise. Double shielded BNC cable was used in the signal path from the pickup coil to the spectrometer to prevent stray rf noise from masking the weak NQR signal.
Figure 4.5: Determination of the optimum NQR tipping angle by varying the rf pulse strength and holding the pulse duration constant at 100 µs. For this experiment the optimum pulse strength is 10.7 G.

To calibrate the coil two sniffer coils were required. The internal sniffer was temporarily inserted inside the tuned RF1 coil at the location of the sample. This sniffer measured induced voltages of $V_i$. A second external sniffer was then positioned and oriented to maximize the magnetic field to be measured. This sniffer measured induced voltages of $V_e$. The voltage was then measured in both sniffers as the pulse strength was varied to find their ratio $S = V_i/V_e$.

Using Faraday’s Law the voltage induced in the internal sniffer is

$$V_i = B_i \omega A_i n_i,$$

where $A_i$ is the area and $n_i$ is the number of turns. Likewise for the external sniffer

$$V_e = B_e \omega A_e n_e.$$  

---

9 A sniffer coil is a few turns of wire of a known area positioned to pick up a time varying magnetic field and the voltage can be measured.
The sample was inserted and the voltage was measured at the external sniffer.

The internal $B_i$ field was

$$B_i = \frac{SV_e}{\omega A_i n_i}. \quad (4.10)$$

It is well known that the NQR signal from a powder has the functional form of a spherical Bessel function of order 1 \cite{9}

$$S_{nqr} \propto \frac{(\sin x - x \cos x)}{(x)^2}, \quad (4.11)$$

where $x = \gamma N \tau B_1$, $\tau$ is the pulse duration, and $B_1$ is the strength of the applied rf. The maximum signal occurs at a tipping angle of 119° or 2.077 rad$^{-1}$:

$$\gamma N \tau B_1 = 2.077. \quad (4.12)$$

With the sample in place, and the RF1 circuit tuned to the NQR frequency of interest, the signal was measured as $B_1$ was varied to generate a calibration curve. The optimum $B_1$ was found experimentally, for a given pulse width, by fitting the signal data to the $j_1(x)$ Bessel function as shown in Fig. (4.5). This calibration provides the optimum pulse strength for the pulse sequence.

### 4.2.3 RF2 Field Applied to the Hydrogen

The RF2 field was produced by a Tomco 1000 W continuous RF power amplifier that was impedance matched to an LC circuit that was tuned to the hydrogen’s Larmor frequency.\footnote{Tomco Technologies, Stepney, Australia} Eight sets of crossed pairs of diodes were used between the amplifier
and the LC circuit to reduce amplifier noise. Using expressions for the magnetic field inside a solenoid, the homogeneity of the coil across the sample was calculated to be 1.5%.

It was expected that the solenoids would interact with each other through mutual inductance and mutual capacitance. One method to minimize these effects was to position the three solenoids so that they were perpendicular. This was especially important for the RF1 coil inside of the RF2 coil, Fig. (4.3). The RF2 coil was fixed on machined posts with respect to the static coil. The RF1 coil was positioned to minimize the induced voltage in RF2 by minimizing the mutual inductance. To do this a signal generator was connected to the RF1 coil and set to the frequency of interest, while the voltage out was set to $V_{RF1}$. The voltage in the RF2 coil, $V_{RF2}$, was then measured. The position of the RF1 coil was manually manipulated until $V_{RF2}$ was minimized. The ratio $V_{RF2}/V_{RF1}$ is a measure of the mutual inductance and varied from 0.001 (well calibrated or perpendicular) to over 0.2 when RF1 was first inserted into the coil.

To calibrate the RF2 coil the $B_1$ field created in the RF2 coil was measured while the input voltage to the RF2 amplifier was varied. The RF2 coil created a field,

$$B = \frac{B_1}{2} \cos(\omega_K t + \phi),$$  \hspace{1cm} (4.13)

where $\omega_K$ is the applied frequency. The field created in the RF2 coil was calibrated with two methods.

The first calibration method was to position a sniffer coil in the RF2 coil at the location of the sample, parallel to the RF2 coils. The RF2 coil was tuned to the frequency of interest and the strength of the rf pulses was varied. The voltage induced in the sniffer coil could then be measured. Using Faraday’s Law as in Eq. (4.8), $B_1$
was then calculated from the measurement of the sniffer voltage. The resulting RF2
calibration factor is in $B_1/V$ (G/V), but the sample was not present during these
measurements. In the next chapter another more accurate method will be used to
calibrate this field with the sample in place and using the NQR signal from the sample.

### 4.3 Arcing and Mutual Inductance

While debugging the RF2 coil it was found that there was a large cross-talk between
the static coil and RF2 coil. The cross-talk was minimized by ensuring that the two
coils were perpendicular to each other, but the noise reduction was not sufficient until
a copper screen was inserted between the static coil and the RF2 coil. Unfortunately,
the copper screen introduced a undesirable side-effect: arcing.\(^{11}\)

The source of the arcing in the RF2 circuit was in two places: the solenoid and the
capacitors. Arcing from the solenoid was fixed by removing turns from the solenoid so
the last wire was further separated from ground, and inserting a Teflon sheet between
the copper shielding and the hot side of the RF2 coil. Arcing over the capacitor
developed as the strength and the duration of the pulses increased. This was reduced
by building up the desired capacitance with three blocks of high-voltage capacitors in
parallel and then in series to achieve the desired capacitance and breakdown voltage,
Fig 4.6. In this case the breakdown voltage of each group was 7.2 kV, thus for
three sets of capacitors the total specified breakdown voltage was 21.6 kV. This
configuration still showed the start of breakdown at a $B_1 \approx 30$ G.\(^{12}\)

An AC analysis of the circuit revealed the magnitude of the voltage across the
inductor to be 13.2 kV [68,70]. The breakdown voltage of air varies from 0.4 to

---

\(^{11}\) The RF2 circuit generated pulses of $B_1 = 14$ G over the sample for durations of up to 2.2 s.

\(^{12}\) Note, this 21.6 kV breakdown voltage does not take into account the physical layout of the circuit
or the frequency at which the capacitors are used, so this specified breakdown voltage is used only for
relative comparisons.
3 kV/mm [71,72], depending on the test method. Therefore, to prevent arcing other high-dielectric materials, such as Kapton tape, electrical tape, QDope, plastic sheeting and Teflon sheeting, were used [34,68,70,73–75]. With these fixes applied, the RF2 circuit could be used for the double resonance experiments, within the limits imposed by the onset of arcing.

![Figure 4.6: Layout of the RF2 tuning capacitors arranged to avoid arcing. The total capacitance for each group of parallel capacitors is the same, \( C_1 = C_2 = C_3 \), so the voltage difference between A and B is divided between them. The breakdown voltage of each capacitor is the same so the total breakdown voltage between A and B is three times the breakdown voltage of one group.](image)

4.4 Multi-pulse Sequence – pPAPS

The debugging of the hardware for this experiment resulted in the development of a unique pulse sequence for signal acquisition. The development of the pulse sequence started with the standard NQR SLSE [59] sequence for an optimally oriented crystallite

\[
90_x - \tau - (90_y - 2\tau - 90_y)_N,
\]  

(4.14)
where $90_x$ is a 90 degree preparatory pulse along the $x$-axis in the rotating frame, $\tau$ is the wait before the start of the refocusing pulses, $90_y$ is a 90 degree pulse 90 degrees out-of-phase from the first pulse, followed by a wait of $2\tau$ in which the signal is sampled, and followed by another refocusing pulse of $90_y$ to end the refocusing block. The refocusing block is repeated $N$ times to acquire the total signal. In this SLSE sequence the refocusing pulses lock the signal so the signal can be accumulated over a longer time which improves the SNR. Data analysis of the SLSE double resonance experiments showed that coherent rf noise was present that needed to be reduced.

Removing noise that is coherent with a pulse, such as ringing, takes advantage of the difference in phase between the noise and the NQR echoes. One approach to reduce this noise is to set the phase of the initial pulses in the SLSE sequence to $\pi$ out of phase from one another, $\pm \pi$ from run to run [76–78]. The NQR echoes have the phase of the preparatory pulse. The phase of the noise caused by ringing, has the phase of the most recent pulse. The proper co-adding of the data from across runs reduces or cancel this type of noise [16,67,79]. This sequence also cancels other types of noise that remains coherent on time scales longer than $T_1$ [13]. Since the $T_1$ of ammonium nitrate is 16.9 s and the noise in the probe was not coherent on such long time scales another method was needed for noise cancellation on short time scales.

The off-resonance behaviors of many sequences have been investigated and show pronounced dips in the signal at specific frequency offsets [80–83]. Comparing the on-resonance and off-resonance behavior of these sequences shows that off-resonance effects can have similar effects as phase shifts [13]. In other words, since sequences with alternated $\pi$ shifts could reduce coherent noise, so could pulse sequences that were off-resonant. Combining the off-resonance effects and the phase-alternated effects leads to a sequence that cancels coherent noise and cancels noise that is constant on short times scales; by careful choice of the amount of off-resonance
the loss of signal can also be avoided. Dips in the signal occur under certain off-
resonance conditions and must be accounted for in the pulse sequence specification.
The sequence developed is called the off-resonance phase-alternating pulse sequence
with a preparatory pulse (pPAPS) or off-resonance pPAPS.

The sequence for a powder sample is

\[
119_{\pm x} - \tau - (119_{x} - 2\tau - 119_{-x} - 2\tau)_N, \tag{4.15}
\]

with all pulses off-resonant and \( \pm x \) indicates that the pulses were along the lab’s \( x \)-
axis. The tip angles were changed from Eq. (4.14) to reflect the optimum excitation
for a powder sample. The phase alternated refocusing block was repeated \( N \) times.
This sequence produced a combination of phase shifts such that the peak signal
detection occurred at an off-resonance of \( \pm (2n + 1)/4\tau \), where \( n \) is an integer. In
the experiments, the signal detection occurs at \( \pm 1/4\tau \). Phase cycling was applied to
col-\-add the echoes and to cancel resonant signals on a short time scale Therefore, the
off-resonant pPAPS sequence changed the phase and utilized the off-resonance of the
pulses to get short time scale noise cancellation without a reduction in signal.

In Fig. (4.7) the spin dynamics of the off-resonance pPAPS sequence is illustrated.
Four sequences are compared; 1) SLSE on-resonance, 2) SLSE off-resonance, 3)
pPAPS on-resonance, and 4) pPAPS off-resonance. The rotating frame single crystal
spin dynamics for each sequence is depicted at specific points in the sequence from
panel (a) to panel (e). The figure is a depiction of the behavior of a spin-1 nuclei
in its interaction representation in fictitious spin-1/2 space where the \( \{x, y, z\} \) axes
respond to the appropriate fictitious spin-1/2 operators. For example, if the \( \omega_x \)
NQR transition is of interest then the axes correspond to \( \{I_{x1}, I_{x2}, I_{x3}\} \). In this space
the behavior of a spin is similar to the NMR \( \{x, y, z\} \) space [4].
Figure 4.7: Comparison of the rotating frame single crystal spin dynamics of the off-resonant pPAPS (row 4) to three other sequences. The sequences are compared by analyzing the amount of signal and noise acquired in the same amount of time. The results for each sequence are given after panel (e), where $S$ is defined as the amount of signal acquired, and $N$ is the amount of noise acquired during the same time. The off-resonant pPAPS sequence results in $S_{total} = 2S$ where the noise is canceled by subtracting alternate windows from each other. The $S_{total}$ for the other sequences contains more noise than accumulated by the off-resonant pPAPS. The off-resonance for this example is $1/(4\tau)$ which produces an evolution of $\pi/2$ for the spins during a wait of $\tau$.

The blue arrow indicates the initial $\langle I_x \rangle$ which is tipped by the first pulse in the sequence onto the $x$-$y$ plane. The green arrow, in panels (c) and (e), indicates the NQR signal that is accumulated. If the NQR signal is located along the $z$-axis then
Table 4.3: Comparison of four multi-pulse sequences showing the signal and noise accumulated during two acquisition windows.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Signal</th>
<th>Noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLSE on-resonance</td>
<td>2S</td>
<td>2N</td>
</tr>
<tr>
<td>SLSE off-resonance</td>
<td>1S</td>
<td>2N</td>
</tr>
<tr>
<td>pPAPS on-resonance</td>
<td>1S</td>
<td>0N</td>
</tr>
<tr>
<td>pPAPS off-resonance</td>
<td>2S</td>
<td>0N</td>
</tr>
</tbody>
</table>

it can’t be detected. The green arrow traces the evolution of the spins during the sequence.

In the first row (1), the evolution of the spins during the on-resonant SLSE is depicted. In panel (a) after a $90_x$ pulse (red arrow) the NQR signal is along the $y$-axis. After a wait of $\tau$, a $90_y$ pulse locks the spins along the $y$-axis. The echo reforms in (c) and is sampled. The second refocusing pulse is applied in panel (d) and again sampled in (e) at the midpoint of the echo. The other sequences are analyzed similarly except that with the off-resonant sequences there is evolution of the spins during the wait between pulses. In Table (4.3) the results of the sequences are compared and the off-resonant pPAPS showed the most promising results.

The experimental off-resonance performance of the pPAPS and SLSE sequences was compared, Fig. (4.8). The data show that the SLSE had its strongest signal on-resonance and dips at $1/4\tau$ while pPAPS was strongest at $1/4\tau$ off-resonance. Sodium nitrite was used in this experiment, with a different probe, to compare the performance of different samples and because the SLSE sequence did not have enough noise cancellation for experiments with the double resonance probe. Figure (4.9) shows the results of an off-resonance frequency sweep with pPAPS, using ammonium
Figure 4.8: Comparison of the pPAPS and SLSE signal as a function of off-resonance, $\Delta \omega/(2\pi)$. The maximum signal occurs for the pPAPS sequence at an off-resonance of $1/4\tau$ while the maximum signal for the SLSE sequence occurs on-resonance. Both sequences demonstrate signal maxima that are periodic with $1/2\tau$, where $\tau = 1.04$ ms and the pulse duration $t = 100 \, \mu$s. The experiments were conducted using 32 g of sodium nitrite at 1.038 MHz with a linewidth of 130 Hz in a probe with a $Q = 9.5$.

nitrate. The strong off-resonance response of the sample is due to the narrow linewidth of the sample. Both experiments confirmed the expected performance. Therefore, for this sample and probe, the pPAPS sequence was combined with an off-resonance offset to provide noise reduction.

4.4.1 Sequence Details

The specific parameters of the off-resonant pPAPS sequence were configured for this particular sample. For this sample, in Earth’s field at the $\omega_y$ transition,
Figure 4.9: The normalized signal for the pPAPS sequence at $\omega_y$ as a function of off-resonance, $\Delta \omega / (2\pi)$, using ammonium nitrate. The maximum signal occurs at an off-resonance of $1/4\tau$ with severe degradation of signal between maxima. All pulses are $\theta = 119^\circ$, a pulse duration $t = 100 \mu s$, and a $\tau = 0.993 \text{ ms}$. Note that the depth of these “dips” approaches 80% which is consistent with samples with a narrow linewidth [81].

$\text{linewidth}(\text{FWHM}) = 53 \pm 20 \text{ Hz}, T_2^* << T_1$, and $T_1 = 16.9 \pm 1.0 \text{ s}$, Appendix B. From these measurements and the $Q$ of the probe the $\tau$ was set to 993 $\mu s$. Considering that $T_{2e} = 4.1 \pm 0.15 \text{ s}$ for a $\tau$ of 1 ms then the number of loops $N$ was set to 1400.$^{13}$ The optimum initial pulse strength, $B_1$, was found experimentally, as described earlier.

