Molecular Structure and Motion in Zero Field Magnetic Resonance

by

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Abstract

Zero field magnetic resonance is well suited for the determination of molecular structure and the study of motion in disordered materials. Experiments performed in zero applied magnetic field avoid the anisotropic broadening in high field nuclear magnetic resonance (NMR) experiments. As a result, molecular structure and subtle effects of motion are more readily observed.

In Chapter 1, the zero field magnetic resonance experiments are introduced. The effects of motion on zero field NMR spectra are the subject of Chapter 2. The chapter begins with an introduction to the Hamiltonian under the effects of motion. This is followed by an experimental example, polycrystalline p-toluic acid. An analytical calculation of the signal function for the hydrogen atoms in hydrogen-bonded p-toluic acid dimers is presented. Experimental spectra are compared to computer simulations based on the analytical calculation. An experiment which monitors the cross-correlation between first and second rank order is introduced. This experiment allows suppression of the zero frequency peak in the zero field spectra. A design of a variable temperature probe, and experimental results at three different temperatures are presented.

Chapter 3 offers a brief introduction to thermotropic liquid crystals, concentrating on a few relevant properties of the nematic phase. Both high field and zero field NMR measurements of CH_2Cl_2 dissolved in a nematic are presented. From these experiments, information on the ordering of the nematic liquid crystalline phase in low and zero applied magnetic field is obtained. Results of a zero field analog of

the Hahn echo and the creation of dipolar order using a zero field analog of the Jeener-Broekaert experiment are also presented.

Chapter 4 presents the results of spectral spin diffusion between two inequivalent methylene deuterons in diethylterephthalate- d_4 . Two-dimensional zero field spectra are presented for two different mixing times, clearly showing the onset of spectral spin diffusion. The effects of a single pulse, and multiple pulse trains on polycrystalline solids are presented in Chapter 5.

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Chapter 1

Introduction

To one only familiar with liquid state NMR, zero field NMR must seem a paradox. One of the interactions that is of interest in high field liquid state experiments, the chemical shift, is irrelevant in zero field. When one considers solids, on the other hand, the solution to the paradox becomes clear. For single crystals, the high field NMR spectra are similar to Figure 1.1. Here the two coupled spin-1/2 nuclei lead to a sharp, well resolved dipole-dipole splitting that depends on the orientation of the internuclear vector with the externally applied magnetic field. Suppose, however, that single crystals of the sample cannot be grown or are difficult to grow, or suppose that the sample is amorphous. Figure 1.1 shows the dipole-dipole coupling spectrum of two coupled spin-1/2 nuclei in a powder in high field. The result of this polycrystalline sample is the famous Pake pattern [1]. Although the Pake pattern allows for straightforward analysis, performing the zero field experiment leads to an even simpler spectrum [2,3].

The powder pattern arises from the application of the magnetic field. When the field is applied, the dipole-dipole coupling Hamiltonian is truncated and becomes dependant upon the angle θ (as $3\cos^2\theta - 1$), where θ is the angle between the

High Field
Crystal

High Field
Powder

Figure 1.1: High field single crystal and high field powder spectra of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$

internuclear vector and the applied magnetic field (see Figure 1.2). Single crystal spectra in Figure 1.3 show that as the crystal rotates to various angles θ , the coupling changes. In the powder where all angles θ are represented, the result is the powder pattern. The shoulders of the pattern arise from the crystallites aligned with the internuclear vectors along the field, the least probable orientation, the horns from those crystallites aligned with the internuclear vectors perpendicular to the field, the most probable orientation.

Zero field NMR circumvents this angular dependence. In the absence of the field, the dipole-dipole coupling is untruncated and is independent of θ . This is so because in zero field, space is isotropic. In isotropic space, all crystallites in the powder have the same coupling and thus, they contribute to the same frequency. The resulting three line spectrum is in Figure 1.4. Although the difference in crystallite orientation does not effect the frequency of the resonance line, it does effect the relative intensity of the three peaks. Figure 1.3 shows the zero field spectra of a single crystal at three different orientations.

The orientation dependence can be explained as follows. Consider the spins themselves as bar magnets, and the evolution in zero field as a precession in the local field of another bar magnet (or magnets). For bar magnets oriented as in Figure 1.5a, the local field of one exerts no torque upon the other. This leads to no precession and thus only a contribution at zero frequency.

The opposite extreme is where the two bar magnets are oriented as in Figure 1.5b. Here, each magnet feels a torque from the other magnet and begins to precess. The result of this orientation is to give rise to the outer peaks only. For crystallite distributions in between these two extremes, one need only break the orientations down into a vector sum of axial and transverse components to find out how much

Figure 1.2: Schematic of two dipole-dipole coupled hydrogen atoms in an applied magnetic field, B . The high magnetic field truncates the dipolar coupling and introduces an angular dependence, θ (the angle between the applied field and the internuclear vector), to the strength of the coupling.

Figure 1.3: Simulated high and zero field NMR spectra of two dipole-dipole coupled spin-1/2 nuclei. Spectra are shown for three single crystal orientations and for a polycrystalline powder. The angles between the internuclear vector and the applied field (high field) or the initial magnetization (zero field) are $\theta = 0^\circ, 45^\circ$ and 90° . In high field, the different crystallite orientations translate into a different NMR frequency. In zero field, the frequency is independent of orientation, only the relative intensities in the peaks change. Thus, as the powder spectrum reveals, zero field NMR often yields better resolved spectra.

I-I Spin Pair

Figure 1.4: Energy levels and allowed transitions for a pair of identical dipole-dipole coupled spin-1/2 nuclei in zero field. Expressed in the principal axis system of the dipolar coupling, the energy levels are $|1\rangle = \frac{1}{\sqrt{2}}(|--\rangle - |++\rangle)$, $|2\rangle = \frac{i}{\sqrt{2}}(|--\rangle + |++\rangle)$, $|3\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle)$, and $|4\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle)$ with corresponding energies $E_1 = -\frac{1}{2}\hbar\omega_D$, $E_2 = -\frac{1}{2}\hbar\omega_D$, $E_3 = \hbar\omega_D$, and $E_4 = 0$ where $\omega_D = \frac{\gamma^2\hbar}{r^3}$. Allowed transitions occur between the triplet energy levels. They are $\omega_{13} = \omega_{23}$ and ω_{12} . The resulting spectrum consists of three lines of equal intensity at $\pm\frac{3}{2}\omega_D$ and at zero frequency.

Figure 1.5: (a) Two bar magnets oriented in this manner will not exert torque on one another. Two dipole-dipole coupled spin-1/2 nuclei belonging to a crystallite oriented with the internuclear vector along the sudden field switching axis will respond similarly and only contribute to a peak at zero frequency. Two bar magnets oriented as in (b) will exert torque on one another and precess. Similarly, a crystallite oriented with the principal axis of the dipolar coupling perpendicular to the applied field will undergo evolution when that field is suddenly removed, thus contributing to peaks at $\pm \frac{3}{2}\omega_D$.

intensity they will contribute to the zero frequency peak or the peak at the dipole frequency.