The pulse strength of the second pulse was also found experimentally. In Fig. (4.10), the second pulse strength was varied and the optimum tipping angle was determined to be the same as the first pulse, $\theta = 119^\circ$ and $t = 100 \mu s$. In $^{13}$See the discussion in Appendix C on using the SNR to determine the number of loops.
fact a tipping angle in the range of 100–130° would produce approximately the same signal. Others have reported that depending on the sample and the sequence the optimum tipping angle for initial and refocusing pulses needs to be experimentally determined [13]. Additional details of the sequence are summarized in Appendix C.

Figure 4.10: For the off-resonance pPAPS with $\Delta \omega/(2\pi) = 1/4\tau$, the tipping angle of the refocusing pulse was varied to find the maximum signal. The preparatory pulse was kept constant at the experimentally predetermined maximum pulse of 119° for a pulse duration of 100 µs. For this sequence and sample the signal is degraded if the tipping angle of the refocusing pulses was greater than ≈130°, in contrast to other NQR spin-1 experiments, so the tipping angle was set to 119° for both pulses.
4.5 Experimental Methods

The sequence for the signal acquisition from the nitrogen in the powder sample starts by saturating the transition under observation with numerous resonant rf pulses of varying strength. The saturation pulses were separated by a 10 ms wait time, which is greater than $T_2$, so the transverse isochromats had dephased, but less than $T_1$, so that relaxation back to thermal equilibrium would be small. The saturation pulses equalized the populations of the two involved energy levels and provided a known initial condition for the model of the system.\textsuperscript{14} The saturation pulses were applied at 36 G because the cross-relaxation at the lower ammonium nitrate resonances, $\omega_z$ and even $\omega_z/2$, is very fast, such that even ramping the static field at 36 G/ms through them would produce a noticeable effect.

Following saturation, the static and rf fields were manipulated to create the double resonance condition for the experiment; see Fig. (4.11) for the general description of a sequence using only a static magnetic field to create the double resonance and Fig. (4.12) for the general description of the sequence used for double resonance experiments created with both a static and a rf magnetic field. Additionally, treating the Zeeman Hamiltonian for a spin-1 system in a small static field as a perturbation to the quadrupole Hamiltonian, using second-order perturbation theory, has shown that there is broadening of the quadrupole frequency due to the Zeeman Hamiltonian which is proportional to $B_0^2$ [52]. Due to this broadening the signal was acquired in Earth's field.

The signal was detected using the off-resonance pPAPS sequence\textsuperscript{15} and was proportional to the population difference at the observed transition. Each data point is typically the result of 16 scans with a recovery delay of 60 s ($\approx 4 \times T_1$) between

\textsuperscript{14}Since the populations are equal if the system was measured at this point the signal would be zero. 
\textsuperscript{15}Most double resonance experiments were performed with an observation frequency $\frac{1}{4\pi}$ off-resonance.
Figure 4.11: General description of the sequence used for double resonance experiments created only with a static magnetic field, $B_0$. The figure shows the $B_0$ applied vs. time during a sequence. While the static field is at $B_{sat}$ a set of saturation pulses are applied to the nitrogen for $t_{sat}$. Next $B_0$ is quickly ramped to $B_{pol}$ for $t_{pol}$ and then $B_0$ is quickly ramped down to $B_{start}$ and swept to $B_{end}$ in $t_{sweep}$. The sweep covers the expected resonance at the field $B_{dr}$ symmetrically. The static field is then reduced to zero and the signal is measured in Earth’s field.

scans. This wait provides time for the spins to return to thermal equilibrium and time for heat dissipation after the application of a large amount of power.

The signal is normalized to the maximum signal obtained from the same sequence but without the double resonance condition, when the sample is in thermal equilibrium. For each experiment, data acquisitions at zero-field were interleaved with acquisitions with the double resonance condition, to compare signal change. Additionally, the resonance frequency was measured before and after an experiment.
Figure 4.12: General description of the sequence used for double resonance experiments created with both a static magnetic field and an rf magnetic field. The figure shows the static magnetic field and the rf (red and dashed lines) applied vs. time during a sequence. While the static field is at $B_{\text{sat}}$ a set of saturation pulses are applied for $t_{\text{sat}}$, not shown. $B_0$ is quickly ramped to $B_{\text{pol}}$ for $t_{\text{pol}}$ and then quickly ramped to $B_{\text{rf}} = \omega_{\text{L}} K / \gamma K$. The static field reaches $B_{\text{rf}}$ at the time $t_{B_{\text{rf}}}$. The rf is applied at the hydrogen’s Larmor frequency starting at $t_{\text{rf start}}$. The strength of the rf pulses are ramped to $B_{1\text{start}}$ and swept to $B_{1\text{end}}$ during $t_{\text{sweep}}$ to cover symmetrically the expected resonance at the field $B_{\text{dr}}$ and turned off while the static field is reduced to zero and then the signal is measured in Earth’s field. Some of these experiments use the adiabatic fast passage technique which is described in Appendix D. Specific details for each experiment are in Appendix E.

to monitor the frequency drift during the experiment, due to various causes such as rf heating.
Chapter 5: Characterization of Double Resonance Cross-Relaxation

A set of experiments were conducted to measure the double resonance cross-relaxation rate, $W_d$, using the probe described in Chapter 4. As a reminder, the general theory from Chapter 2 identified three double resonance conditions:

1. Static double resonance: $|\omega_{NQR}| = \gamma_H B_0$, where $\omega_{NQR}$ is one of three characteristic nitrogen NQR frequencies: $\omega_x$, $\omega_y$, and $\omega_z$, and $\gamma_H B_0$ is the hydrogen’s Larmor frequency,

2. Rabi double resonance: $|\omega_{NQR}| = \gamma_H B_1$, where $B_1$ is the strength of the field rotating at $\gamma_H B_0$ and applied perpendicular to the static magnetic field,

3. Rabi plus Larmor double resonance: $|\omega_{NQR}| = \gamma_H B_0 \pm \gamma_H B_1$.

These three double resonance conditions can be created at any of the three NQR transition frequencies. The nine conditions are listed in Table (2.1) each with a different cross-relaxation rate. But before $W_d$ could be measured for the Rabi and Rabi plus Larmor double resonance conditions the rotating field was calibrated.

5.1 Rabi Oscillation Experiment

The Rabi oscillation experiment was used to calibrate the rf field in the RF2 coil and is described in Fig. (5.1). The experiment was performed with the sample and all components in place and was used as a more accurate calibration than the RF2 calibration experiment described in Chapter 4. A calibration factor between the
observed sniffer voltage and the rotating field $B_1$ was determined. This calibration experiment was similar to the experiment described in Fig. (3.3), except that an rf pulse was added that under specific conditions flips the magnetization of the $^1$H. The pulse was applied at the Larmor frequency and resulted in a signal

$$S_y = A \cos (\gamma H B_1 t_{pw}) + B,$$

where $t_{pw}$ is the pulse width and $A$ and $B$ are constants. This is a common experiment in the NMR community, which results in a “nutation” graph that shows the Rabi oscillations, Fig. (5.2). The peaks and troughs are identified by

$$\gamma H B_1 t_{pw} = n\pi,$$

where $n$ is an integer $\geq 0$. The peaks correspond to a maximum when $n$ is odd and the troughs correspond to a minimum when $n$ is even. The nutation curve data end when $B_1 \approx 30$ G due to arcing and not due to amplifier limitations.

Using Eq. (5.1) and the data in Fig. (5.2), $B_1$ could be calculated once the actual pulse duration was adjusted for the shape of the pulse. The programmed pulse duration was 50 $\mu$s, but they were not perfectly square pulses, thus an effective pulse duration of 38.6 $\mu$s was calculated. Therefore, the first peak is $B_1 = 3.05 \pm 0.05$ G. The resulting calibration factor in rotating field $B_1$ per V, at the sniffer, is 11.75 $\pm$ 0.25 G/V, and is in agreement with, but is more accurate than, the calibration determined by using the sniffer coil inside the RF2 coil in Chapter 4.

Next, a sequence combining a “$\pi$” pulse with a sequence from Chapter 3, which matches multiple NQR frequencies, results in a dramatic improvement in the SNR for ammonium nitrate. Then the different cross-relaxation rates for the various double resonance conditions are calculated and measured.
Figure 5.1: Experimental sequence to observe Rabi oscillations. The static magnetic field applied during the Rabi oscillation sequence is presented. First, the $\omega_y$ transition is saturated while $B_0 = 36$ G. Then, $B_0$ is quickly ramped to 108.5 G for $t_{pol} = 2$ s (108.5 G is halfway between $\omega_x/\gamma_H$ and $\omega_y/\gamma_H$, so those double resonance conditions are not matched). Next, the static field is ramped quickly down to the $B_{rf} = 85.5$ G and an rf pulse at $\nu = 0.362$ MHz is applied that tips the $^1$H’s polarization. Next, the $\omega_z$ double resonance condition ($B_z = |\omega_z|/\gamma_H$) is slowly swept through and $\omega_y$ is measured in Earth’s field. The sweep covers $B_z \pm 6$ G, at a rate of 0.6 G/ms, well within the instrument’s capabilities.

5.2 SNR Improvement – Double Resonance with Spin-flip

The most dramatic improvement in SNR is demonstrated with a modification to a sequence that is described in Chapter 3, Fig. (3.3). The sequence matches the static field to $|\omega_y|/\gamma_H$ and then sweeps the static field through $|\omega_z|/\gamma_H$ before the $|\omega_y|/\gamma_H$
signal is measured. As shown in Fig. (3.3) (dotted line) the sequence leads to a reduction in signal. One possibility to reverse this loss of signal, as suggested in Ref. [7], would be to flip the polarization of the hydrogen atoms adiabatically before sweeping through $B_0 = |\omega_z|/\gamma_K$. Another method to flip the $^1$H polarization is to apply a “$\pi$” pulse. Either way, the gain in signal would then be dictated by [8]

$$
\langle I_{y3}\rangle = \langle I_{y3}^0\rangle \left( 1 + \frac{1}{2 + 4/(3R)|\omega_y|} \frac{\omega_x}{|\omega_y|} \right),
$$

(5.3)
or \( \langle I_{y3} \rangle = 1.50 \langle I_{y3}^0 \rangle \) for ammonium nitrate. In Fig. (5.3) the resulting signal from the sequence is presented and shows a gain in signal of 1.47 ± 0.02 which is close to the predicted gain and an increase in relaxation by a factor of 5.6. The relaxation for the \(^{14}\text{N} \) has been reduced from 16.9 s ± 1.0 s to 3.0 ± 0.2 s by using this double resonance sequence. Overall this sequence shows an improvement in SNR of 3.5 ± 0.1, for a fixed period of time, which is equivalent to reducing the total time to acquire the same amount of signal by a factor of 12. This sequence shows similar total signal size as the sequence in Fig. (3.2) in Chapter 3. But in that sequence all three NQR transitions are swept, from highest to lowest, to produce an SNR improvement of 2.3. The sequence is similar to that described in Fig. (5.1) and the “\( \pi \)” pulse is determined from the calibration in Fig. (5.2).

The measured relaxation time for this case is \( T_{1\text{DR}} = 3.0 ± 0.2 \) s, somewhat less than the previously measured hydrogen \( T_1 \). This is consistent with numerical predictions for the data (2.7 ± 0.3 s) using the previously measured hydrogen \( T_1 = 3.1 ± 0.4 \) s. This fast rate is helped by a sharp initial increase of signal which accompanies the \(|\omega_z|\) level crossing.

5.3 Measuring the Peaks and Widths of the Double Resonance Conditions

In Chapter 3, all three of the static double resonance conditions were investigated, but only for the \( \omega_y \) static double resonance condition was a rate of \( W_y^0 = 103 ± 22 \) s\(^{-1} \) measured. In this chapter the results of experiments using all three types of double resonances conditions are described. Specifically, the double resonance conditions that are created and studied are
Figure 5.3: Experimental $T_{1N}$ data (●) for a double resonance sequence which shows increases in both recovery time and signal, and matches calculations using the spin-temperature model. After saturating the $\omega_y$ transition, the field is ramped to $B_0 = |\omega_y| / \gamma_H$ for the wait time shown on the horizontal axis. A $\pi$-pulse is then applied to flip the $^1H$ polarization and then $B_0$ is slowly swept through $B_0 = |\omega_z| / \gamma_H$. The measured $\omega_y$ NQR signal demonstrates an SNR improvement of $3.5 \pm 0.1$. For comparison the $T_{1N}$ in zero-field (○) is also shown. The lines are fit to $S = A(1 - e^{-t/T_1})$.

1. Static double resonance at $\omega_z$, $|\omega_z| = \gamma_H B_0$.
2. Rabi double resonance at $\omega_z$, $|\omega_z| = \gamma_H B_1$.
3. Static double resonance at $\omega_y$, $|\omega_y| = \gamma_H B_0$.
4. Rabi plus Larmor double resonance at $\omega_y$, $|\omega_y| = \gamma_H B_0 + \gamma_H B_1$.

For these conditions the maximum $^{14}\text{N}$ signal, the width of the double resonance, and the cross-relaxation rate will be measured and compared to the theory in Chapter 2 and the results from Chapter 3.
The theory developed in Chapter 3 applies to any of the static only double resonance conditions. Thus, for double resonance conditions 1) and 3) above, the signal equation, Eq. (3.18), and the table of solutions, Table (3.1), apply. Assuming that \( W_d \gg \rho \gg W_x, W_y, W_z \), then the solution includes three rates: one rate is dominated by cross-relaxation (\( \lambda_D \)), a second is proportional to \( K \) autorelaxation (\( \lambda_K \)), and a third is characterized by the \( I \) autorelaxation (\( \lambda_I \)). For this sample, only one rate will dominate under different time frames, since the rates are an order of magnitude or more apart. For ammonium nitrate the previously measured \( W_d \) is approximately 100 s\(^{-1}\) which is much greater than \( \rho = 0.33 \) s\(^{-1}\) which is also greater than all the \(^{14}\)N autorelaxation rates. The corresponding nitrogen autorelaxation rates are given by \( W_x = 0.033 \) s\(^{-1}\), \( W_y = 0.015 \) s\(^{-1}\), and \( W_z = 0.024 \) s\(^{-1}\). During the double resonance the spin dynamics will be dominated by \( W_d \).

The solution to the other double resonance conditions that utilize the Rabi rotating field, 2) and 4) above, follows the same procedure as in Chapter 3. The rate equations are formed from Eq. (2.93) for a specific double resonance condition. The solution to the rate equations is again based on the assumption \( W_d \gg \rho \gg W_x, W_y, W_z \), but in the rotating frame \( \rho = 1/T_{1H} \rho \) and \( K'_q \) is replaced by \( \tilde{K}'_{x'} \). The previous assumption still holds because for our sample \( 1/T_{1H} \rho \approx 1/T_{1H} \). Therefore, the solutions to the rate equations, Eq. (2.93), for these double resonance conditions will have the same eigenvalues as in Table (3.1).

The return to thermal equilibrium is thus governed by

\[
(\delta I_{x3}, \delta I_{y3}, \delta I_{z3}, \delta \tilde{K}_{x'}) = a_D V_D e^{-\lambda_D t} + a_K V_K e^{-\lambda_K t} + a_I V_I e^{-\lambda_I t} + C, \tag{5.4}
\]

where \( a_D, a_K, \) and \( a_I \) depend on the initial conditions of the system, and \( C \) is a constant vector that is the particular homogeneous solution to Eq. (2.93). This
general form of the solution is valid for both conditions 2) and 4). Most importantly
the “fast” eigenvalues, $\lambda_D$, which embody the cross-relaxation rates, are of the same
form as the static double resonance condition $\lambda_D$. For the Rabi and the Rabi plus
Larmor double resonance condition $\lambda_D = (2 + 4/(3R))W_d$, and $W_d$ will dominate
during cross-relaxation.

Finding the peaks, $B_{\text{resonant}}$, and the characteristic widths, $\Delta$, of the different
double resonance conditions is a necessary precondition for the measurement and
understanding of $W_d$ for each condition. The measurement of $W_d$, Eq. 2.81, depends
on the amount of the resonance condition that is swept during an experiment,
characterized by

$$h = \frac{\int_{B_{\text{low}}}^{B_{\text{high}}} \exp\left(-\frac{B^2}{2\Delta^2}\right)dB}{(\sqrt{2\pi}\Delta)}. \quad (5.5)$$

Some of the widths have been previously presented: see Table (4.2) for the widths of
the static double resonance conditions at $\gamma_H B_0 = |\omega_z|$ and $\gamma_H B_0 = |\omega_y|$. Additionally,
the magnitude of the nitrogen signal after the double resonance allows us to compare
the different types of double resonance conditions for potential use in explosives
detection solutions.

5.3.1 Rabi Double Resonance at $\omega_z$

The Rabi double resonance, $\gamma_H B_1 = |\omega_z|$, peak and width are measured by using the
sequence described in Fig. (5.4):\footnote{Additional details about this sequence are in Appendix E. The Rabi double resonance, $\gamma_H B_1 = |\omega_z|$, data are collected using a sequence described in Appendix E: Fig. (E.2) with parameters specified in both Table (E.3) and Table (E.2), row 5. Note this is not an adiabatic half passage experiment.} In a static field of $B_0$ the continuous perpendicular
rf creates an effective field in the rotating frame. Under these experimental conditions
the hydrogens in the rotating frame \( \langle \tilde{K}_x' \rangle \) resonantly couple with the nitrogens \( \langle I_{3z} \rangle \) through dipolar coupling when \( \gamma_H B_1 = |\omega_z| \). While the continuous rf is applied the hydrogens effectively cause the nitrogens’ population levels to attain a common spin temperature at the cross-relaxation rate. When the energy levels are matched between the two systems, the dipolar coupling, specifically the static part, provides a means for the energy-conserving flip-flop transitions. This sequence indirectly detects, through the nitrogen, the hydrogen’s polarization in the rotating frame \( \langle \tilde{K}_x' \rangle \), in a solid, at static field \(< 120 \text{ G}\). This is particularly surprising because the linewidth of hydrogen under these conditions is \( \Delta^2 = 2.7 \text{ G}^2 \) (6.9 kHz) while the linewidth of nitrogen is \( 53 \pm 29 \text{ Hz} \). So, the nitrogen can be used to indirectly detect a very broad system.

The double resonance peak and the width are found by varying \( B_1 \) while holding the other parameters of the experiment constant. The results are show in Fig. (5.5) for 2120 ms pulses. The peak signal, \( S_{\text{peak}} \), for the continuous rf of duration 2120 ms, is centered at a \( B_1 = 19 \pm 1 \text{ G} \), but the expected value was 20.7 G. The expected value incorporates the exact calculation of the \( I \) Zeeman and quadrupole energy levels and transition frequencies for these conditions, which may explain why the peak in Fig. (5.5) is not symmetric. The measured FWHM is \( 7.2 \pm 0.6 \text{ G} \), which is broader than expected from previous data.

The signal size, \( S_{\text{peak}} \approx 0.5 \), is comparable to the data obtained with the static double resonance condition at \( \omega_z \), Fig. (3.3) (red solid squares). The size of the signal at all three rf durations compares well to the signal evolution under the static condition. This implies that the relaxation mechanisms occurring during both conditions have similar rates and bodes well for the use of this technique in explosives detection.

Rabi double resonances at \( \gamma_H B_1 = |\omega_z| \) and \( \gamma_H B_1 = |\omega_z/2| \) are shown in Fig. (5.5).
Figure 5.4: Experimental sequence used to find the Rabi double resonance at $\gamma_H B_1 = |\omega_z|$. A set of $^{14}$N saturation pulses are applied in a static field of 36 G. The field is ramped to $B_{rf}$ in 3 ms, and then the rf field (red) of amplitude $B_1$ is applied for $t_{match}$. In this figure the field is applied for 200 ms; the static field is then lowered to Earth’s field in 3 ms. The $\omega_y$ signal is measured as $B_1$ is varied to find the resonances. The rotating field strength, $B_1$, is measured at the midpoint of the pulse. The rotating field strength linearly increases by about 1.0 % over the duration of the continuous pulses and is part of the measured error.

The resonance at $\gamma_H B_1 = |\omega_z/2|$ shows a resonance created by the simultaneous flipping of two hydrogens at the same time (a double spin-flip). While the double spin-flip double resonance is not treated theoretically in this work, the experimental data indicate a significant and fast signal gain which could be pursued for use in NQR spectroscopy and possibly explosives detection. In Ref. [84] high-field cycling experiments with rf applied parallel to the static field created other double resonance conditions that take advantage of the solid-effect and provide a new NQR spectroscopy technique. While both experiments in Fig. (5.5) show similar resonances the rotating field was controlled more linearly in the main graph. To the author’s knowledge this is
the first time this type of Rabi NQR cross-relaxation experiment has been conducted, most likely due to the high power required and working at such a low frequency.

Figure 5.5: Detection of Rabi double resonances at $\gamma_H B_1 = |\omega_z|$ and $\gamma_H B_1 = |\omega_z/2|$ with a pulse duration of 2120 ms. The normalized $\omega_y$ signal is measured as $B_1$ is varied. The arrows identify the two resonances that are detected at $\gamma_H B_1 = |\omega_z|$ and $\gamma_H B_1 = |\omega_z/2|$. In the inset is the normalized $\omega_y$ signal, measured as $B_1$ is varied for three values of the continuous rf: 200 ms (blue), 1120 ms (red), and 2120 ms (black). Two resonances are detected at $\gamma_H B_1 = |\omega_z|$ and $\gamma_H B_1 = |\omega_z/2|$. Error bars of ±0.02 are removed for clarity.
5.3.2 Rabi Plus Larmor Double Resonance at $\omega_y$

In this experiment $B_1$ is varied to find the $\omega_y$ Rabi plus Larmor double resonance. Under these experimental conditions the $^1\text{H}$ in the rotating frame resonantly couple with the $^{14}\text{N}$ through dipolar coupling. While the continuous rf is applied the $^1\text{H}$ effectively cause the $^{14}\text{N}$'s populations to come to a common spin-temperature at the cross-relaxation rate. When the energy levels are matched between the two systems, the static dipolar coupling provides a means for the energy-conserving flip-flop transitions. This double resonance condition is created using the sequence in Fig. (5.6)\(^2\), which is an adiabatic half passage (AHP) experiment [85]. The adiabatic half passage experiment is described in more detail in Appendix D. The AHP technique was needed because of instrumental limitations. Without the technique the $^1\text{H}$ would dephase in the time required for the rf amplifier to ramp to the desired $B_1$. By using the AHP technique the $^1\text{H}$ are slowly brought into the desired $B_{rf}$ level and at the same time the $B_1$ is ramped to the desired level. Again, to the author’s knowledge this is the first implementation of this double resonance condition for any system. The results are show in Fig. (5.7) for 40 ms pulses.

The peak double resonance signal occurs at $B_1 = 14.0 \pm 0.14$ G which is the expected value for this condition. The peak’s FWHM is $3.4 \pm 0.4$ G which is narrower then the other conditions. The peak signal size $S_{\text{peak}} = 0.87 \pm 0.03$ compares well to the data obtained with the static double resonance condition at $\omega_y$, Fig. (3.1) (open squares). In Fig. (3.1) at $t = 6$ s the signal is $S_{\text{peak}} = 0.8$. This again provides evidence that the rotating double resonance conditions will produce similar SNR improvements as the static double resonance conditions. The width of this double resonance is significantly smaller then the other widths but, when close to resonance

\(^2\)Additional details about this sequence are in Appendix E. The Rabi plus Larmor double resonance, $\gamma_H B_0 + \gamma_H B_1 = |\omega_y|$, data are collected using a adiabatic half passage experiment sequence described in Appendix E: Fig. (E.2) with parameters specified in both Table (E.3) and Table (E.2), row 7.
Figure 5.6: Experimental sequence to detect the Rabi plus Larmor double resonance $\gamma_H B_0 + \gamma_H B_1 = |\omega_y|$. A sequence of saturation pulses are applied to the $^{14}\text{N}$ in 36 G. The static field is ramped quickly to 108.5 G, above the expected resonance condition, and is maintained for 6 s. The rf field is then applied at the Larmor frequency of the $^1\text{H}$ at $B_1$ (red dashed line) while $B_0$ (black line) is reduced adiabatically to $B_{rf}$ to miss the $\omega_y$ resonance. The static field is reduced to meet the conditions of adiabatic half passage \[85\]. The rf total pulse duration, $t_{\text{match}}$, is 40 ms. The static field is then reduced to zero so that the $\omega_z$ condition is not matched. The signal at $\omega_y$ is then measured in Earth’s field. $B_1$ is varied to find the double resonance condition $\gamma_H B_0 + \gamma_H B_1 = \omega_y$.

in the rotating frame, as indicated by Eq. (2.56), the homogenous dipolar coupling corresponding to $\Delta_K$, is reduced by a factor of 2 over the static case.

The measured initial condition, without any double resonance, is $0.36 \pm 0.05$, which agrees with the predicted value of 0.32 due to the partial return of $^{14}\text{N}$ to thermal equilibrium. As $B_1$ is increased the measured signal quickly increases to $0.5 \pm 0.03$; then the signal peaks at the resonance condition, $B_1 = 14$ G. Above the resonance condition, $B_1 > 14$ G, the signal drops to $0.35 \pm 0.03$ as expected. This discrepancy in the signal size below resonance is most likely due to a partial resonance with both $\omega_z/2$ and $\omega_z$. Above this double resonance peak the next resonance
condition is $\omega_z = \omega_{0K} + \omega_{1K}$, which occurs at a $B_1 \approx 33$ G, so the signal should be the same as with no double resonance, which the data show.

Figure 5.7: Detection of the Rabi plus Larmor double resonance condition $\gamma HB_1 + \gamma HB_0 = |\omega_y|$: vary $B_1$ as $B_0$ is held constant and apply $B_1$ for 40 ms. The signal peak occurs at the predicted $B_1$ of 14.0 G. In this sequence $B_0$ is 85.5 G. The zero field value for $\omega_y$, with no resonance, is 0.32. The FWHM of this resonance condition is $3.4 \pm 0.4$ G (Gaussian fit).

The resonance widths and peaks for the four double resonance conditions have been measured and are summarized in Table (5.1). The width describes the range over which the double resonance occurs and to what extent. It is important because the cross-relaxation is effective only while the matching field is within this range. As discussed in Chapter 2, for each condition there are different sources of broadening, as shown in Table (2.2), including apparatus-dependent field inhomogeneities. Therefore the experimental measurements of $\Delta$ are utilized to calculate $W^0_d$ and characterize the cross-relaxation conditions. In Tables (5.1) and (5.2) key parameters of the
Table 5.1: Peaks and widths of the double resonance conditions. The peak of the double resonance condition is listed in the $B_{\text{resonance}}$ column. The next column is the measured FWHM and the final column is the $\Delta$ for this double resonance condition. $B_{\text{high}}$ and $B_{\text{low}}$ are in Table (5.2).

<table>
<thead>
<tr>
<th>Double resonance condition</th>
<th>$B_{\text{resonance}}$ Measured (G)</th>
<th>$B_{\text{resonance}}$ Predicted (G)</th>
<th>FWHM (G)</th>
<th>$\Delta$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_z</td>
<td>$</td>
<td>18.9 ± 0.3</td>
<td>18.7</td>
</tr>
<tr>
<td>$\gamma_H B_1 =</td>
<td>\omega_z</td>
<td>$</td>
<td>19.0 ± 1.0</td>
<td>20.7</td>
</tr>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
<td>99.8 ± 1.5</td>
<td>99.1</td>
</tr>
<tr>
<td>$\gamma_H B_1 + \gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
<td>14.0 ± 0.1</td>
<td>14.0</td>
</tr>
</tbody>
</table>

sequence used to measure the double resonance widths for the different conditions are summarized.

## 5.4 Cross-Relaxation Rates

### 5.4.1 Effective Cross-Relaxation

The cross-relaxation depends on the amount of the resonance condition that is swept during an experiment, which depends on $\Delta$ and the experimental setup for each double resonance condition, Table (5.1). While the field is being swept through the resonance condition the $^1\text{H}$ and $^{14}\text{N}$ nuclei can cross-relax. Experimentally, the cross-relaxation rate is measured by varying the amount of time spent sweeping through the double resonance condition of interest while holding $\Delta B = B_{\text{high}} - B_{\text{low}}$ constant. This is characterized by a sweep rate. This sweep rate is $\frac{dB_0}{dt}$ for the static double resonance experiments and $\frac{dB_1}{dt}$ for the other double resonance conditions, Table (5.1). During
Table 5.2: Parameters to measure double resonance widths. Each sequence maintains the same start and stop limits for the static or rf field, but varies the amount of time that it takes to sweep from the $B_{\text{low}}$ to $B_{\text{high}}$. In the “Sweep” column is the difference, $\Delta B = B_{\text{high}} - B_{\text{low}}$, for the static or rf field controlled during the experiment. The shortest and longest durations, in ms, are listed in this table. The instrumental limitation for the $\frac{dB}{dt}$ is 36 G/ms while the limit for $\frac{dB}{dt}$ is 150 G/ms.

<table>
<thead>
<tr>
<th>Double resonance condition</th>
<th>Shortest (ms)</th>
<th>Longest (ms)</th>
<th>Sweep $\Delta B$ (G)</th>
<th>$B_{\text{low}}$ (G)</th>
<th>$B_{\text{high}}$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_z</td>
<td>$</td>
<td>0.352</td>
<td>420</td>
<td>12.0 ± 0.1</td>
</tr>
<tr>
<td>$\gamma_H B_1 =</td>
<td>\omega_z</td>
<td>$</td>
<td>0.05</td>
<td>200</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
<td>1.0</td>
<td>400</td>
<td>16.0 ± 0.2</td>
</tr>
<tr>
<td>$\gamma_H B_1 + \gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
<td>0.1</td>
<td>200</td>
<td>5.0 ± 0.1</td>
</tr>
</tbody>
</table>

In an experiment the effective cross-relaxation rate is measured and then the peak cross-relaxation rate was calculated.