The value of the zero field NMR experiment cannot be readily appreciated with this simple example. This thesis will hopefully convey, however, the usefulness of the experiment to samples such as liquid crystals, or samples where motion is present.

Another type of experiment discussed in this thesis is zero field NQR of deuterium [2,3]. Deuterium is a quadrupolar nucleus with a spin angular momentum of 1. The high field spectrum of a single deuterium site in a molecule is quite similar to the spectrum of two dipole-dipole coupled spin-1/2 nuclei. The zero field spectrum, on the other hand, is in most cases quite different. Both the zero field energy level diagram and schematic zero field spectrum for deuterium are shown in Figure 1.6. The sharp peaks of the zero field spectrum allow an easy calculation of the quadrupolar coupling constant, e^2qQ , and the asymmetry parameter, η . Assignment of these values from a the high field spectrum is much more laborious.

The value of the zero field NQR experiment becomes much more prominent when dealing with more than one deuterium site. Figure 1.7 shows the high field and zero field spectra of perdeuterated diethylterephthalate. Here the high field spectrum is sharp, but the superposition of the powder patterns from different quadrupolar sites makes the assignment of the peaks difficult. In the zero field spectrum, four distinct regions corresponding to the ν_+ and ν_- lines of the aromatic and methylene, the methyl resonances and the ν_0 lines (in order of decreasing frequency) are observed. From this spectrum, quadrupole coupling constants and small asymmetry parameters can be calculated and assigned to five inequivalent sites (two aromatic, two methylene and one methyl) in this molecule. The quadrupolar coupling constant and asymmetry parameter are quite sensitive to the local environment of the

Figure 1.6: Energy level diagram and allowed transitions for a single spin-1 nucleus with $\eta \neq 0$ in zero field. In the principal axis system of the electric quadrupole the energy levels are $|1\rangle = \frac{1}{\sqrt{2}}(|-1\rangle - |+1\rangle)$, $|2\rangle = \frac{i}{\sqrt{2}}(|-1\rangle + |+1\rangle)$, and $|3\rangle = |0\rangle$ with corresponding energies $E_1 = (1 - \eta)A_q$, $E_2 = (1 + \eta)A_q$, and $E_3 = -2A_q$. Transitions occur between all three levels at frequencies corresponding to ν_+ , ν_- and ν_0 where $\nu_0 = \nu_+ - \nu_-$. When $\eta = 0$, the $|1\rangle$ and $|2\rangle$ energy levels are degenerate and the spectrum reduces to three lines similar to the zero field spectrum of two dipolar coupled spin-1/2 nuclei.

Figure 1.7: (a) High field (4.2 T) spectrum and (b) zero field spectrum of perdeuterated diethylterephthalate. In the high field spectrum, three powder patterns are superimposed upon one another. In the zero field spectrum, on the other hand, the ν_+ and ν_- lines of the different chemical groups; aromatic, methylene and methyl, and the ν_0 lines are separate and distinct.

quadrupolar nucleus. Thus, one would expect different, characteristic deuterium to see different characteristic spectra depending upon, for example, motion, type of bond and proximity to the aromatic rings.

A quick glance at the periodic table suggests that if zero field NMR is useful for obtaining spectral parameters for deuterium, then it might be suitable for much of the periodic table as well. In fact, much spectroscopy has been done in zero field on other quadrupolar nuclei, as well as, deuterium [4,5]. The difference, however, is that those previous studies were frequency domain experiments whereas this experiment is a time domain experiment. The problem with the frequency domain experiments is that the low frequency ν_0 lines often cannot be resolved due to power broadening [6]. This is especially true for small values of η . Although A_q and η can be assigned from the ν_- and ν_+ lines alone, the ν_0 line is necessary for proper assignment of which ν_- line corresponds to which ν_+ line when more than one inequivalent quadrupolar site is present.

1.1 The Hamiltonians

Two interactions, the dipole-dipole or dipolar and the quadrupolar, are important in this thesis. Due to their importance, a brief introduction is in order.

1.1.1 Dipolar

The dipole-dipole Hamiltonian for two coupled spins is

$$H_D = -\frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} \left[\frac{3(\mathbf{I}_1 \cdot \mathbf{r})(\mathbf{I}_2 \cdot \mathbf{r})}{r_{12}^2} - \mathbf{I}_1 \cdot \mathbf{I}_2 \right] \quad (1.1)$$

where r_{12} is the internuclear vector. Often, the Hamiltonian is written in a principal axis system where the z-axis is along the internuclear vector

$$H_D = -\frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} (3I_{1z} I_{2z} - \mathbf{I}_1 \cdot \mathbf{I}_2) \quad (1.2)$$

When expressed in an arbitrary frame, the Hamiltonian can be broken down into the sum of six terms, the dipolar alphabet, as

$$H_D = -\frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} [A + B + C + D + E + F] \quad (1.3)$$

$$A = I_{1z} I_{2z} (1 - 3 \cos^2 \theta)$$

$$B = -\frac{1}{4} (I_1^+ I_2^- + I_1^- I_2^+) (1 - 3 \cos^2 \theta)$$

$$C = -\frac{3}{2} (I_1^+ I_{2z} + I_{1z} I_2^+) \sin \theta \cos \theta e^{-i\phi}$$

$$D = -\frac{3}{2} (I_1^- I_{2z} + I_{1z} I_2^-) \sin \theta \cos \theta e^{i\phi}$$

$$E = -\frac{3}{4} I_1^+ I_2^+ \sin^2 \theta e^{-2i\phi}$$

$$F = -\frac{3}{4} I_1^- I_2^- \sin^2 \theta e^{2i\phi}$$

where the angles θ and ϕ relate the principal axis frame to the applied magnetic field.

In the presence of a large applied magnetic field, the Hamiltonian is truncated to give the secular Hamiltonian consisting of the A and B terms only

$$H_D^0 = -\frac{\gamma_1 \gamma_2 \hbar}{2r_{12}^3} [3I_{1z} I_{2z} - \mathbf{I}_1 \cdot \mathbf{I}_2] (3 \cos^2 \theta - 1) \quad (1.4)$$

The Hamiltonian can also be represented in spherical notation

$$H_D = \frac{\gamma_1 \gamma_2 \hbar}{2r_{12}^3} \sum_{m=-2}^{+2} (-1)^m A_{2m} T_{2-m} \quad (1.5)$$

Where A_{2m} are the spatial components and T_{2-m} the spin components of the Hamiltonian.

1.1.2 Quadrupolar

The Hamiltonian for the quadrupolar nucleus interacting with the electric field gradient at the nucleus is

$$H_Q = A_q[3I_z^2 - \mathbf{I}^2 + \eta(I_x^2 - I_y^2)] \quad (1.6)$$

with $A_q = \frac{e^2qQ}{4I(2I-1)}$ and the asymmetry parameter, η . The asymmetry parameter is a measure of the deviation of the electric field gradient from cylindrical symmetry. The value of the asymmetry parameter is restricted to $0 \leq \eta \leq 1$.