The calculation of the peak cross-relaxation rate is based on Eq. (2.81), repeated here for reference,

$$W_d^0 = \frac{W_{\text{exp}} (B_{\text{high}} - B_{\text{low}})}{\int_{B_{\text{low}}}^{B_{\text{high}}} \exp(- \frac{\Delta B^2}{2G_A^2}) dB} \quad (5.6)$$

$$= \frac{W_{\text{exp}} (\Delta B)}{G_A}, \quad (5.7)$$

where $W_{\text{exp}}$ is the measured effective cross-relaxation, $\Delta B = B_{\text{high}} - B_{\text{low}}$ is the experimental sweep, and $G_A = \int_{B_{\text{low}}}^{B_{\text{high}}} \exp(- \frac{\Delta B^2}{2G_A^2}) dB$ is the effective width of the measured cross-relaxation.
5.4.2 Characterizing $W_d$ at $\omega_z$

The static double resonance, $\gamma_H B_0 = |\omega_z|$, and the Rabi double resonance, $\gamma_H B_1 = |\omega_z|$, cross-relaxation rates are measured by using two sequences described in Fig. (5.8) panes (a) and (b). The results of the static double resonance condition $\gamma_H B_0 = |\omega_z|$ (blue stars and dashed line) and the Rabi double resonance $\gamma_H B_1 = |\omega_z|$ (red squares) are presented in panes (c) and (d) vs. the inverse sweep rate.

<table>
<thead>
<tr>
<th>Double resonance condition</th>
<th>“Fast” fit parameter $R_{fitfast}$ (ms/G)</th>
<th>“Slow” fit parameter $R_{fitslow}$ (ms/G)</th>
<th>% Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_z</td>
<td>$</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>$\gamma_H B_1 =</td>
<td>\omega_z</td>
<td>$</td>
<td>0.63 ± 0.23</td>
</tr>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
<td>0.28 ± 0.05</td>
</tr>
<tr>
<td>$\gamma_H B_1 + \gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
<td>0.45 ± 0.08</td>
</tr>
</tbody>
</table>

The normalized $\omega_y$ signal vs. the inverse sweep rate for these two double resonance conditions is presented in panes (c) and (d). The $x$-axis is the inverse sweep rate $(\frac{dB_2}{dt})$ or $(\frac{dB_1}{dt})$, as appropriate, in ms/G. In pane (c) the inverse sweep rate is presented on a log scale. In panes (c) and (d) the signal for both these double resonance conditions quickly reaches 0.36 which agrees with previous results for
the $|\omega_z|$ transition, Fig. (3.3). The data for the static double resonance condition, $\gamma_H B_0 = |\omega_z|$ (blue stars), can be fit using the model in Chapter 3 and results in a $W_d = 140 \pm 20$ s$^{-1}$. Because this experiment provides finer grained data a bi-exponential is fit to the data, pane (c). The data for both these conditions are fit to bi-exponentials and the “fast” and “slow” fit parameters are in Table (5.3). These fit parameters are related to the solution for $\lambda_D$ from Table (3.1)

$$\lambda_D = \frac{1}{R_{fit} \Delta B} = \left(2 + \frac{4}{3R} \right) W_{d,exp}. \quad (5.8)$$

The calculation of the peak cross-relaxation rate takes into account the fact that only part of the gaussian shaped resonance condition is covered during the experiment. The calculation of the peak cross-relaxation rate is

$$W_0^d = \frac{W_{d,exp} \Delta B}{G_A} \quad (5.9)$$

$$W_0^d = \frac{1}{R_{fit}(2 + \frac{4}{3R})G_A} \quad (5.10)$$

The measured values for $W_0^d$ are in Table (5.4). The measured “fast” $W_0^d$ for the static double resonance condition $\gamma_H B_0 = |\omega_z|$ is approximately 4 times faster than $W_0^d$ for the Rabi double resonance condition $\gamma_H B_1 = |\omega_z|$. The “fast” cross-relaxation rate is more appropriate for the comparison because of the assumptions used in the solution to the rate equations and the time constraints on the use of time-dependent perturbation theory [10,44].

The theoretical cross-relaxation rate for both of these conditions can be calculated using Eq. (2.71), the positions of the atoms in ammonium nitrate from Ref. [38], the
Table 5.4: Comparison of measured and theoretical $W^0_d$ rates in s$^{-1}$

| Double resonance condition | Static $\gamma_H B_0 = |\omega_z|$ | Rabi $\gamma_H B_1 = |\omega_z|$ | Static $\gamma_H B_0 = |\omega_y|$ | Combined $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$ |
|----------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| “Fast” $W^0_d$             | $350 \pm 32$                    | $100 \pm 40$                    | $230 \pm 40$                    | $260 \pm 50$                    |
| “Slow” $W^0_d$             | $36 \pm 8$                      | $13 \pm 9$                      | $29 \pm 11$                     | $32 \pm 12$                     |
| “Single” $W^0_d$           | $190 \pm 80$                    | $32 \pm 14$                     | $90 \pm 14$                     | $140 \pm 22$                    |
| Single $W^0_d$ from model  | $140 \pm 24$                    | $100 \pm 40$                    |                                  |                                  |
| Theoretical $W^0_d$        | $310$                           | $110$                           | $350$                           | $160$                           |

proposed PAS frame from Ref. [60], the geometric term, $F_{ik}$ from Table (2.1), and the experimental widths from Table (5.1). For the static double resonance condition a cross-relaxation rate of 440 s$^{-1}$ was calculated without any averaging due to motion. A rapid reorientation of the ammonium ion, on the order of $10^{11}$ s$^{-1}$, has been observed [51]. Since this motion is much much faster than $W^0_d$ it is incorporated into the model by taken the average geometric term $F_{ik}$ from the nitrogen to the four hydrogens of each ion instead of the individual terms: all the rates with and without motion for all the double resonance conditions are presented in Table (5.5). This averaging reduces the rate to 310 s$^{-1}$ which is close to the measured $W^0_{dfast}$ of $550 \pm 180$ s$^{-1}$.

For the Rabi double resonance condition $\gamma_H B_1 = |\omega_z|$ the theoretical cross-relaxation rate was calculated to be 110 s$^{-1}$ with motion and $W^0_{dfast} = 140 \pm 100$ s$^{-1}$ is measured. For both cases the theoretical cross-relaxation rates agree with the

---

3 The calculation includes all hydrogen nuclei within a 10 Å radius from the chosen nitrogen atom.
Table 5.5: Theoretical double resonance cross-relaxation rates with and without the fast reorientation of the hydrogen’s motion included. The calculation for each rate uses the experimentally measured $\Delta$ for each condition.

<table>
<thead>
<tr>
<th>Double resonance condition</th>
<th>Theoretical $W_d^0$ s$^{-1}$ with motion</th>
<th>Theoretical $W_d^0$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_z</td>
<td>$</td>
</tr>
<tr>
<td>$\gamma_H B_1 =</td>
<td>\omega_z</td>
<td>$</td>
</tr>
<tr>
<td>$\gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
</tr>
<tr>
<td>$\gamma_H B_1 + \gamma_H B_0 =</td>
<td>\omega_y</td>
<td>$</td>
</tr>
</tbody>
</table>

measured “fast” cross-relaxation rates. These results are summarized in Table (5.4).

Also in Table (5.4), for the static double resonance conditions, the full numerical model developed in Chapter 3 is used to calculate the rates. The results of this calculation are in the row “Single $W_d^0$ from model.” This model was used in Chapter 3 to calculate, for the $\omega_y$ static double resonance condition, $W_d^0 = 103 \pm 22$ s$^{-1}$. In comparison, the theoretical result is $W_d^0 = 400$ s$^{-1}$.\(^4\) The experimental data below 1 ms were not available in that experiment and therefore $W_{d_{fast}}^0$ could not be determined. Essentially, the $W_d^0 = 103 \pm 22$ s$^{-1}$ measured is $W_{d_{slow}}^0$. This $W_{d_{slow}}^0$ differs by a factor of four from the theoretical prediction. A theoretical difficulty is that at longer times the assumptions of perturbation theory are no longer valid. Therefore, this approach is valid only for calculating $W_{d_{fast}}^0$. For the experiments in this chapter the data time resolution is significantly improved compared to the experiments in Chapter 3 and is sufficient to resolve the $W_{d_{fast}}^0$ rate.

As a further consistency check, the data were fit to a single exponential and those

\(^4\)This rate is different from the rates in Table (5.4) because of different experimental conditions.
data are presented in Table (5.4) in the row “Single” $W_d^0$. This fit was poor but sufficient to indicate that a rate on the order of $100 \text{ s}^{-1}$ dominates at this slow time scale, except for the Rabi double resonance condition which is even slower. These rates are consistent with the results of the model (“Single $W_d^0$ from model” above) but differs from the expected “fast” rate by a factor of 3.5. Due to this discrepancy these “slow” rates deserve further investigation.

The sequence used to determine $W_d^0$ for the static double resonance condition $\gamma_H B_0 = |\omega_z|$ is described in Fig. (5.8) pane (a). The sequence used to determine $W_d^0$ for the Rabi double resonance condition $\gamma_H B_1 = |\omega_z|$ is described in Fig. (5.8) pane (b). The static field, $B_0$, (black) and the rf amplitude, $B_1$, (red dashed line, axis on the right) are plotted during the sequence to measure $W_d$ for the double resonance condition $\gamma_H B_1 = |\omega_z|$

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Additional details about these sequences are in Appendix E. The static double resonance, $\gamma_H B_0 = |\omega_z|$, data are collected using a sequence described in Appendix E: Fig. (E.1) with parameters specified in Table (E.1) row 2. The Rabi double resonance, $\gamma_H B_1 = |\omega_z|$, data are collected using a sequence described in Appendix E: Fig. (E.2) with parameters specified in both Table (E.3) and Table (E.2), row 6. Note this is not an adiabatic half passage experiment.
Figure 5.8: The static, $\gamma_H B_0 = |\omega_z|$, and Rabi double resonance, $\gamma_H B_1 = |\omega_z|$, crossrelaxation rates are measured by using two sequences described in panes (a) and (b). The results of the static double resonance condition (blue stars and dashed line) and the Rabi double resonance condition (red squares) are presented in panes (c) and (d) vs. the inverse sweep rate. The measured “fast” $W_d$ is within the error bars of the theoretical calculations. The theoretical and measured $W_d$ for the static double resonance condition are approximately 3–4 times faster than the $W_d$ for the Rabi double resonance condition, Table (5.4).
5.4.3 Characterizing $W_d$ at $\omega_y$

The static double resonance, $\gamma_H B_0 = |\omega_y|$, and the Rabi plus Larmor double resonance, $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$, cross-relaxation rates are measured by using two sequences described in Fig. (5.9) panes (a) and (b). The results of the static double resonance condition (blue stars and dashed line) and the Rabi plus Larmor double resonance (red squares and line) are presented in panes (c) and (d). The normalized $\omega_y$ signal vs. the inverse sweep rate for these two double resonance conditions are presented in panes (c) and (d). The $x$-axis is the inverse sweep rate ($\frac{dB}{dt}$) or ($\frac{dB_1}{dt}$), as appropriate in ms/G. In pane (c) the inverse sweep rate is presented on a log scale.

In panes (c) and (d) the signal for both these double resonance conditions quickly approaches 1.0 which agrees with previous results for the $\omega_y$ transition, Fig. (3.1). At longer times, not shown, the spin temperature model predicts a steady state normalized signal of 1.04 and 1.05 ± 0.2 is measured for these double resonance conditions. The data for the static double resonance condition, $\gamma_H B_0 = |\omega_y|$ (blue stars), can be fit using the model in Chapter 3 and result in a $W_0^d = 100 \pm 40$ s$^{-1}$, but the data for both these conditions are fit to bi-exponentials and the “fast” and “slow” fit parameters are in Table (5.3). Using the procedure from the previous section the measured values for $W_0^d$ are presented in Table (5.4). The measured $W_0^d$ for the static double resonance condition is approximately the same as $W_0^d$ for the Rabi plus Larmor double resonance condition.

The $W_0^d$ for the static double resonance condition $\gamma_H B_0 = |\omega_y|$ is measured to be $W_{d,fast}^0 = 260 \pm 32$ s$^{-1}$. Using the previously described procedure a theoretical cross-relaxation rate of 350 s$^{-1}$ was calculated, close to the measured $W_{d,fast}^0$. The $W_0^d$ for the Rabi plus Larmor double resonance condition $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$ is measured to be $W_{d,fast}^0 = 300 \pm 40$ s$^{-1}$ and calculated to be 160 s$^{-1}$.

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The sequence used to determine $W_d^0$ for the static double resonance condition $\gamma_H B_0 = |\omega_y|$ is described in Fig. (5.9) pane (a). The initial polarization time was 6.2 s; this time was chosen to minimize the difference between the expected relaxation of the $^{14}$N and the polarization of the $^1$H in this field. During this period the $^{14}$N relaxes back to 0.32 of the thermal equilibrium value.

The sequence used to determine $W_d^0$ for the Rabi plus Larmor double resonance condition, $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$, is described in Fig. (5.9) pane (b). The static field, $B_0$, (black line) and the rf amplitude, $B_1$, (red dashed line) are plotted during the sequence. This is a AHP experiment, described in Appendix D.

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$^6$Additional details about these sequences are in Appendix E. The static double resonance, $\gamma_H B_0 = |\omega_y|$, data are collected using a sequence described in Appendix E: Fig. (E.1) with parameters specified in Table (E.1) row 4. The Rabi pulse Larmor double resonance, $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$, data are collected using a sequence described in Appendix E: Fig. (E.2) with parameters specified in both Table (E.3) and Table (E.2), row 8. Note this is an adiabatic half passage experiment.
Figure 5.9: The static double resonance, $\gamma_H B_0 = |\omega_y|$, and the Rabi plus Larmor double resonance, $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$, cross-relaxation rates are measured by using two sequences described in panes (a) and (b). The results of the static double resonance condition $\gamma_H B_0 = |\omega_y|$ (blue stars and dashed line) and the Rabi plus Larmor double resonance (red squares) are presented in panes (c) and (d) vs. the inverse sweep rate. The $W_d$ for the static double resonance condition $\gamma_H B_0 = |\omega_y|$ is approximately the same as $W_d$ for the Rabi plus Larmor double resonance condition.
5.5 Dipolar Coupling Strength from Cross-Relaxation Rates

Both the experimental and theoretical $W_d^0$ rates are calculated using the experimental $\Delta$. Comparisons among them are valid under the conditions discussed and with the realization that these rates are partially determined by the experimental conditions. A more fundamental characteristic, has been defined in Chapter 2, and is $\omega_D^2$, the dipolar coupling strength

$$\omega_D^2 = \gamma_k W_d^0 \sqrt{2\pi} \Delta.$$  \hspace{1cm} (5.11)

For all the double resonance conditions these dipolar coupling strengths are presented in Table (5.6) in units of $10^6 \text{ s}^{-2}$. This dipolar coupling parameter is $\gamma_k$ times the square of the dipolar field experienced by the nitrogen due to the motionally averaged hydrogens and independent of experimental conditions. In Table (5.6) the theoretical and the measured values of the “fast” $\omega_D^2$ are in good agreement.

The theory in Chapter 2 reveals that the cross-relaxation rate of Rabi plus Larmor double resonance condition should be 1/4 the rate at the other conditions. This is seen by looking at the $F_{ik}$ terms in Table (2.1). Comparing the static double resonance at $\omega_y$ and the Rabi plus Larmor double resonance at $\omega_y$, the factor of 1/4 is in the theoretical calculations but is not shown experimentally and should be investigated.
Table 5.6: Comparison of measured and theoretical $\omega_D^2 \times 10^6$ s$^{-2}$.

| Double resonance condition | Static ($\gamma_H B_0 = |\omega_z|$) | Rabi ($\gamma_H B_1 = |\omega_z|$) | Static ($\gamma_H B_0 = |\omega_y|$) | Combined ($\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$) |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| “Fast” $\omega_D^2$         | 58.1 ± 5.3                      | 20.1 ± 8.5                      | 40.8 ± 7.5                      | 25.4 ± 4.7                      |
| “Slow” $\omega_D^2$         | 6.0 ± 1.3                       | 2.6 ± 1.8                       | 5.1 ± 1.9                       | 3.1 ± 1.1                       |
| % Fast                      | 60 ± 3                          | 40 ± 11                         | 66 ± 8                          | 57 ± 7                          |
| $\Delta$ (G)                | 2.5 ± 0.3                       | 3.1 ± 0.1                       | 2.6 ± 0.3                       | 1.6 ± 0.1                       |
| “Single” $\omega_D^2$       | 32.0 ± 12.8                     | 6.5 ± 2.7                       | 15.4 ± 2.5                      | 13.4 ± 2.1                      |
| Single $\omega_D^2$         | 23.3 ± 4.0                      |                                 | 17.5 ± 7.0                      |                                 |
| from model                  |                                 |                                 |                                 |                                 |
| Theoretical $\omega_D^2$    | 51.4                            | 22.1                            | 61.3                            | 15.3                            |
5.6 Conclusions

Utilizing double resonance cross-relaxation, the relaxation rate of the $^{14}$N as well as the $^{14}$N signal size in systems with $^1$H-$^{14}$N has been increased. A model of this system has been developed that treats the motionally averaged heterogeneous secular dipolar Hamiltonian as a perturbation of the combined quadrupole and Zeeman Hamiltonians. This model reveals three double resonance conditions, involving static and rf fields and expressions for the cross-relaxation rate ($W_d$). The terms that contribute to $W_d$ for each double resonance condition are presented in Table (2.1). The static double resonance is created by matching $\gamma_H B_0 = |\omega_{NQR}|$. The Rabi double resonance condition is created by matching $\gamma_H B_1 = |\omega_{NQR}|$, where $B_1$ is applied perpendicular to $B_0$ at the $^1$H Larmor frequency. The Rabi plus Larmor double resonance condition is created by matching $\gamma_H B_1 + \gamma_H B_0 = |\omega_{NQR}|$. In all three cases, the polarized $^1$H is observed by cross-polarization with the $^{14}$N at the double resonance condition and the $^{14}$N’s signal is detected in Earth’s field. For the Rabi and Rabi plus Larmor conditions the double resonance occurs in the rotating frame. In all cases the double resonance cross-relaxation is mediated by energy conserving “flip-flop” transitions through the static part of the dipolar coupling. The cross-relaxation can lead to a significant and quick increase in the $^{14}$N signal characterized by $W_d^0$, $\Delta$, and $\omega_d^2$.

This simple two-spin model is extended to the powder ensemble and predicts the spin dynamics for three different types of double resonance. The solutions to the rate equations, Eq. (2.93), for these double resonance conditions have the eigenvalues in Table (3.1). The experiments, together with the derived expressions, suggest that cross-relaxation during double resonance is dominated by the static dipolar coupling, in which the effective coupling is reduced, or averaged out, by molecular motion within the crystal. The theoretical results are generally applicable to other spin
systems. This model is general and not limited only to ammonium nitrate or $^1$H-$^{14}$N or even applicable to only spin-1/2 spin-1 systems but is applicable to any spin-1/2 to fictitious spin-1/2 system. The best results will be in spin systems where the spin -1/2 autorelaxation rate is much greater than the spin $I$ autorelaxation rate.

The two rotating double resonance conditions have been implemented for the first time with results in Fig. (5.5) and Fig. (5.7). Four double resonance conditions are characterized by measuring the peak, width, and signal size, in Table (5.1), to determine the cross-relaxation rates and coupling strength. For all three types of double resonance, the $\omega_D^2$ dipolar coupling strength, which is an experimental independent measure of the cross-relaxation, is measured and compared to the theoretical predictions, Table (5.6). Three of the measured “fast” rates compare well to the predictions. One example is the static double resonance condition at $\omega_y$: the “fast” $\omega_D^2 = 45.7 \pm 5.6 \times 10^6 \text{s}^{-2}$ compares well to the theoretical $61.3 \times 10^6 \text{s}^{-2}$.

These “fast” cross-relaxation rates are utilized and a significant improvement in SNR is demonstrated with a low field static double resonance sequence. The double resonance condition is created by matching the Larmor frequency of the $^1$H to the $^{14}$N NQR transition frequencies, $\gamma_H B_0 = |\omega_y|$, then flipping the $^1$H polarization by a $\pi$ pulse, and then sweeping the $\omega_z$ transition. The experiments show, for ammonium nitrate, an SNR improvement of $3.5 \pm 0.1$ and match the predictions of the model, Fig. (5.3). Other double resonance conditions were characterized, such as the sequence that matches all three nitrogen transitions and results in a SNR increase of $2.3 \pm 0.1$ as shown in Fig. (3.2). All the results from these double-resonance experiments fit the predictions of the spin-temperature model fairly well, with only slight discrepancies. Note that the spin-temperature model allows the calculation of only the final conditions of an experiment not the rates. The rates are calculated using the model from Chapter 2.
Using these double resonance techniques a significant cross-relaxation rate in ammonium nitrate between the nitrogen of NO$_3^-$ and the hydrogen of NH$_4^+$ has been measured. The measured $W_{d,fast}$ is close to the motionally average theoretical $W^0_d$s, for all three types of double resonance conditions, Table (5.4). One example is the static double resonance condition at $\omega_y$: the “fast” $W^0_d = 260 \pm 32$ s$^{-1}$ compares to the theoretical 350 s$^{-1}$ rate. This measured “fast” $W^0_d$ rate is $\approx$8000 times larger than the $^{14}$N $W_x$ autorelaxation rate.

These “fast” $W^0_d$ rates and the experimental data indicate that the cross-relaxation occurs on the order of 10–20 ms in this sample. Thus, the maximum cross-polarization occurs on this time scale, which constrains the detection requirements. The typical detection technique is to sweep through the resonance condition which has the advantage of compensating for the unknown temperature of the sample in the field. The measurements of these rates now place time constraints on the sweep to optimize the detected signal due to gains from this cross-relaxation.

The $^{14}$N signals from the rotating double resonance conditions are similar to the signals from the static double resonance conditions. This implies that the improvement in SNR is similar to the static double resonance condition. The data indicate that equivalent improvements in SNR can be achieved by using any of the three resonance conditions. This is an exciting but preliminary result, since only a few experiments have been conducted with these new double resonance conditions. This has important implications for the engineering of future explosives detection systems. Additionally, the techniques presented here have the potential for even greater gains in SNR when optimized just for explosives detection. Furthermore, while the double spin-flip double resonance is not treated theoretically in this work, the experimental data indicate a significant and fast signal gain which could be pursued for use in NQR spectroscopy and possibly explosives detection, Fig. (5.5).
The experiments for the rotating double resonance conditions resulted in a few experimental methods that are applicable to similar problems. The off-resonant pPAPS sequence changes the phase and the off-resonance of the pulses to get coherent rf noise and short time-scale noise cancellation without a loss in signal. The Rabi oscillation sequence provides an excellent means of calibrating for these double resonance conditions, Fig. (5.2), and the spin-flip technique, Fig. (5.3), can also be used for explosives detection.

As mentioned in Chapter 2 Section 2.1.10, the measurement of the cross-relaxation rates can be used to determine distance independent of the powder average. The theory indicates that if six of the double resonance cross-relaxation rates can be measured then a precise determination of the motionally averaged distance in a system can by calculated essentially factoring out the effect of the powder.

Besides contributing new possibilities to explosives detection these double resonance conditions provide new experimental techniques. Two of these double resonance conditions, the Rabi and Rabi plus Larmor, allow us to measure $\langle \tilde{K}_x' \rangle$, the transverse component of $K$ in the rotating frame. The rotating double resonance conditions indirectly detect, through the nitrogen, the hydrogen's polarization in the rotating frame $\langle \tilde{K}_x' \rangle$, in a solid, at static field <120 G. This is particularly surprising because the linewidth of hydrogen, for this sample, under these conditions is $\Delta^2 = 2.7 \text{ G}^2$ (6.9 kHz) while the linewidth of nitrogen is only $53 \pm 29 \text{ Hz}$. Therefore, the nitrogen can be effectively used to indirectly detect $^1\text{H}$ in low-field: this is a possible spectroscopic technique.

While this chapter focuses on strong rf pulses that show promise for enhanced explosives detection, among other benefits, the next chapter explores how weak rf pulses can contribute to explosives detection.
Chapter 6: NQR Single Pulse Echoes

6.1 Introduction

The use of NQR for the detection of contraband material has received significant attention because of its ease of implementation and ability to uniquely identify illicit substances [1–4].\(^1\) Practical considerations push NQR detection technology to operate at lower magnetic fields for reduced power requirements, larger detection volumes, and safe operation around delicate instrumentation. Therefore, to improve the NQR detection capability it is important to understand the spin dynamics which occurs in samples irradiated by weak rf pulses. One clear manifestation of the spin dynamics in this regime is the appearance of an echo after a single pulse, of duration \(t_1\), in samples that have a distribution of electric field gradients (EFG’s) which result in an inhomogeneously broadened line, referred to as EIB – Electric field gradient Inhomogeneously Broadened. In Fig. (6.1) the echo effect on the experimental signal (\(\bigcirc\)) can clearly be seen as compared to delta function pulses (solid line). While these data are for \(\gamma B_1/\sigma = 2.6\), where \(\gamma\) is the gyromagnetic ratio, \(B_1\) is the amplitude of the applied rf, and \(\sigma\) is the linewidth (half-width at half maximum) of the sample, the data will demonstrate that more pronounced single-pulse echoes (SPEs) occur when \(\gamma B_1/\sigma\) is even lower. The signal size, timing, and optimal pulse duration to observe these SPEs and compare them to the traditional echo from a double pulse in this low field regime is explored theoretically.

\(^1\)Parts of this chapter were published as: D. Prescott, J. Miller, C. Tourigny, K. Sauer, Nuclear quadrupole resonance single-pulse echoes, J. of Mag. Res. 194 (2008) 1.
Figure 6.1: By comparing the signal from RDX due to a delta-like pulse to the signal from a weaker pulse the formation of an NQR SPE is demonstrated. The normalized NQR signal in Fourier space vs. tipping angle for a single pulse of $B_1=51 \, \text{G}$ closely follows the predicted NQR signal [9] (solid line) while the (○) shows the signal for a pulse of 2.3 G, which produces an echo. The arrows highlight the occurrence of the maximum echo. The vertical line, at 119°, shows the point of maximum expected FID due to a delta-like pulse.

The first observation of single-pulse echoes was by Bloom[86] in 1954 using water in a very inhomogeneous magnetic field. Since then, they have been detected in a number of other physical systems, such as: magnetically ordered solids[87–91], crystals with large dynamic frequency shifts[92], or an optically thin molecular sample subjected to a Stark-pulse[93]. It has long been debated the exact method of formation of these observed echoes[88,94–96], and under what conditions they are formed—whether for large inhomogeneous broadening alone[86], or with the addition of significant inhomogeneity in the Rabi frequencies[88], or for rf excitation far detuned from the
center frequency[97–99]. These echoes, however, share in common the experimental observation of the signal’s peak at times comparable to the duration of the excitation pulse, typically after a tipping pulse \( \geq 360^\circ \). In contrast, our data shows a SPE which occurs for an average effective tipping angle close to \( 270^\circ \), and whose signal peaks much closer to the falling edge of the pulse. This SPE, which is closely related to the more traditional double-pulse echo (DPE)[100], can be most easily observed under conditions of inhomogeneous line broadening and inhomogeneous Rabi frequencies, which in the case of NQR corresponds to a large EIB and a distribution of crystallite directions as found in a powder sample. Figure (6.1) demonstrates the increase in signal because of this echo effect under these conditions.

### 6.2 Theory

To demonstrate the formation of NQR SPEs a system dominated by the nuclear quadrupole interaction and subjected to a single resonant rf pulse is modeled. Included in the model are off-resonance effects due to the linewidth. Additionally, the assumption is made that relaxation is negligible during the pulse and that the wait time between data acquisitions is much greater than both the spin-lattice relaxation time \( T_1 \) and the spin-spin relaxation time \( T_2 \) (in contrast to multipulse SPEs[101]).

This admittedly simplified model is sufficient to show how the NQR SPE forms and to predict the conditions for a maximum echo. A SPE is defined as the occurrence of a single maximum of the signal magnitude which occurs after the end of the rf pulse. Those signals where the maximum occurs at the end of the rf pulse are deemed to be a “free decay.”

The development of the SPE is modeled by the density matrix \( \rho(t) \) for the total Hamiltonian \( H_T = H_0 + H_1 \), where \( H_0 \) is the dominant Hamiltonian and \( H_1 \) is
the perturbation Hamiltonian. The dominant Hamiltonian is proportional to the quadrupole Hamiltonian and for ease of calculation the quadrupole Hamiltonian, for spin-1, can be defined with respect to fictitious spin-$\frac{1}{2}$ operators [9,44,45] as,

$$H_Q = \hbar \{ \omega_x I_{x3} + \frac{1}{3} (\omega_y - \omega_z) I_{x4} \}, \quad (6.1)$$

where $\langle I_{x3} \rangle = \frac{N_y - N_z}{2N}$ (half the difference in population of the highest eigenstate $N_y$, and the lowest eigenstate $N_z$, over the total number of spin-1 atoms $N$). The definition of the three characteristic transition frequencies ($|\omega_x| > |\omega_y| > |\omega_z|$), Fig. (1.1), and the operator $I_{x4}$ (which does not contribute to the signal) can be found in Appendix A. The fictitious spin-$\frac{1}{2}$ formalism allows us to treat a multi-level system as a two level system when only one transition is involved, for instance $\omega_x$. While the focus is on the case of spin-1, because of the sample, the results are generally applicable to any non-degenerate two level system coupled by an rf field, i.e. either a spin-$\frac{1}{2}$ or a fictitious spin-$\frac{1}{2}$ system[25].

The interaction of the nuclei with the rf pulse of frequency $\omega_{rf}$ and the off-resonant part of the quadrupole Hamiltonian is treated as a perturbation. Therefore, the dominant Hamiltonian is written as, $H_0 \equiv \frac{\omega_{rf}}{\omega_x} H_Q$, and the perturbing Hamiltonian as, $H_1 = H_{rf} + V$, where $V \equiv -\Delta \omega \omega_x H_Q$ and $\Delta \omega \equiv \omega_{rf} - \omega_x$ describe the resonance offset effects created by the EIB[102]. The rf Hamiltonian for the $\omega_x$ transition is $H_{rf} = -\gamma \hbar \mathbf{I} \cdot \mathbf{B}_1 \cos(\omega_{rf} t + \phi_1)$ where $\omega_{rf}$ is applied at $\overline{\omega}_x$, the mean value of $\omega_x$ or the first moment of the lineshape[24]. The rotation angle of the pulse is $\theta = \gamma B_1 t_1$. Note, this model is limited to systems such that the frequency difference between the NQR levels is much greater than the linewidth of the transition.