1.2 The Sudden Experiment

Ideally, a time domain experiment is performed by simply placing a sample in a pickup coil, applying a resonant magnetic pulse to disturb the thermal equilibrium spin state populations, and collecting the data in real time. For certain quadrupolar nuclei this scheme is possible. In most cases, however, this method, while appealing, is unrealistic. The problem with such an approach is twofold: sensitivity of the conventional Faraday detector increases with frequency, and sensitivity depends upon polarization of the sample. Sensitivity of a Faraday detector can be expressed as follows

$$|\varepsilon| \sim d\phi/dt \sim \omega M \quad (1.7)$$

where ε , the electromagnetic force, will be related to a measured voltage induced in the coil; ϕ is the magnetic flux through the coil; ω is the resonance frequency; and M is the polarization.

The frequencies of interest in this thesis are proton-proton dipole-dipole couplings (~ 1 -50kHz) and deuterium quadrupole couplings (~ 150 kHz). These frequencies are not high enough to be detected directly using a conventional Faraday detector.

Sensitivity in NMR is increased by placing the sample in a larger magnetic field. When sample is placed in an external magnetic field, the resonance frequency increases linearly with applied field strength (this of course in the high field limit where the Zeeman frequency is much larger than the local interaction). Polarization given by the Curie Law, increases with applied magnetic field strength as:

$$M_0 = \frac{N\gamma^2\hbar^2 I(I+1)B_0}{3kT} \quad (1.8)$$

Thus, the magnetization (polarization) is dependent upon the number of spins N , the gyromagnetic ratio (which will determine the energy level separation in the field), the static field strength B_0 , and the temperature T . In the absence of an applied field, B_0 is the local field. Local fields in these experiments are ~ 10 G for proton-proton dipole couplings to ~ 200 G for deuterium quadrupole couplings. These values are certainly much smaller than the $10^4 - 10^5$ G of superconducting magnets.

To avoid the insensitivity of the coil at low frequencies and to ensure a large polarization, both preparation and detection are performed in high field. The experiment proceeds as follows. After allowing the sample to reach equilibrium magnetization in a large magnetic field, the field is suddenly switched off. Following the sudden transition to zero field, $[\rho_0, H_{z,f}] \neq 0$ ($\rho_0 = I_{z,L}$, magnetization in the laboratory frame along the z -axis) and evolution is initiated. At this point, it would be desirable to measure the zero field FID (free induction decay) directly, in zero field, and in real time. However, although we now have a large polarization, the frequencies are still too low for the Faraday detector. Detection can, however, be performed back in the high magnetic field. After the sudden transition to zero field disturbs the equilibrium, evolution is allowed to proceed for a time t_1 . The large static magnetic field is then reapplied, thereby locking a component of the magnetization, and the magnetization measured, in high field, in t_2 . By repeating this field cycling scheme

for an increasingly incremented zero field time interval, t_1 , the magnetization as a function of t_1 is monitored, and the FID, or strictly speaking, an interferogram is plotted out point by point.

Thus, the zero field experiment is a two-dimensional experiment [7]. The initial high field period is analogous to the preparation, the first field cycle is analogous to the pulse that initiates t_1 , while the second field cycle is analogous to the pulse that terminates t_1 . Once in high field, another pulse initiates t_2 . For most of the zero field experiments, however, the information in t_2 will be ignored, and t_2 simply used to monitor t_1 . It is possible, however, to perform a true two-dimensional high field versus zero field experiment where both time dimensions are monitored. Such an experiment was performed by Zax and Bielecki [2]. This experiment shows the correlation between the lines in zero field and the powder pattern in high field. Computer simulations for a single spin-1 or two dipolar coupled spins-1/2 with zero and nonzero η have been done [8].

In the experiments performed here the preparation and detection are performed in a superconducting magnet and, as a result, field switching is most easily implemented as a two step process. Instead of switching off the 4.2 kG superconducting magnet, the sample is pneumatically shuttled out of the magnet bore, into the fringe field (100 or 300 G). Once in the fringe field, a secondary electromagnet is suddenly switched on to cancel the fringe field and initiate the zero field evolution period. At the end of t_1 , the electromagnet is switched off, and the sample shuttled back into the high field region where the magnetization is measured. This is schematically shown in Figure 1.8.

In practice, the low field section is a bit more complicated than previously described. The electromagnet in low field has two desired properties: high homogeneity

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Figure 1.8: Schematic of the experimental field cycle. After preparation in the large magnetic field B_0 , the sample is shuttled pneumatically out of the magnet to an intermediate field, B_{int} , where $B_{int} > B_{loc}$. This step is performed adiabatically. The intermediate field is then reduced to zero suddenly and t_1 , the zero field period, initiated. Sudden reapplication of B_{int} terminates t_1 and preserves the z component of magnetization. The sample is then adiabatically returned to B_0 where the signal, $S(t_1)$, is detected.

and fast switching. A highly homogeneous field dictates that the coil be large in volume compared to the sample. Large volume in turn leads to a larger inductance in the coil and therefore a slow response time. To avoid this problem, the low field section consists of two coils. One is large, homogeneous, and slow switching; the other is small and rapid switching. A typical low field cycle and a schematic of the apparatus appear in Figure 1.9. Implementation of the field cycle is as follows. After the sample arrives in the fringe field, the small intermediate field (IF) coil is switched on. The field direction of the small coil adds to the fringe field. At the same time, the large coil is switched on; its field opposes the fringe field. When the large, or bucking coil is fully on, the small coil is suddenly switched off, and zero field is attained. A scheme opposite to this is followed at the end of the zero field period. Note that the field generated by the small coil need not be related to the intensity of the fringe field, but must meet the criteria of equation 1.9.

When implementing the field cycle, there are a number of timing and field strength parameters that need to be taken into consideration. The sample must be removed adiabatically from the superconducting magnet. Here, adiabatic in both the thermodynamical and quantum mechanical sense are important. The sample should be removed faster than T_1 , thus preserving polarization. And, the sample should be removed slowly enough such that the spins are always in a state of internal equilibrium, that is, slower than T_2 .

The fringe field where the sample stops (also the field generated by the IF coil) must be larger than the local interaction; the Larmor frequency must be greater than any of the natural zero field frequencies. A value for the minimum field strength necessary is determined by the following equation

$$B_i = \omega_{max}/\gamma \quad (1.9)$$

Figure 1.9: Schematic of the low field coils, and graphs of field vs. time for the switching of the electromagnetic coils. The field, B_0 , corresponds to the high field (4.2 T) generated by the superconducting magnet. The coils B_1 and B_2 correspond to the zero field (bucking) coil and the intermediate field (IF) coil, respectively. B_1 is homogeneous and slow switching, B_2 is less homogeneous and rapid switching. At right, the field profiles of the different coils are illustrated. The top drawing shows the fringe field of the superconducting magnet, B_0 , experienced by the sample as it shuttles to and from the low field region. In the middle two drawings, the switching of the bucking coil, B_1 , and the fast switching IF coil, B_2 , are shown. The combination of the three leads to the field cycle shown at the bottom.

where B_i is the intermediate or fringe field, ω_{max} is the maximum zero field frequency of the sample, and γ is the gyromagnetic ratio of the nucleus. For dipole-dipole coupled protons, a 100 G intermediate field is used. For deuterium, the intermediate field is 300 G.

An intermediate field that is not strong enough will lead to two problems. First, if the intermediate field approaches the minimum field strength of equation 1.9, level crossings or avoided crossings may occur. Second, below the minimum field strength, the state of the system will be not well defined. Phase errors and other distortions in the spectra result from these problems.

The next step then is the sudden removal of the intermediate field. This sudden switching time, τ_s , must be faster than the largest natural zero field frequency ω_{max}

$$\tau_s \ll 1/\omega_{max} \quad (1.10)$$

The switching time for the IF coil of 0.3 μ sec meets this criteria.

More complete discussions of the zero field experiment are found elsewhere [2,47, 48].

1.2.1 Calculation of the Signal

The signal as a function of time spent in zero field, t_1 , is calculated as an expectation value of the detected operator. In the sudden experiment, the detected operator is $I_{z,L}$ (magnetization in the laboratory frame along the z-axis). Thus, the signal is

$$S(t_1) = Tr\{I_{z,L}\rho(t_1)\} \quad (1.11)$$

where $\rho(t_1)$ is the density operator after time evolution under the zero field Hamiltonian. This time evolution of the initial state, $\rho(0)$, is

$$\rho(t_1) = e^{-iH_{zf}t_1}\rho(0)e^{iH_{zf}t_1} \quad (1.12)$$

In the sudden experiment the initial state is $I_{z,L}$. To simplify the calculation the initial state is rotated into the molecular frame where calculation of the evolution under the zero field Hamiltonian is most conveniently expressed. This is accomplished by the use of a rotation operator $R(\alpha, \beta, \gamma) = R(\Omega)$ [20]. After evolution, rotation back into the laboratory frame allows the expectation value with $I_{z,L}$ to be calculated. Thus, the signal function is

$$S_{\Omega}(t_1) = \text{Tr}\{I_{z,L}R^{-1}e^{-iH_{z,L}t_1}R\rho_L(0)R^{-1}e^{iH_{z,L}t_1}R\} \quad (1.13)$$

At this point, the signal function contains angular dependence, Ω , relating the individual crystallite orientations to the laboratory frame. The signal function must be integrated over all possible orientations to yield the powder average

$$S(t_1) = \int_{\Omega} S_{\Omega}(t_1)P(\Omega)d\Omega \quad (1.14)$$

where $P(\Omega)d\Omega = \sin\beta d\beta d\alpha d\gamma$.

The calculated signal for the sudden experiment of two dipole-dipole coupled spin-1/2 nuclei is

$$S(t_1) = \frac{1}{3}[1 + 2\cos(\frac{3}{2}\omega_D t_1)] \quad (1.15)$$

This fits the experimental signal with 1/3 of the intensity at zero frequency and 2/3 of the intensity at $\pm\frac{3}{2}\omega_D$.

For a spin-1 nucleus with an asymmetry parameter, η , the calculated signal is

$$S(t_1) = \frac{1}{3}\{\cos[2\eta A_q t_1/\hbar] + \cos[(3 - \eta)A_q t_1/\hbar] + \cos[(3 + \eta)A_q t_1/\hbar]\} \quad (1.16)$$

this fits the experimental signal with 1/3 of the signal at ν_0 (the first term), ν_- (the second term), and ν_+ (the third term).

1.3 The Adiabatic Demagnetization Experiment

An alternative to the sudden experiment, and one that is frequently discussed in this thesis, is complete adiabatic demagnetization to zero field. In the adiabatic demagnetization experiment, dc magnetic field pulses initiate and terminate the zero field period where evolution occurs. The field cycle is shown in Figure 1.10a.

Following a complete demagnetization to zero field, the eigenstates of the spin system in the sample will be those of the zero field Hamiltonian [12]. This will occur, however, only if the demagnetization is adiabatic in the quantum mechanical sense. That is, the rate of demagnetization must be slower than the natural frequencies of the sample.

$$1/\tau_{\text{demag}} \ll \omega_{\text{natural}} \quad (1.17)$$

This criterion is easily met in the experiments performed here. Adiabatic demagnetization in the thermodynamic sense is desired to preserve the populations. However, in many samples relaxation in low fields is rapid.

The adiabatic demagnetization from the high field to the intermediate field (100 or 300 G) was already described. Once in the intermediate field, instead of switching on the bucking coil and the IF coil, only the bucking coil is switched on. The field cycle follows the trajectory in Figure 1.10b. The final demagnetization rate can be adjusted by adding or removing inductance in series with the bucking coil. With the present instrumentation, the time to demagnetize from the low field to zero field can be adjusted from 1 to 40ms, a value that easily satisfies equation 1.17.

Once in zero field, $[\rho_0, H_{zf}] = 0$ and no evolution occurs. To initiate evolution a dc pulse is applied. The direction of the pulse in the lab frame is unimportant. all three orthogonal directions lead to the identical result. After t_1 , a second pulse along the same laboratory axis as the first pulse is applied to terminate the zero field

Figure 1.10: (a) Schematic of the field cycle used in the complete demagnetization to zero field experiment. Following demagnetization to zero field, evolution is initiated by a dc field pulse, θ . t_1 is terminated by a pulse θ' and the sample adiabatically returned to high field where the signal, $S(t_1, \theta, \theta')$, is sampled. (b) A schematic of the field cycle depicted in (a) with the characteristics of the coils included. After the sample is pneumatically shuttled to the intermediate field, the bucking coil is switched on and the field decreases exponentially to zero. Following the zero field period, the bucking coil is switched off, the field increasing exponentially to the intermediate field, and the sample shuttled from the intermediate field up to high field.

period, the bucking coil is switched off, and the sample returned to high field for the detection period.

As one might expect, application of the pulsed dc fields is not arbitrary. Indeed, the effects of the pulsed dc fields on the spin system in zero field are analogous to RF pulses in high field. The flip angle θ of the dc pulse will depend upon the pulse length, τ , and the dc field strength B as

$$\theta = \gamma B \tau \quad (1.18)$$

The best method for determining θ as a function of τ is to perform a calibration experiment in which a single pulse is applied in zero field. Such an experiment can be easily done in either of two ways illustrated in Figure 1.11. In the first method, the sample is suddenly brought to zero field, and immediately a pulse of width τ is applied. Following termination of the pulse, the intermediate field is suddenly reapplied and the magnetization measured in high field as a function of τ . Given the initial condition of $\rho_0 = I_{x,L}$ prior to the pulse, this method only works for measuring the flip angle dependence of transverse coils. An example of such a coil calibration curve is shown in Figure 1.12a. Note that the precise determination of a 90° pulse, often the pulse length desired, will not be precise with this method. In the second method, the initial state prior to the pulse will be some form of zero field order. Spatial symmetry of this initial condition allows this method to be used for all three orthogonal coils. A resulting coil calibration curve is shown in Figure 1.12b. With complete demagnetization to zero field, the 90° pulse as well as every 90° increment afterwards is readily interpreted. This method of coil calibration is quite similar to the time domain low field NMR experiment of Strombotne and Hahn [13]. The only difference is that they used a sudden transition back to high field following the low field period.