Thus, the density matrix $\rho(t)$ evolves under the Liouville equation, $\dot{\rho} \hbar = i[\rho, H_0 + \dot{\rho} \hbar = i[\rho, H_0 +
$H_1$, which in the interaction representation of $H_0$ becomes, \( \dot{\rho} = i \{ \rho, \tilde{H}_1 \} \), where \( \dot{\rho} = e^{iH_0t/\hbar} \rho e^{-iH_0t/\hbar} \) and \( \tilde{H}_1 = \tilde{H}_{rf} + \tilde{V} = e^{iH_0t/\hbar} (H_{rf} + V) e^{-iH_0t/\hbar} \). Using the secular approximation\[44\],

\[
\tilde{H}_{rf} = -\hbar \omega_1 (I_{x1} \cos \phi_1 + I_{x2} \sin \phi_1),
\]

(6.2)

where the effective Rabi frequency, \( \omega_1 = \gamma B_1 \cos \xi \), and \( \xi \) is the angle between the direction of the applied field and \( \hat{x} \) of the principle axes frame of the EFG [24]. \( \dot{\rho} \) is then calculated in the fictitious spin-\( \frac{1}{2} \) space.

In this space there is a coordinate frame for each NQR frequency [4,9]. For the \( \omega_x \) NQR frequency \( \dot{\rho} \) is described in the \( \hat{I}_{x1}, \hat{I}_{x2}, \hat{I}_{x3} \) subspace. Figure (6.2) shows the rotation of \( \dot{\rho} \) during an rf pulse for different resonance offsets in a single crystal. After a pulse of \( t_1 \),

\[
\dot{\rho}(t_1) = e^{-i\tilde{H}_1t_1/\hbar} \rho(0) e^{i\tilde{H}_1t_1/\hbar},
\]

(6.3)

where \( \tilde{H}_1 = -\omega_1 \hbar \hat{n} \) creates nutation at a rate of \( \omega_1 = \sqrt{\Delta \omega^2 + \omega_1^2} \) around the axis \( \hat{n} = \cos \alpha \cos \phi_1 \hat{I}_{x1} + \cos \alpha \sin \phi_1 \hat{I}_{x2} + \sin \alpha \hat{I}_{x3} \). Starting from thermal equilibrium and in the high temperature limit, \( \rho(0) = -\hbar \omega_x I_{x3}/(3kT) \), where the terms which do not contribute to the final signal have been neglected. The deviation of the rotation axis from the \( \hat{I}_{x1} - \hat{I}_{x2} \) plane is, \( \alpha = \arctan \frac{\Delta \omega}{\omega_1} \), as shown in inset of Fig. (6.2). After the rf pulse, the different spin isochromats rephase to form an echo, as shown by the horizontal lines on the surface of the sphere. This reversal of spins creates the NQR SPEs that are observed. Therefore the resonance offset, acting as an additional rotation in the \( \hat{I}_{x3} \) direction, serves both to separate the isochromats during the pulse and refocuses them afterwards. The actual refocusing occurs over an extent of
Figure 6.2: The rotation of $\tilde{\rho}$ by the effective rf excitation in the presence of resonance offset effects shows the formation of the SPE. The spin isochromats start at all along $I_{x3}$, are subjected to a $254^\circ$ pulse with $\phi = 0$, and then evolve till they rephase at (B) where an echo is formed at approximately the time $1/\gamma B_1$ after the pulse. The on-resonance spin is labeled $a$ and the amount of resonance offset for each spin progresses to the two spins subjected to the most resonance offset labeled $\pm b$, $b = \gamma B_1/2$.

time, creating an echo which is smeared out temporally. A similar echo effect occurs for a powder sample, but the $I_{x1}$ component of the rotation varies depending on the orientation of the crystallite with respect to the applied radio-frequency. The $I_{x3}$ component of rotation, however does not vary depending on the crystallite orientation; therefore there is less variation in the nutation rate, $\omega_t$, than when there is no off-resonance component in the rotation. For a powder, this means that the EFG inhomogeneities compensates for the Rabi inhomogeneities in a weak-field limit for a rotation of approximately $340^\circ$. 

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Proceeding from Eq. (6.3), at a time $\tau_1$ after the pulse,

$$
\hat{\rho}(t_1 + \tau_1) = -\frac{\hbar\omega_x}{3kT} \left( \frac{I_x^3}{2} (\cos^2 \alpha \cos \Theta_1 + \sin^2 \alpha) - (iI_+D_1 e^{i\delta_1} e^{i(\Delta\omega\tau_1 - \phi_1)}) \right) + h.c.,
$$

where $\Theta_1 = \omega t_1$, $D_1 = \cos \alpha (\sin^2 \Theta_1 + (1 - \cos \Theta_1)^2 \sin^2 \alpha)^{1/2}$, $\delta_1 = \arctan \left( \frac{1 - \cos \Theta_1 \sin \alpha}{\sin \Theta_1} \right)$, and $h.c.$ stands for the Hermitian conjugate. Note that $\Theta$ refers to the effective rotation each spin is subject to while $\theta$ refers to the rotation angle of the rf pulse that is applied during a pulse sequence.

The observable of interest is $<I_x>_{SPE} = \text{Tr}(\rho I_x)$ and using the expressions for fictitious spin-$\frac{1}{2}$, it is determined that,

$$
<I_x>_{SPE} = i\frac{\hbar\omega_x e^{-i\omega_x t}}{6kT} e^{i(\Delta\omega\tau_1 - \phi_1)} D_1 e^{i\delta_1} + c.c.,
$$

where $c.c.$ is the complex conjugate of the first term. This expression is similar to those seen for magnetization in spin-$\frac{1}{2}$ systems subject to Larmor inhomogeneous broadening[97].

To gain insight into the appearance of the SPE, the limit when $\gamma B_1 \gg \Delta \omega$ is analyzed. To first order in $\frac{\Delta \omega}{\gamma B_1}$

$$
\delta_1 \approx \frac{\tan(\gamma B_1 t_1 \cos \xi/2)}{\gamma B_1 \cos \xi} \Delta \omega,
$$

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and

\[ D_1 \approx \sin(\gamma B_1 t_1 \cos \xi), \quad (6.7) \]

where \( \delta_1 \) is the phase and \( D_1 \) is the echo amplitude. An echo-like behavior will occur when the coefficient in front of \( \Delta \omega \) in Eq. (6.6) is negative, i.e., \( 180^\circ < \gamma B_1 t_1 \cos \xi < 360^\circ \). The amplitude, \( D_1 \), is maximum in this range when \( \gamma B_1 t_1 \cos \xi \) is \( 270^\circ \). Under this condition, the echo would occur at \( \tau_1 = \frac{1}{\gamma B_1 \cos \xi} \), which clearly demonstrates the smaller the excitation field, \( B_1 \), the increased time, after the pulse, before the occurrence of the echo.

A signal is observed from the rf pick-up coil with its axis of symmetry along the \( \hat{x} \)-axis. For a powder the average over all possible directions is,

\[
\text{Signal}_{\text{powder}} = \frac{1}{2} \int \int <I_x>_{\text{SPE}} f(\Delta \omega) \cos \xi \sin \xi \, d\xi \, d\Delta \omega, \quad (6.8)
\]

where \( f(\Delta \omega) \) gives the shape of the resonance line. Experimentally the line shapes are Lorentzian, therefore in the foregoing \( f(\Delta \omega) \) is assumed to have a Lorentzian distribution.

To compare the SPE to the DPE, the spin dynamics after a second pulse of the same strength and frequency is
\[ \langle I_x \rangle = \frac{i\hbar \omega_x}{6kT} e^{-i\omega_s t} \{ \]

\[ e^{i(\Delta \omega_{t_2} + \delta_2 - \phi_2)} D_2 (\cos^2 \alpha \cos \Theta_1 + \sin^2 \alpha) \]

\[ + \frac{D_1}{2} e^{i(\Delta \omega(t_1 + t_2) + \delta_1 - \phi_1)} \]

\[ \{ \cos^2 \alpha + \cos \Theta_2 (1 + \sin^2 \alpha) + 2i \sin \Theta_2 \sin \alpha \} \]

\[ - e^{i(\Delta \omega(t_2 - t_1) - \delta_1 - (2\phi_2 - \phi_1))} \]

\[ \{ \cos^2 \alpha + \cos \Theta_2 (\sin^2 \alpha - 1) \} \} + c.c., \]

where \( \Theta_2, \delta_2, \) and \( D_2 \) are defined with respect to the second pulse of width \( t_2 \) and phase \( \phi_2. \)

Figure 6.3: SPE and DPE sequence timing diagram. Note, \( t_2 \) is the time after the second pulse and that \( t = t_1 + \tau_1 + t_2 + \tau_2 \) is the total time.

The first term in Eq. (6.9) corresponds to a free induction decay (FID) from the second pulse, the second term to the FID from the first pulse, and the third term to the DPE, \( \langle I_x \rangle_{DPE} \). One can easily see the third term is the DPE from the fact that the phase goes to zero at \( \tau_2 = \tau_1 \) in the presence of any resonance offset and
in the limit of delta-function pulses. The echo signal for a powder after a double-pulse “Exorcise” [103] sequence, that is phase cycled to leave only the echo, is then calculated from $< I_x >_{DPE}$.

Additionally, the inclusion of the resonance offset effects in Eq. (6.9), predicts the delay ($\Delta \tau$) of the DPE. This delay is defined as the difference between the occurrence of the peak of the DPE due to a weak-pulse with resonance offset effects, compared to the occurrence of the peak of the DPE due to a delta-pulse. Equivalently, $\Delta \tau = t_{echo} - \tau_1$, where $t_{echo}$ is the time of the maximum echo as shown in Fig. (6.3). The model predicts that the delay in the appearance of the maximum DPE approaches $\Delta \tau = 0.62t_1$ at large values of $\gamma B_1/\sigma$ in a powder and is only 2% less at small values of $\gamma B_1/\sigma$. This increased delay compares well to the prediction by Slichter[24] of $\Delta \tau = 2t_1/\pi$ in the case of protons in a static magnetic field irradiated by a perpendicular rf.

Using the model, the SPE, DPE and FID characteristics of a powder and a crystal are plotted in Fig. (6.4). For each value of $\gamma B_1/\sigma$ the rotation angle(s) ($\theta_1$ and/or $\theta_2$) needed to produce the maximum $\text{Signal}_{total}$ are optimized, where $\text{Signal}_{total}$ is the total integrated magnitude of the signal over time and is equivalent to the amplitude in Fourier space at $\omega_x$. In pane (a) the maximum $\sigma \text{Signal}_{total}$ is plotted because it highlights the behavior independent of the line width with constant line shape. The sequence used to generate the DPE has no time between pulses and is phase cycled to leave only the echo. Both the SPE and DPE signals are normalized to the maximum FID due to a delta-pulse with the optimum rotation angle. The time of occurrence of the peak, after the last pulse, is shown in (d) in units of $\sigma t_{echo}$ radians.

Inspecting the graphs, as $\gamma B_1/\sigma$ increases, pane (d) shows that for both a powder and a crystal the maximum SPE occurs near the end of the pulse and nothing distinguishes it from a “free decay.” Additionally, as $\gamma B_1/\sigma$ increases, the other
Figure 6.4: NQR FID, SPE, and DPE characteristics are shown as a function of $\gamma B_1/\sigma$ for both a powder (bottom four panes) and a crystal (top four panes): (a) shows the normalized maximum total signal for each pulse in dimensionless units of $\sigma Signal_{\text{total}}$, (b) shows the normalized maximum signal amplitude in time, (c) shows the rotation angles for the maximum in (a), and (d) shows the time of occurrence of the maximum in (b).

characteristics approach the values predicted by delta-pulse theory. For instance, for the crystal, at large $\gamma B_1/\sigma$, the FID, SPE, and DPE $Signal_{\text{total}}$ approaches 1, while the powder DPE signal approaches 0.83. Also, at large $\gamma B_1/\sigma$, the DPE rotation angles for a powder approach $\theta_1 = 119^\circ$ and $\theta_2 = 238^\circ$ vs. $\theta_1 = 90^\circ$ and $\theta_2 = 180^\circ$ for a crystal. In particular, for large values of $\gamma B_1/\sigma$, notice that for a crystal the DPE
and SPE $\sigma_{Signal_{total}}$ are similar but for a powder the DPE and SPE $\sigma_{Signal_{total}}$ differ significantly.

Contrast this with the $\sigma_{Signal_{total}}$ at small values of $\gamma B_1/\sigma$: for both a powder and a crystal, the DPE and SPE $\sigma_{Signal_{total}}$ are not significantly different. In fact, for a powder, as $\gamma B_1/\sigma$ decreases, the SPE $\sigma_{Signal_{total}}$ approaches the DPE $\sigma_{Signal_{total}}$ and exceeds it. This implies that the SPE behaves like the DPE, with no time between pulses and when it is phase cycled to leave only the echo. Also notice that the maximum amplitude of the signal is reduced, but the $\sigma_{Signal_{total}}$ is not. This means the signal will be stretched out in time, which is shown in the experimental data. Further, in this regime, both the optimum rotation angles and the corresponding $\sigma_{Signal_{total}}$ for a FID signal are decreasing as the dephasing during the pulse starts to dominate the spin dynamics. In comparison, the peak of the SPE occurs further from the end of the pulse, for small values of $\gamma B/\sigma$, allowing for more of the signal to be observed.

The largest variation in the SPE $\sigma_{Signal_{total}}$ occurs in a powder between the $\sigma_{Signal_{total}}$ after an ideal delta-function pulse and the $\sigma_{Signal_{total}}$ after a weak rf producing a small $\gamma B_1/\sigma$ ratio. Thus, increased Rabi inhomogeneous broadening contributes to the detection of these SPEs. Therefore, the model predicts that the SPE will be most noticeable in a powder with small $\gamma B_1/\sigma$ ratios. A small $\gamma B_1/\sigma$ results when the rf pulse is weak and/or the resonance has a large linewidth. Additionally, in this regime the SPE $\sigma_{Signal_{total}}$ is comparable to and can be somewhat greater than the DPE $\sigma_{Signal_{total}}$, as confirmed experimentally in Fig. (6.5).
6.3 Experimental Conditions

The NQR SPE and DPE experiments were conducted at room temperature with two powder samples that contain $^{14}\text{N}$ nuclei: 17 g of the military grade explosive RDX ($\text{C}_3\text{H}_6\text{N}_6\text{O}_6$) at the NQR frequency $|\nu_y| = 3.36$ MHz with a linewidth, full-width at half-max (FWHM), of $524 \pm 25$ Hz, and 40 g of glycine hemihydrochloride ($\text{C}_4\text{H}_{10}\text{N}_2\text{O}_4\text{HCL}$) at the $\nu_x$ frequency of 0.834 MHz with a linewidth of $780 \pm 30$ Hz. Both samples have a predominantly Lorentzian shaped linewidth profile.

The experiments were conducted using a TecMag NQR spectrometer and a different probe for each sample. The probe consisted of the sample at the center of the tuned rf coil which was inside a Faraday cage to minimize rf interference. The probe for the glycine hemihydrochloride experiments had a $Q$ of 30 while the probe for RDX experiments had a $Q$ of 150.