Figure 1.11: Two methods for determining flip angle, θ , as a function of pulse width, τ . In (a) the sample is suddenly brought to zero field. Following a delay of $0.1 \mu\text{sec}$ (which allows the intermediate field to reach zero), a dc field pulse of width, τ is applied. When the dc pulse field is turned off, a second $0.1 \mu\text{sec}$ delay precedes the sudden reapplication of the field and trip to high field where $S(\tau)$ is monitored. With an initial condition of $I_{x,L}$ prior to the pulse, this field cycle works only for measuring the flip angle dependence of transverse coils. A sample calibration curve is presented in Figure 1.12a. (b) After the sample is brought adiabatically to zero field, a dc pulse of length τ is applied. Following the pulse, the sample is adiabatically returned to high field where $S(\tau)$ is monitored. With an initial condition of zero field order, all three orthogonal coils are calibrated with this method. A sample calibration curve is presented in Figure 1.12b.

Figure 1.12: (a) Coil calibration curve of a transverse coil determined by the method described in Figure 1.11a. (b) Coil calibration curve determined by the field cycle of Figure 1.11b.

The decay of the pulse calibration curves is attributed primarily to inhomogeneity in the pulsed dc field. This effect can be drastically lessened by increasing the size of the coil (with the trade-off in slower rise time or larger power requirements), decreasing the volume of the sample, using a better coil design, or by using composite pulses.

While performing these experiments, the pulse strengths were varied over a wide range, but usually within a range such that pulse widths varied from 0.8 to 5 μsec for a 90° pulse for protons.

Calculation of the signal in the adiabatic demagnetization two pulse experiment is straightforward with one exception; the initial condition is often not well known. However the initial condition has the constraint that ρ_0 must commute with the zero field Hamiltonian. In large, infinitely coupled spin systems, where spin temperature arguments are completely valid, the initial condition is readily described. Such systems, however, are impractical to study by zero field NMR. In the spin systems that are of most interest for zero field experiments, small isolated dipolar coupled spin systems or quadrupolar nuclei, the spin temperature hypothesis does not hold. As a result, all we can say with certainty is that $[\rho_0, H_{zf}] = 0$. Zax has arrived at a possible value of $\rho_0 \propto (3I_z^2 - I^2) + (I_x^2 - I_y^2)$ for isolated pairs of spin-1/2 nuclei or isolated spin-1 nuclei [30].

Calculation of the signal is similar to that previously discussed for the sudden experiment. Here, however, the initial density operator is in the molecular frame and must be rotated to the laboratory frame where the dc pulses are applied. The signal function is expressed as

$$S_N(t_1) = \text{Tr} \{ \rho(0) R e^{-i\theta' I_{z,L}} R^{-1} e^{-iH_{zf} t_1} R e^{-i\theta I_{z,L}} R^{-1} \rho(0) R e^{i\theta I_{z,L}} R^{-1} e^{iH_{zf} t_1} R e^{i\theta' I_{z,L}} R^{-1} \} \quad (1.19)$$

where the pulses are applied, in this example, along the laboratory z-axis. The magnetization detected in high field is assumed to be proportional to the initial state. This assumption is based on the symmetry of the demagnetization/remagnetization.

To ensure a proper response from the pulses, two criteria should be followed: the strength of the pulse should be larger than the largest spin interaction, and the pulse length sufficiently short such that evolution is negligible during the pulse time. the excitation bandwidth, $\Delta\omega$, of the dc pulse is related to the pulse length by

$$\Delta\omega \simeq 1/\tau \quad (1.20)$$

For deuterium this dictates that a 90° pulse must be shorter than $5 \mu\text{sec}$.

The effect of the initial pulse is to rotate a portion of the populations into coherences. Evolution of the coherences under the zero field Hamiltonian will then occur. The effect of the second pulse is to rotate these coherences back into populations.

If this experiment is to be performed on, for example, a pair of spin-1/2 nuclei, an initial pulse of $\theta = 90^\circ$ will give maximum signal. The terminating pulse will give the most signal if $\theta' = -\theta$. $\theta' = \theta$ will work, but the magnetization will be opposed to the field and therefore decreased by T_1 .

In principle, the signal for this experiment should be identical to that of the sudden experiment. In practice, however, the signal, although identical in phase and relative intensity of the peaks, is less in absolute intensity. Certainly, this can be explained by details that are usually ignored such as level crossings between less than completely isolated spins or groups of spins, and more effective relaxation in the lower fields.

Although this field cycle is not as good from the point of view of signal-to-noise as the sudden experiment, it is worthwhile because this field cycle is an important tool in deuterium NQR. This important experiment involves the indirect observation

of the deuterium spectrum via direct observation of the protons.

Briefly, the experiment proceeds as follows. After polarization in high field the sample is adiabatically shuttled to zero field. During the demagnetization, in the low field region, the energy levels of the protons and deuterons will be equal. At this point, the populations of the energy levels come into contact and equalize. Once in zero field, a pulse is chosen such that deuteron evolution is initiated while the protons remain undisturbed. After t_1 , the termination pulse is applied, the sample passed through the energy level equalization point in low field where the deuterons pass zero field evolution information to the protons, and the sample returned to high field where detection is performed on the protons.

Certainly the detection of deuterium can be accomplished directly, so is why indirect detection used? Due to the difference in gyromagnetic ratios of the proton and deuteron, the equilibrium magnetization of these nuclei in high field is quite different. Thus, the signal intensity from an identical number of spins would be greater for the protons. Additionally, as shown previously, the sensitivity of the detector depends upon the frequency, and the resonance frequency of protons in high field is higher than that of deuterons by a factor of six. This results in a larger signal from the protons.

These reasons are straightforward enough, but two other major factors contribute to the value of this experiment. First, the T_1 of protons is often more suitable for the zero field experiments than the deuteron T_1 , which is often inconveniently long, or too short to survive shuttling. In the indirect detection experiment, proton T_1 is the relevant time. Second, even though spin temperature arguments are not strictly correct (remember, only small spin systems are considered), one can assign a spin temperature to the two spin systems. Where a spin temperature treatment is fully

valid, the proton spin system will be colder by a factor of ~ 15 when the sample is in high field. This colder spin temperature is due to the larger energy level separation of the protons compared to the deuterons in high field. It is known, however, that the energy level separation in zero field is reversed. Therefore, somewhere along the demagnetization pathway, the energy levels contact one another and equalize their populations. This polarization transfer results in a large increase in deuteron polarization. Diagrams of the energy levels of protons and deuterons as the field goes from high field to zero field are displayed in Figure 1.13. From this, we can see that the energy levels of the protons and deuterons will equalize in a field of approximately 10 to 50 G.

Once in zero field, a dc pulse initiates evolution. The excitation bandwidth of this pulse is stated in equation 1.20. With pulse times of 0.8 to 5 μsec , the bandwidth of the dc pulse will be large enough to excite both the protons and deuterons. We do not, however, want the protons to undergo any evolution during the zero field period, for to do so would certainly complicate and degrade the deuteron signal. This is because of the proton-deuteron level matching and polarization transfer that occurs during the remagnetization step. To avoid this, all that is required is to apply a 2π pulse to the protons. Such a pulse will be a 60° pulse for the deuterons, quite sufficient to create coherences that evolve during the zero field period.

To terminate the zero field period and bring these coherences back into populations, a -2π proton pulse is applied. Upon remagnetization, the deuteron populations will have changed and an equalization of populations will occur again. This, then, is what is measured back in high field when the proton magnetization is detected.

In summary, the advantages to this technique are threefold: increased sensitivity

Figure 1.13: Transition frequency for protons and deuterons vs. applied magnetic field strength in low field. Where the proton and deuteron frequencies match, transfer of polarization from one nucleus to the other is possible. This transfer allows indirect detection of the deuterons through the protons. Also, the energy level match often results in a large increase in the deuteron polarization.

of proton detection, enhanced polarization of the deuterons resulting from the level crossing, and the more favorable dependence upon proton T_1 . A disadvantage is the loss of intensity information in the spectrum. This loss of intensity information results from an inequitable polarization transfer, owing to different contact times, between the various levels of the deuterons.

One should be aware that many of the ideas discussed above for the field cycling experiments are not new. Experiments involving low field and zero field magnetic resonance are well established [13,14,4,5]. Field cycling techniques are also employed in the study of demagnetization effects and low field relaxation [11,12,9,10]. The experiments discussed here differ from those previous experiments, which are predominantly frequency domain experiments. Certain quadrupolar nuclei, on the other hand, such as ^{35}Cl where the zero field frequencies are 35MHz, are directly detected in the time domain. Also, new experiments involving directly detected low field and zero field signals with a dc SQUID are currently underway [17,18,19,21,22,23].

1.4 High Field Detection

Once the sample is returned to the high magnetic field, the signal as a function of t_1 must be recorded. In an experiment where one is interested in the zero field spectrum by itself, the magnitude of the high field signal as a function of t_1 is the important quantity (the initial amplitude of the high field FID). An initial 90°_x , followed by the application of a θ_y pulse train allows repeated sampling of the initial FID amplitude. This detection sequence is known as pulsed spin-locking [24,25,26, 27]. Another sequence, valuable for separating the signals from a multicomponent system on the basis of differing T_2 's, employs a 180°_z pulse prior to the spin-lock pulse train. These sequences are depicted in Figure 1.14. In practice, the pulsed

Figure 1.14: High field detection sequences. (a) Application of the pulsed spin-lock train of multiple echos allows multiple sampling of the echo amplitudes. The echo amplitudes are averaged for increased signal-to-noise and assigned as a single t_1 point. The best angle for the echo pulses, usually between 45° and 90° , is determined empirically. (b) This sequence is employed with samples such as liquid crystal/solute mixtures where the signals from the two components can be separated on the basis of differing T_2 values.

spinlocking does improve the signal-to-noise ratio by an appreciable amount. The increase in signal-to-noise varies widely from sample to sample due to differences in the ability of a specific sample to be spin-locked. Some samples spin-lock 1000 or more points, others less than 100.

To remove the effects of drift in the dc level of the spectrometer, the phase of the initial pulse in the spinlock sequence is cycled between x and π . Phase cycling is performed for each t_1 point. This 180° phase shift of the initial phase inverts the spinlock signal. The dc offset of the spectrometer is not, however, inverted. Thus, by subtracting the two spinlock signals, the effect of the spectrometer drift is negated.

1.5 The Apparatus

The experimental apparatus is briefly described; more detailed descriptions can be found elsewhere [47,48]. All of the experiments were performed on a homebuilt NMR spectrometer. The heart of the spectrometer is a 4.2 T superconducting magnet where the proton Larmor frequency is 185 MHz. The bore, minus room temperature shims, which were not used in these experiments, is 89 mm, providing plenty of room to work with. The RF transmitter on the spectrometer is suited fairly well for the pulsed spin-lock detection sequence. The transmitter amplifier typically generates 500-600 W, although could run up to 1000 W. The RF pulses have a rise time of ~ 50 nsec. Receiver ringdown time is in the 3-20 μ sec range. Most of the spin-locking in these experiments was performed with a 20-40 μ sec delay between the spin-lock pulses, allowing ample time for ringdown before sampling the echo.

A schematic of the field cycling apparatus and the superconducting magnet is shown in Figure 1.15. Compared to most magnets, this one has a long (75cm) support stand. As the plot in Figure 1.16 of the residual field versus distance from

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Figure 1.15: (a) Schematic of the superconducting magnet, field cycling apparatus, high and low field regions. (b) Enlarged view of the high field NMR probe. The sample container rides up and down in a 10 mm o.d. glass shuttle tube (the inner diameter of the tube is 8 mm). The positioning of the sample shuttle in the RF coil and the low field coils is done by shuttle stops. The low field apparatus depicted in (c) consists of the zero field or bucking coil (labelled in the figure as the shielding coil), a composite coil made of two unequal length solenoids, and the 1F (auxiliary) coil or coils. The T-fitting serves two purposes. This fitting allows positioning of the sample stop and enables the connection to the pneumatic valves used for sample shuttling. The sample holder pictured in (d) is machined from Kel-F.

the magnet bottom shows, this amount of space below the magnet is useful if a 100 G bucking coil is used in low field. A. Bielecki's thesis [47] includes a discussion of the bucking coil design. A schematic of the pulsed dc field coils, axial to and transverse to the superconducting magnet's principal axis, is shown in Figure 1.17.

Most of the high field detection was done with a probe based on a modified saddle coil. A schematic is shown in Figure 1.18. The latter experiments were performed with an improved high field coil design. This design shown in Figure 1.19 is a Helmholtz coil.

Shuttling of the sample is done pneumatically. High pressure air is stepped down by a series of regulators, and is then directed to the switches. Typical air pressures used for shuttling were 2-6 psi. The sample container is shuttled between high and low field in a time as short as 100 msec, or more typically 200-300 msec.

Figure 1.16: Plot of magnetic field vs. distance from the bottom of the superconducting magnet dewar. The high field center of the superconducting magnet (42 kG) is ~ 35 cm above the bottom of the magnet, which is the zero point on this graph. Experiments on protons and indirect detection of deuterons are performed in a 100 G fringe field (~ 50 cm from the magnet dewar), and direct detection of deuterons in a 300 G fringe field (~ 20 cm from the dewar).

Three Orthogonal Coil Design

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Figure 1.17: Design for three orthogonal intermediate field coils. The nylon coil form is machined to hold two saddle coils and a solenoid coil. The solenoid is parallel to the superconducting magnet. The coil form fits snugly around the shuttle tube.

Top View

Side View

Figure 1.18: Schematic of the modified saddle coil employed in most of the experiments, both proton and deuteron high field detection, discussed in this thesis. The center hole (10 mm i.d.) is machined such that the shuttle tube fits snugly. The outer two holes allow the coil to be firmly attached to the probe base as depicted in Figure 1.15b.