6.4 Experimental Results

The theory developed in the previous section allows us to select samples and design experiments to demonstrate and explore these NQR SPEs. The theory indicates the SPEs will be easier to detect as $\gamma B_1/\sigma$ is reduced since the echo signal will be temporally removed from the experimental deadtime. Using a reduced $\gamma B_1/\sigma$ of 0.43, the appearance and development of the SPE is demonstrated in the inset of Fig. (6.5). The SPE is produced with a pulse of $t_1 = 5$ ms, $B_1 = 0.54$ G, and $\theta_1 = 300^\circ$: $\theta_1$ is selected to generate the maximum SPE by referring to Fig. (6.4)(c). The delta-like pulse (strong-pulse) is $t_1 = 31 \mu$s, $B_1 = 35$ G, and $\theta_1 = 119^\circ$. The SPE clearly appears with fast initial rise and an asymmetrical tail.

$T_2$ effects also impact the echo signal. The theoretical echo data in the inset of Fig. (6.5) is adjusted down by 20 % to fit the experimental echo signal profile. The
adjustment reflects $T_2$ effects during the pulse.

Figure 6.5: In the inset, the emergence of the SPE is demonstrated using glycine hemihydrochloride. The echo (solid line) is shown in comparison to the FID from a delta-like pulse (dashed line). In the main graph is a comparison of the SPE, DPE and the optimum FID signal showing the experimental $Signal_{total}$ for each pulse sequence excluding deadtime. The SPE (solid line) due to a pulse of $B_1 = 1.3$ G is compared to the DPE (dashed line) due to pulses of $B_1 = 1.3$ G and the optimum FID (dotted line) of $B_1 = 35$ G. Under these conditions the SPE $Signal_{total}$ is larger than the DPE and the FID $Signal_{total}$. The deadtime in the main graph is 0.25 ms and is 0.2 ms in the inset.

A further demonstration of the SPE is shown in Fig. (6.6) as the pulse length is increased. The lower graph shows the experimental (dots) and the theoretical (line, Eq. (6.8)) normalized SPE signal as $\theta$ is varied for the same pulse length as in the top graph. In the top graphs of Fig. (6.6) the most negative values indicated the time of occurrence of the maximum theoretical SPE for a particular $\theta$. In (a) and (d) a strong delta-like rf pulse does not show an echo while in (c) and (f) the black
region shows the emergence of the SPE echo with a much weaker rf pulse. Notice that as \( t_1 \) is increased the FID maximum amplitude decreases and the SPE maximum amplitude increases. In (c) and (f) a pulse of \( t_1 = 2.4 \text{ ms} \) is used to irradiate glycine hemihydrochloride, which has a larger linewidth than RDX, and the echo reaches a maximum where predicted (\( \theta = 340^\circ \)) and is more noticeable.

Figure 6.6: Development of an SPE as the pulse length is increased. The top graphs are contour plots of the normalized theoretical SPE signal for specific \( \theta \)'s (x-axis) as the echo evolves in time (y-axis). The bottom graphs show the signal vs. \( \theta \) for the same pulse length as the top graph. In (a) and (d) there is no observable echo after a pulse of \( t_1 = 100 \mu\text{s} \), using RDX, while in (c) and (f) there is a noticeable echo—the black region in (c). In (b) and (e), again using RDX, the echo starts to form about 0.25 ms after a pulse of \( t_1 = 500 \mu\text{s} \) at \( \theta = 345^\circ \). In (c) and (f), using glycine hemihydrochloride, the echo is maximum about 0.5 ms after a pulse of \( t_1 = 2.4 \text{ ms} \). Arrow in (f) points out maximum echo.

Additionally, under certain conditions, the SPE \( \text{Signal}_{total} \) is greater than the DPE \( \text{Signal}_{total} \). In Fig. (6.5), a comparison of the SPE and DPE and the optimum
FID $\text{Signal}_{\text{total}}$ using glycine hemihydrochloride is shown. The SPE and DPE were generated with rf pulses to create the same $\gamma B_1/\sigma$ ratio. The SPE signal, created with $B_1 = 1.3$ G, $t_1 = 2.4$ ms and $\theta_1 = 345^\circ$ (solid line), is compared to the DPE signal, created with pulses of $B_1 = 1.3$ G, $\theta_1 = 116^\circ$ and $\theta_2 = 187^\circ$ (dashed line). The optimum FID is also presented (dotted line - same pulse parameters as in the inset).

The experimental $\sigma \text{Signal}_{\text{total}}$, excluding deadtime, and normalized to the optimum FID, is shown for each pulse. The SPE $\sigma \text{Signal}_{\text{total}} (0.94 \pm 0.02)$ is greater than the DPE $\sigma \text{Signal}_{\text{total}} (0.78 \pm 0.02)$. Theoretically the SPE $\sigma \text{Signal}_{\text{total}}$ is predicted to be 0.96 while the DPE $\sigma \text{Signal}_{\text{total}}$ is 0.98. One possible cause of this difference between predicted and actual DPE $\sigma \text{Signal}_{\text{total}}$ is the breaking of the spin-locking [104] by using phase cycling in the DPE sequence. The phase cycling removes all but the DPE from the signal, but at the cost of breaking the spin-locking, hence, the signal would be lower than predicted. If a lower $\gamma B_1/\sigma$ ratio is used the calculations (Fig. (6.4)a) for a powder show that the SPE will be greater than the DPE $\sigma \text{Signal}_{\text{total}}$, even without this spin-locking effect.

In comparison to the FID both the SPE and DPE $\sigma \text{Signal}_{\text{total}}$ are approximately twice the FID $\sigma \text{Signal}_{\text{total}}$, if the deadtime is taken into account, which shows the potential increase in attainable signal when using these pulse sequences in comparison to the FID. The FID from the strong-pulse has a sharply decreasing amplitude and may be difficult to detect experimentally due to the implementation dependent deadtime. In contrast, the occurrence of the SPE is significantly removed from the trailing edge of the pulse so it is easier to detect experimentally.

In Fig. (6.7), the delay ($\Delta \tau$), predicted by the model, of the occurrence of the DPE is demonstrated. The delay is the difference between the theoretical predictions and the predictions using an ideal delta-pulse. The pulse to generate the DPE is $B_1 = 1.3$ G, $\theta_1 = 116^\circ$, and $\theta_2 = 187^\circ$, while $\theta_1$ and $\theta_2$ are optimized for maximum
DPE signal by referring to Fig. (6.4)(c). Data shows the peak normalized signal decreasing with increasing $\tau_1$, while there is a consistent delay in the formation of the echo. In Fig. (6.7), the echo signal is shown and each data point is the average of 200 $\mu$s of data. The raw echo time data are then fit to a Gaussian (solid lines) because it has been shaped by the pulse and the numerical simulations predict that it is roughly Gaussian under these conditions. The fit of the four data sets result in a $T_2 = 7.6 \pm 0.1$ ms, with a Gaussian standard deviation of $1.32 \pm 0.01$ ms, in comparison to a predicted value of 1.53 ms, and a consistent delay of $\Delta\tau = 0.56 \pm 0.01$ ms in comparison to 0.51 ms. The predictions are generated using Eq. (6.9) and
the differences could be due to non-ideal pulses, and relaxation effects.

6.5 Conclusion

NQR SPEs have been detected for the first time and are well modeled by a theory that incorporates EFG inhomogeneous broadening. The theory demonstrates that the echoes are created by the dephasing and rephasing of the individual spin isochromats that are present in a material with a large EIB. The SPEs occur in a powder when $\theta$ is $\approx 340^\circ$ and they reach a maximum with a low $\gamma B_1/\sigma$ ratio and they disappear at large $\gamma B_1/\sigma$ ratios. This combination of requirements explains why the NQR SPEs have not been observed in previous NQR experiments. Echoes have been observed and predicted by theory in glycine hemihydrochloride and RDX. The theory and experiments allow us to characterize SPEs as temporally asymmetric with a fast initial rise. While the experimental confirmation of this theory utilized samples with a large EIB and a powder sample, which contribute to inhomogeneous Rabi broadening, this theory should be applicable to other systems with inhomogeneous line broadening and inhomogeneous Rabi broadening whatever the cause. A comparison of the theories for SPEs and DPEs shows that the SPE behaves like a DPE with no time between pulses and that the SPE $Signal_{total}$ can be greater than the DPE $Signal_{total}$ under certain conditions. This is shown using glycine hemihydrochloride and a pulse such that $\gamma B_1/\sigma = 1.03$. An analysis of the DPE, using this model, also provides additional insight into the experimentally observed increased delay of the DPE. The delay of the DPE ($\Delta \tau$) is the difference between the theoretical predictions and the predictions using an ideal delta-pulse. The theory predicts $\Delta \tau = 0.62 t_1$ at large values of $\gamma B_1/\sigma$ in a powder and is only 2% less at small values of $\gamma B_1/\sigma$ and this is confirmed by experiments. Therefore, using these techniques, pulse sequences for the detection of
contraband over a large volume can be tuned for an optimum SPE or DPE signal.
Appendix A: Fictitious Spin-$\frac{1}{2}$ Operators

For spin-1 the eigenfunctions of $I_z$ are $|+1\rangle, |-1\rangle,$ and $|0\rangle$. The eigenfunctions of $H_Q$ in the principal axis frame of the electric field gradient are: $|y\rangle = (|+1\rangle + |-1\rangle)/\sqrt{2}, |x\rangle = (|+1\rangle - |-1\rangle)/\sqrt{2}$, and $|z\rangle = |0\rangle$, and have the corresponding eigenenergies: $E_y, E_x,$ and $E_z$. The NQR transition frequencies are: $\omega_x=(E_y-E_z)/\hbar$, $\omega_y=(E_z-E_x)/\hbar$, and $\omega_z=(E_x-E_y)/\hbar$.

The fictitious spin-$\frac{1}{2}$ operators are:

\begin{align*}
I_{x1} &= \frac{1}{2} I_x; & I_{y1} &= \frac{1}{2} I_y; & I_{z1} &= \frac{1}{2} I_z; \\
I_{x2} &= \frac{1}{2} (I_y I_z + I_z I_y); & I_{y2} &= \frac{1}{2} (I_x I_z + I_z I_x); & I_{z2} &= \frac{1}{2} (I_x I_y + I_y I_x); \\
I_{x3} &= \frac{1}{2} (I_x^2 - I_y^2); & I_{y3} &= \frac{1}{2} (I_z^2 - I_x^2); & I_{z3} &= \frac{1}{2} (I_y^2 - I_z^2); \\
I_{x4} &= I_{y3} - I_{z3}; & I_{y4} &= I_{z3} - I_{x3}; & I_{z4} &= I_{x3} - I_{y3},
\end{align*}

and $I_{x\pm} = (I_{x1} \pm i I_{x2})/2$.

These operators meet the condition $I_{x3} + I_{y3} + I_{z3} = 0$, and the power of these operators is in the commutation relationships. A few examples are

\begin{align*}
[I_{p,i}, I_{p,j}] &= 0, \quad (A.1) \\
[I_{p,i}, I_{p,j}] &= i I_{p,k}, \quad (A.2)
\end{align*}

where $i, j, k$ are cyclic and where $p \in (x, y, z)$. 
Appendix B: Ammonium Nitrate Measurements

Table B.1: Ammonium nitrate $T_2$, $T_2^*$, and $T_{2e}$ measurements.

|       | $\omega_y$ | Measure $\omega_y$ at $\gamma_H B_0 = |\omega_z|$ | $\omega_x$ | Measure $\omega_x$ at $\gamma_H B_0 = |\omega_z|$ |
|-------|------------|-----------------------------------------------|------------|-----------------------------------------------|
| $T_2$ | 8 ± 0.7 ms | 2.8 ± 1 ms                                   | 8.9 ± 0.9 ms | 1.45 ± 0.3 ms                                 |
| $T_2^*$| 6 ± 2 ms  | 2.5 ± 0.5 ms                                 | 5.5 ± 0.5 ms | 1.7 ± 0.3 ms                                 |
| $T_{2e}$ at 4.1 ± 0.2 s | 8.3 ± 0.6 ms | 1.8 ± 0.1 s                                 | 8.3 ± 0.6 ms |

Measurements of $T_2$, $T_2^*$, and $T_{2e}$ for four experimental conditions are presented in Table (B.1). The rate of decay of the signal once it is tipped into the $x$-$y$ plane is characterized by $T_2^*$. The spin-spin relaxation time or transverse relaxation, $T_2$, is related to $T_2^*$ by

$$1/T_2^* = 1/T_2 + \gamma \Delta H,$$

where $\Delta H$ the field inhomogeneity [34]. For a relaxation process dominated by the quadrupole interaction the field inhomogeneity is caused by differences in the EFG, for a relaxation process dominated by the Zeeman interaction it is caused by the magnetic field inhomogeneities. In a multipulse sequence, such as SLSE, the second and subsequent pulses cause the spins to refocus and form an echo and the echo signal will decay at a rate characterized by $T_{2e}$. Figure (3.5) shows an example of the change in $T_{2e}$ in a static magnetic field and is discussed in section 3.3.3. $T_2$, $T_2^*$, and $T_{2e}$ are shorter on resonance due to the increased effectiveness of the dipolar coupling at this
condition. This creates linewidth broadening such that over time fewer spins are in phase, corresponding to a loss in signal.

In the column labeled $\omega_y$ in Table (B.1), $T_2$, $T_2^*$, and $T_{2e}$ for $\omega_y$ are measured in Earth’s field. All the $T_{2e}$ measurements are made with a $\tau = 1$ ms. In the next column, those parameters are measured when the double resonance condition $\gamma_H B_0 = |\omega_z|$ is satisfied. In the third $T_2$, $T_2^*$, and $T_{2e}$ for $\omega_x$ in Earth’s field are measured. And in the final column those parameters are measured when the double resonance condition $\gamma_H B_0 = |\omega_z|$ is satisfied. The sample is 800 g of 99.5 % pure ammonium nitrate in solenoid with a filling factor of $\frac{2}{3}$. The data was acquired over a temperature range of 22 °C to 30 °C.
Appendix C: pPAPS

The preparatory pulse phase alternated pulse sequence (pPAPS) includes phase cycling. The pPAPS sequence

\[ t_1 - \tau_1 - (t_2 - \tau_2 - \text{Acq}1 - t_3 - \tau_2 - \text{Acq}2)_N, \]  

(C.1)

where \( t_1, t_2 = t_3 \) are pulse durations, and Acq1 and Acq2 represent the acquisition of the signal data. All pulses are off-resonant at \( \Delta \nu = 1/4 \tau \) and the phases of the pulses and acquisitions are specified in Table (C.1).

![Figure C.1: Timing for pPAPS sequence. \( t_1, t_2, \) and \( t_3 \) are the optimized pulse durations, Acq1 and Acq2 represent the acquisition of the signal data. \( \tau = t_1 + \tau_1 = 993 \, \mu s \). The acquisition and refocusing part of the sequence is repeated \( N \) times.](image)

The pulses are optimized by finding the pulse rotation that creates the largest signal, which is theoretically \( \gamma_N B_1 t_1 = 2.077 \), where \( t_1 \) is the pulse width. All the pulse widths are set to 100 \( \mu s \) and the \( t_1 \) pulse is followed by a wait of \( \tau_1 = 893 \, \mu s \), thus \( \tau = t_1 + \tau_1 = 993 \, \mu s \). The duration of \( t_2 + \tau_2 + \text{Acq}1 = 2\tau \).

The \( (t_2 - \tau_2 - \text{Acq}1 - t_3 - \tau_2 - \text{Acq}2) \) is then repeated for 1400 loops or about 5.6 s. The number of loops was calculated from the optimal SNR of this sequence.
$t_2$ is followed by a wait with Acq1 starting near the midpoint of the echo. The total time of the acquisition is 1032 µs. $t_3 + \tau_2 + \text{Acq2} = 2\tau$.