Figure 1.19: Helmholtz coil and coil form used for high field detection. This coil form has a built-in sample shuttle. The coil form screws into the aluminum probe base, in addition to attachment to the probe base as in Figure 1.15b.

Chapter 2

Motion

The dipole-dipole coupling discussed in the Introduction is for static coupled spins. What happens when the spins are not static? To answer this question, consider the simplest case of two coupled spin-1/2 nuclei. Previous studies in high field have shown [31] and theoretical calculations of motion in zero field [32,33,34,35] reveal that motion alters the dipole-dipole coupling. To simplify matters, all of the motions discussed below are considered to be fast on a time scale of the dipole-dipole couplings. And, the jump rates are fast such that the molecule spends its time in a particular site, not somewhere along the jump.

The dipole-dipole Hamiltonian introduced previously is axially symmetric. That is, if we take the internuclear vector to be the z axis, the x and y axes are indistinguishable. This, however, is not always the case in a dipole-dipole coupling. Motion can disturb the equivalence of the x and y axes, thereby breaking the axial symmetry. The nonaxially symmetric dipole coupling has a readily identifiable effect on the energy levels, and therefore the spectrum. As Figure 2.1 shows, the motion splits the degeneracy of the $|+\rangle$ and $|-\rangle$ levels. Thus, for two coupled spin-1/2 nuclei, the motion induces a quadrupolar-like Hamiltonian with an asymmetry parameter

Figure 2.1: Energy level diagrams and simulated spectra for two homonuclear dipole-dipole coupled spin-1/2 nuclei in zero field. The singlet state is not shown. In the absence of motion, the $|+\rangle$ and $|-\rangle$ states are degenerate. Motion (specifically two site jumps) lifts the degeneracy in the $|+\rangle$ and $|-\rangle$ states. This lifting of the degeneracy results in a markedly different spectrum in the presence and absence of motion. Motion splits the line that appears in the static spectrum at $\frac{3}{2}\omega_D$. Arrows indicate the allowed transitions.

η. The asymmetric dipolar Hamiltonian is then

$$H_D = \frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} [3I_{1z}I_{2z} - \mathbf{I}_1 \cdot \mathbf{I}_2 + \eta(I_{1x}I_{2x} - I_{1y}I_{2y})] \quad (2.1)$$

a Hamiltonian quite similar to a spin-1 quadrupolar Hamiltonian. Thus, we can often treat the two coupled spin-1/2 nuclei as an effective spin-1 nucleus.

One can make a classical analogy of the coupling between two bar magnets to explain the axial and nonaxial coupling. In the axial case shown in Figure 2.2, the magnets (analogous to the dipole moments of a spin-1/2 nucleus) are stationary and the coupling between them lies on a cylinder. As Figure 2.2 reveals, motion serves to make the x axis (in the plane of the paper) different than the y axis (out of the plane of the paper). Here, the motion is in the plane of the paper.

Simulated high field and zero field powder spectra for two coupled spin-1/2 nuclei undergoing different types of motion are presented in the paper by Meier et al [33]. Additional simulated spectra of motion in zero field are found in the paper of Jonson et al [32]. As the simulations reveal, motion in high field results in a modification of the powder pattern. In zero field, however, motion lifts the degeneracy of the $|+\rangle$ and $|-\rangle$ states thereby changing the number of allowed transitions from two to three. This introduces a drastically different character to the zero field spectrum in the presence versus the absence of motion.

2.1 The Toluic Acid Dimer

A few samples have been studied in depth with the zero field technique to gain greater insight into their motion. One of the samples, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ exhibits, when the spin system is diluted by partial random deuteration, librations of the water molecule [36,37,38]. Another beautiful example of motion is CH_2Cl_2 dissolved

Figure 2.2: Schematic of two bar magnets, which represent the dipolar coupling of two spin-1/2 nuclei. When the bar magnets are static, the coupling between them is along the z -axis, with the x -axis, in the plane of the paper, and y -axis, out of the plane of the paper, equivalent. In the presence of motion the coupling no longer lies along a cylinder. Instead, the coupling along the x -axis is smeared out and is no longer equivalent to the coupling along the y -axis.

in a biaxial smectic-E liquid crystal[38,39,41]. In this system, the CH_2Cl_2 molecules jump between different orientations in the herringbone lattice of the liquid crystals.

The example to be discussed at length here is solid p-toluic acid (p-methyl benzoic acid) [44]. This sample, like many carboxylic acids, forms hydrogen-bonded dimers in the solid state [42,43], see Figure 2.3. These H-bonded dimers exhibit interesting, small amplitude motions. As shown previously in single-crystal studies by X-ray crystallography [42,43] and NMR [31], the carboxylic protons in this crystalline solid are in a state of dynamic disorder at room temperature. This means that one orientation of the internuclear vector is not preferred over the other, and exchange between the two orientations is occurring. Additionally, ^{17}O NQR experiments [45] have demonstrated, through an averaging of the quadrupolar tensor, that the hydrogen atoms jump between oxygen atoms rather than undergoing 180° flips about the C-C vector. In their single-crystal NMR study, Meier et al [31] concluded that the hydrogen bonded protons undergo correlated jumps. Such correlated motions should be readily observable in the zero field NMR spectrum, even for a polycrystalline sample.

2.1.1 Theory

Although the H-bonded protons in this sample were previously determined to undergo correlated jumps, let us consider the general case of the hydrogen atoms being either static, or undergoing correlated or uncorrelated jumps. These three scenarios are depicted in Figure 2.3. In the most general case, the average dipole-dipole coupling tensor is written

$$\mathbf{D} = P_1\mathbf{D}_1 + P_2\mathbf{D}_2 + P_3\mathbf{D}_3 + P_4\mathbf{D}_4 \quad (2.2)$$

p-Toluic Acid Dimer

Figure 2.3: Hydrogen bonded dimer of *p*-toluic acid. Jumps of the two hydrogen atoms between molecules in the dimer yield four possible orientations of the dipole-dipole coupling tensor (1, 2, 3, and 4). Shown below are the possible configurations for the two proton dynamics in the carboxylic acid dimer. (a) The static limit. In (b) the uncorrelated motion of the two protons results in all four possible orientations of the internuclear vector. The jumps in (c) are correlated and the proton-proton internuclear vector interchanges between orientations 1 and 2. The jumps between orientations 1 and 2 are described by the angle α . At room temperature, orientations 1 and 2 are assumed to be equally populated and therefore the principal axes of the average of the average dipole coupling tensor will correspond to a frame where the x -axis is along the carboxyl C-C vector and the y -axis is also in the plane of the drawing. A motionally induced asymmetry in the averaged dipolar coupling will result for either (b) or (c).