The optimal number of loops is determined by modeling the signal and the noise. It is well known that the noise is proportional to the $\sqrt{t}$, where $t$ is time. The NQR signal from a multipulse sequence is

$$S \propto \int_0^t (1 - e^{-t'/T_2}) dt',$$  \hspace{1cm} (C.2)

and therefore the SNR is

$$\text{SNR} \propto \int_0^t (1 - e^{-t'/T_2}) dt'/\sqrt{t}.$$  \hspace{1cm} (C.3)

This is optimized when $t = 1.25 \ T_{2e}$ [13].

There are at least three factors in determining the loop time, $\tau$. The first is the pulse duration and shape to obtain the optimum NQR signal. Once the pulse duration is determined then the sequence parameters should then be set so that the echo midpoint starts later than $t_{\text{deadtime}}$. 


Table C.1: The pPAPS phase cycling sequence. The columns are the phases of each pulse or acquisition in the pPAPS sequence. Each row corresponds to one scan and all eight are required for the phase cycling to implement the desired pPAPS sequence.

<table>
<thead>
<tr>
<th>Pulse 1</th>
<th>Pulse 2</th>
<th>Acq 1</th>
<th>Pulse 3</th>
<th>Acq 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>π</td>
<td>π</td>
<td>0</td>
<td>π</td>
</tr>
<tr>
<td>π</td>
<td>π</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>π/2</td>
<td>π/2</td>
<td>3π/2</td>
<td>3π/2</td>
<td>3π/2</td>
</tr>
<tr>
<td>3π/2</td>
<td>π/2</td>
<td>π/2</td>
<td>3π/2</td>
<td>π/2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>π</td>
<td>π</td>
<td>π</td>
</tr>
<tr>
<td>π</td>
<td>0</td>
<td>0</td>
<td>π</td>
<td>0</td>
</tr>
<tr>
<td>π/2</td>
<td>3π/2</td>
<td>3π/2</td>
<td>π/2</td>
<td>3π/2</td>
</tr>
<tr>
<td>3π/2</td>
<td>3π/2</td>
<td>π/2</td>
<td>π/2</td>
<td>π/2</td>
</tr>
</tbody>
</table>
Appendix D: Adiabatic Fast Passage

The Adiabatic Fast Passage (AFP) [24,34] experiment takes advantage of the fact that if the static field is changed slowly (adiabatically) then the \(^1\)H magnetization follows the effective field in the rotating frame.\(^1\) The AFP experiment starts with the sample in a static field and the rf applied perpendicular to it and far from the Larmor frequency in that static field. As \(B_0\) is lowered to approach the resonance condition \(\gamma_H B_0 = \omega_{1K}\) the effective field, and therefore the \(^1\)H magnetization, aligns with \(B_1\). If the sweep is terminated on resonance it is called adiabatic half passage (AHP) [85]. Continuing the sweep past resonance inverts the nuclear magnetization, “adiabatic inversion”. If the rate of the sweep fulfils the criteria for AFP, Eq. (D.1), then the \(^1\)H magnetization will follow the effective field and at the “half passage” condition, exactly on resonance, the \(^1\)H magnetization will lie along the direction of \(B_1\). In this configuration the Rabi plus Larmor double resonance condition can be met.

There are two conditions for the AFP in solids [25]. The static field must change slowly compared to the rf: \(\frac{1}{B_1} |dB_0/dt| \ll \gamma_H B_1\) and the field must change faster than the \(^1\)H spins relax \(\frac{1}{T_{1H}} \ll \frac{1}{B_1} |dB_0/dt|\) which gives the combined constraint:

\[
\frac{1}{T_{1H}} \ll \frac{1}{B_1} |dB_0/dt| \ll \gamma_H B_1, \tag{D.1}
\]

where \(T_{1H}\) is the hydrogen’s relaxation time.

The experiment is setup to met the AFP condition, Eq. (D.1). Assuming \(T_{1H} \approx 3\) s and that the fastest \(dB_0/dt\), without causing oscillations in the static field, is 3600 G/s.

\(^1\)This is also known as adiabatic demagnetization in the rotating frame.
Therefore the largest $B_1$ needed for this experiment, 28 G, meets the conditions. As a further test the rf Rabi oscillations experiment, described in Chapter 4, was implemented using these parameters, instead of using the $\pi$ pulse, and produced similar results to Fig. (5.2).
Appendix E: Sequences for Double Resonance Experiments

There were two main types of sequences used for the experiments. The sequences are described generally in Fig. (E.1) and Fig. (E.2). The main difference was that the sequence in Fig. (E.2) includes the rf that was needed to create some of the double resonance conditions.

E.1 Static Only Double Resonance Experiments

The static field only experiments used the sequence described in Fig. (E.1) with the parameters from Table (E.1). These sequences were used to find the resonance peak, the resonance peak width and measure $W_d$ for static only double resonance conditions.

Table E.1: Static double resonance experiment parameters for the sequence described in Fig. (E.1). The $B_0$ in the table indicates that $B_0$ is set for each experiment, as when trying to find the resonance condition.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$B_{sat}$</th>
<th>$t_{sat}$</th>
<th>$B_{pol}$</th>
<th>$t_{pol}$</th>
<th>$B_{start}$</th>
<th>$t_{sweep}$</th>
<th>$B_{end}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Peak at $\omega_{0K} =</td>
<td>\omega_z</td>
<td>$</td>
<td>36 G</td>
<td>200 ms</td>
<td>27.3 G</td>
<td>20 ms</td>
<td>$B_0$</td>
</tr>
<tr>
<td>2) $W_d$ at $</td>
<td>\omega_z</td>
<td>$</td>
<td>36 G</td>
<td>200 ms</td>
<td>36 G</td>
<td>1 ms</td>
<td>24 G</td>
</tr>
<tr>
<td>3) Peak at $\omega_{0K} =</td>
<td>\omega_y</td>
<td>$</td>
<td>36 G</td>
<td>200 ms</td>
<td>108.5 G</td>
<td>20 ms</td>
<td>$B_0$</td>
</tr>
<tr>
<td>4) $W_d$ at $</td>
<td>\omega_y</td>
<td>$</td>
<td>36 G</td>
<td>200 ms</td>
<td>108.5 G</td>
<td>6.2 s</td>
<td>107.5 G</td>
</tr>
</tbody>
</table>

\footnote{These figures are also included in Chapter 4.}
Figure E.1: General description of the sequence used for double resonance experiments created only with a static magnetic field, $B_0$. The figure shows the $B_0$ applied vs. time during a sequence. While the static field is at $B_{sat}$ a set of saturation pulses are applied for $t_{sat}$. Next $B_0$ is quickly ramped to $B_{pol}$ for $t_{pol}$ and then $B_0$ is quickly ramped down to $B_{start}$ and swept to $B_{end}$ in $t_{sweep}$. The sweep covers the expected resonance at the field $B_{dr}$ symmetrically. The static field is then reduced to zero and the signal is measured in Earth’s field.

### E.2 RF2 Field Experiments

The experiments which require a rf field as part of the double resonance used the sequence described in Fig. (E.2) with the parameters from Table (E.3) for $B_0$ and Table (E.2) for $B_1$.

**Experimental sequence used to determine $W_d$ for the static double resonance condition** $\gamma_H B_0 = |\omega_z|$. In Fig. (5.8) pane (a), the static magnetic field is shown during the sequence. First, a sequence of $^{14}$N saturation pulses are applied at 36 G then the field is quickly ramped down to 24 G and swept to 12 G, which covers the $\omega_z$ FWHM = $5.9 \pm 0.6$ G. The duration of the sweep, $t_{sweep}$, is varied. A typical time of 4 ms is shown in the figure. The resulting $\omega_y$ signal is
Table E.2: Rabi and Larmor double resonance experiment parameters for $B_1$ in the sequence described in Fig. (E.2). The $B_1$ in the table indicates that $B_1$ is set for each experiment, as when trying to find the resonance condition.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$t_{rf \text{start}}$</th>
<th>$B_{\text{1 start}}$</th>
<th>$t_{\text{sweep}}$</th>
<th>$B_{\text{1 start}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5) Peak at $\omega_{1\text{K}}/2 =</td>
<td>\omega_z</td>
<td>$</td>
<td>0</td>
<td>$B_1$</td>
</tr>
<tr>
<td>6) $W_d$ at $\omega_{1\text{K}}/2 =</td>
<td>\omega_z</td>
<td>$</td>
<td>0</td>
<td>33 G</td>
</tr>
<tr>
<td>7) Peak at $\omega_{1\text{K}}/2 + \omega_{0\text{K}} =</td>
<td>\omega_y</td>
<td>$</td>
<td>-1 ms</td>
<td>$B_1$</td>
</tr>
<tr>
<td>8) $W_d$ at $\omega_{1\text{K}}/2 + \omega_{0\text{K}} =</td>
<td>\omega_y</td>
<td>$</td>
<td>-1 ms</td>
<td>23 G</td>
</tr>
</tbody>
</table>

Table E.3: Rabi and Larmor double resonance experiment parameters for $B_0$ in the sequence described in Fig. (E.2). $B_{rf} = \omega_{1\text{K}}/\gamma_K$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$B_{\text{sat}}$</th>
<th>$t_{\text{sat}}$</th>
<th>$B_{\text{pol}}$</th>
<th>$t_{\text{pol}}$</th>
<th>$B_{rf}$</th>
<th>$t_{B_{rf}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5) Peak at $\omega_{1\text{K}}/2 =</td>
<td>\omega_z</td>
<td>$</td>
<td>36 G</td>
<td>200 ms</td>
<td>$B_{rf}$</td>
<td>1 ms</td>
</tr>
<tr>
<td>6) $W_d$ at $\omega_{1\text{K}}/2 =</td>
<td>\omega_z</td>
<td>$</td>
<td>36 G</td>
<td>346.8 ms</td>
<td>108.5 G</td>
<td>20.25 ms</td>
</tr>
<tr>
<td>7) Peak at $\omega_{1\text{K}}/2 + \omega_{0\text{K}} =</td>
<td>\omega_y</td>
<td>$</td>
<td>36 G</td>
<td>200 ms</td>
<td>108.5 G</td>
<td>6 s</td>
</tr>
<tr>
<td>8) $W_d$ at $\omega_{1\text{K}}/2 + \omega_{0\text{K}} =</td>
<td>\omega_y</td>
<td>$</td>
<td>36 G</td>
<td>346.8 ms</td>
<td>108.5 G</td>
<td>6 s</td>
</tr>
</tbody>
</table>

then measured in Earth’s field. Changing the static field much quicker that 36 G/ms results in oscillations in the static field. The results of this experiment are in panes (c) and (d) (blue stars and dashed line).

**Experimental sequence used to determine $W_d$ for the Rabi double resonance condition** $\gamma_H B_1 = |\omega_z|$. In Fig. (5.8) pane (b), the static field, $B_0$, (black) and the rf amplitude, $B_1$, (red dashed line, axis on the right) are plotted during the sequence to measure $W_d$ for the double resonance condition $\gamma_H B_1 = |\omega_z|$ which is also an indirect measure of $K_{x'}$. First, a sequence of $^{14}\text{N}$ saturation pulses
Figure E.2: General description of the sequence used for double resonance experiments created with both a static magnetic field and an rf magnetic field. The figure shows the static magnetic field and the rf (red and dashed lines) applied vs. time during a sequence. While the static field is at $B_{\text{sat}}$ a set of saturation pulses are applied for $t_{\text{sat}}$, not shown. $B_0$ is quickly ramped to $B_{\text{pol}}$ for $t_{\text{pol}}$ and then quickly ramped to $B_{\text{rf}} = \omega_{1K}/\gamma_K$. The static field reaches $B_{\text{rf}}$ at the time $t_{B_{\text{rf}}}$. The rf is applied at the hydrogen’s Larmor frequency starting at $t_{\text{rf start}}$. The strength of the rf pulses are ramped to $B_{1\text{start}}$ and swept to $B_{1\text{end}}$ during $t_{\text{sweep}}$ to cover symmetrically the expected resonance at the field $B_{dr}$ and turned off while the static field is reduced to zero and then the signal is measured in Earth’s field.

are applied at 36 G, and the field is quickly ramped to 108 G for 20.25 ms. Then the field is ramped to $B_{rf}$ in 0.735 µs at 12.2 G/ms, slow enough not to create instrument caused oscillations in the static field and fast enough not to excite $\omega_y$. The rf is applied at the Larmor frequency (362 kHz, $B_{rf}$=85.5 G) and slowly increased to $B_1$=33 G and then swept to 43 G. The duration of the sweep, $t_{\text{sweep}}$, is varied. In this figure $t_{\text{sweep}} = 4$ ms. This is not an adiabatic fast passage experiment since the rf is not turned on until the static field reaches $B_{rf}$.

Experimental sequence used to determine $W_d$ for the static double resonance condition $\gamma_H B_0 = |\omega_y|$. This experimental sequence is also an indirect
measure of $\hat{K}_{x'}$. First, a sequence of saturation pulses are applied to the $^{14}\text{N}$ in 36 G. The static field is ramped quickly to 108 G for 6.2 s. The static magnetic field, $B_0$ (black line) is plotted during the sequence starting just before the sweep. The static field is lowered and the expected $\omega_y/\gamma_H$ condition, $99.07 \pm 8$ G is swept. The time of the sweep is varied from 0.2 ms to 1 s. After the sweep, $B_0$ is lowered quickly to zero so that the $\gamma_H B_0 = |\omega_z|$ resonance is not met. The signal at $\omega_y$ is then measured in Earth’s field.

**Experimental sequence used to determine $W_d$ for the Rabi plus Larmor double resonance condition**, $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$. In Fig. (5.9) pane (b), the static field, $B_0$, (black line) and the rf amplitude, $B_1$, (red dashed line) are plotted during the sequence. First, a sequence of $^{14}\text{N}$ saturation pulses are applied at 36 G then the field is quickly ramped to 108.5 G for 6.2 s. A adiabatic half passage (AHP) experiment is then performed, described in Appendix D. The $B_1$ is turned on and applied at 362 kHz which is not the Larmor frequency. $B_0$ is then slowly lowered to $B_{rf}$ at a rate of 31 G/ms. $B_1$ is also slowly increased so that the magnetization follows the $B_1$. The AHP tips the magnetization of the $^1\text{H}$ by $\pi/2$ so that the double resonance condition $\gamma_H B_1 + \gamma_H B_0 = |\omega_y|$ is met. When $B_1$ reaches 23 G it is swept to 33 G to cover the expected value of the resonance condition, $B_1=28$ G $\pm$ 5 G. The FWHM for the static double resonance at $\omega_y$ is 6.2G $\pm$ 0.8 G. If the sweep began before 23 G a double resonance at 18.9 G would be created and if it continued to increase above 33 G then another double resonance condition at 36 G would be met, thus it was limited to between 23 G and 33 G. The duration of the sweep is varied and the $\omega_y$ signal is measured.
Bibliography
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David Prescott’s initial career was in software design and development of a variety of programs and products morphing into a career as a Internet international telecommunications management consultant. After being enticed by the promise of quantum computing Mr. Prescott decided to pursue a Ph.D. in atomic physics. During his studies at GMU he has published two articles and presented talks and posters at six conferences.