where P_n is the fractional population of orientation n . The tensors, $\mathbf{D}_n$, describe the dipole-dipole coupling for the two protons in a particular orientation, as explained in the caption to Figure 2.3. A few simplifications to this expression can be made immediately. First, when the tensor is viewed in the molecular based frame of Figure 2.3, the interproton vectors 3 and 4 are equivalent and thus $\mathbf{D}_3 = \mathbf{D}_4$, unlike the interproton vectors 1 and 2, which have a different dependence on the jump angle α . Additionally, at room temperature, interproton vectors 1 and 2 are assumed to be equally populated, as are 3 and 4. With these simplifications, equation 2.2 becomes

$$\mathbf{D} = P_1(\mathbf{D}_1 + \mathbf{D}_2) + 2P_3\mathbf{D}_3 \quad (2.3)$$

Writing the average dipole-dipole coupling tensor requires all dipole-dipole couplings to be in a common frame. If we choose the molecule based frame (xyz) of Figure 2.3 where the x -axis is taken along the carboxyl C-C vector and the y -axis bisects the angle 2α , the internuclear vectors 3 and 4 are in the common frame while the internuclear vectors 1 and 2 need to be rotated into the common frame. The unusual choice of y instead of z as the principle axis in this coordinate system follows the convention of Meier et al [31]. This unusual convention also leads us to label the axially symmetric tensor of, for example, interproton vector 1, as $D_{xx} = D_{xx}$ and $-D_{yy} = 2D_{zz}$. Recall that a static dipole-dipole tensor is cylindrically symmetric and traceless.

The dipole-dipole tensor in the frame of interproton vector 1 is then

$$\mathbf{D}_1 = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} \quad (2.4)$$

To express this tensor in the common frame described above, we have to rotate as

follows $R(\alpha)\mathbf{D}_1R^{-1}(\alpha) = \mathbf{D}_{1(cf)}$ where

$$R(\alpha) = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (2.5)$$

The rotation gives $\mathbf{D}_1$ in the common frame as

$$\mathbf{D}_{1(cf)} = \begin{pmatrix} \cos^2 \alpha D_{xx} + \sin^2 \alpha D_{yy} & \cos \alpha \sin \alpha (D_{yy} - D_{xx}) & 0 \\ \cos \alpha \sin \alpha (D_{yy} - D_{xx}) & \sin^2 \alpha D_{xx} + \cos^2 \alpha D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} \quad (2.6)$$

$\mathbf{D}_2$ is rotated into the common frame by the opposite rotation applied to $\mathbf{D}_1$;

$$\mathbf{D}_{2(cf)} = R^{-1}(\alpha)\mathbf{D}_2R(\alpha).$$

Using $D_{xx} = D_{zz}$ and $2D_{xx} = -D_{yy}$

$$\mathbf{D}_{1(cf)} = D_{xx} \begin{pmatrix} 1 - 3 \sin^2 \alpha & -3 \cos \alpha \sin \alpha & 0 \\ -3 \cos \alpha \sin \alpha & 1 - 3 \cos^2 \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (2.7)$$

and

$$\mathbf{D}_{2(cf)} = D_{xx} \begin{pmatrix} 1 - 3 \sin^2 \alpha & 3 \cos \alpha \sin \alpha & 0 \\ 3 \cos \alpha \sin \alpha & 1 - 3 \cos^2 \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (2.8)$$

Since $\mathbf{D}_3$ and $\mathbf{D}_4$ are already in the common frame, they can be written as

$$\mathbf{D}_3 = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} \quad (2.9)$$

or

$$\mathbf{D}_3 = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & -2D_{xx} & 0 \\ 0 & 0 & D_{xx} \end{pmatrix} \quad (2.10)$$

$\mathbf{D}_4$ is identical to $\mathbf{D}_3$.

Now, to get the average dipole coupling tensor for this system, the four couplings ($\mathbf{D}_{1(cf)}$, $\mathbf{D}_{1(cf)}$, $\mathbf{D}_3$, and $\mathbf{D}_4$) must be summed using equation 2.2.

Before writing the resultant sum, let us call D_{xx} for coupling 1 and coupling 2 in the common frame, D_1 , and D_{xx} for coupling 3 and 4, D_3 . D_{xx} for coupling 3 can then be written $D_1 D_3 / D_1$. Here $D_n = \hbar \gamma^2 / r_n^3$. Summing up as in equation 2.3 with the simplifications and assumptions of populations at room temperature, we get the average dipole-dipole coupling tensor

$$\mathbf{D} = D_1 \times \begin{pmatrix} 2P_1(1 - 3\sin^2 \alpha) + 2\frac{D_3}{D_1}P_3 & 0 & 0 \\ 0 & 2P_1(1 - 3\cos^2 \alpha) - 4\frac{D_3}{D_1}P_3 & 0 \\ 0 & 0 & 2P_1 + 2\frac{D_3}{D_1}P_3 \end{pmatrix} \quad (2.11)$$

The normalized zero field signal is calculated via the standard method introduced in the Introduction to be

$$S(t_1) = 1/3[\cos \omega_{12}t_1 + \cos \omega_{13}t_1 + \cos \omega_{23}t_1] \quad (2.12)$$

Thus, one expects three lines of equal intensity at the frequencies corresponding to the differences in eigenvalues derived from equation 2.11. These frequencies are

$$\begin{aligned} \omega_{12} &= D_1[6P_1(\sin^2 \alpha - \cos^2 \alpha) - 6\frac{D_3}{D_1}P_3] \\ \omega_{13} &= D_1[6P_1 \sin^2 \alpha] \\ \omega_{23} &= D_1[6P_1 \cos^2 \alpha + 6\frac{D_3}{D_1}P_3] \end{aligned}$$

2.1.2 Results

The proton zero field NMR spectrum, obtained by the sudden experiment, of p-toluic acid at room temperature appears in Figure 2.4. The spectra contain the splittings in the high frequency lines, reflecting the asymmetry of the average dipolar coupling. The predicted low frequency peak, however, is masked by a large zero frequency peak. This large nonevolving peak arises from residual protons. The p-toluic acid sample used was ~60% deuterated on the acid sites and 98% deuterated elsewhere. By diluting the acid site protons, coupling between dimers is reduced and the splitting of the lines is better resolved.

Simulated zero field spectra for static protons, as well as correlated and uncorrelated jumps, were produced for comparison to the experimental spectrum as follows. The value of D_3 is based on the internuclear distances taken from X-ray crystallographic data for pentafluorobenzoic acid. Pentafluorobenzoic acid is a molecule of related structure whose carboxyl hydrogen atoms show no disorder at room temperature and is thus a suitable model compound. From the X-ray data, I determined $r_3 = r_4$ to be 2.23 Å. Simulated spectra for the static ($P_1 = 1.0$), correlated ($P_1 = P_2 = 0.5$, $P_3 = P_4 = 0$), and uncorrelated ($P_1 = P_2 = P_3 = P_4 = 0.25$) cases appear in Figure 2.5. Comparison to the experimental spectra indicates that correlated jumps between two orientations are the most plausible situation. The values of r_1 and α derived from the experiment are $r_1 = 2.33 \pm 0.05$ Å and $\alpha = 16.0 \pm 2^\circ$, which are in good agreement with results previously reported by Meier et al from single crystal experiments in high field. The values of r_1 and α were determined by varying these two parameters until they fit the experimental data.

Figure 2.4: Experimental zero field NMR spectra of *p*-toluic acid ~60% deuterated on the acid sites and 98% deuterated elsewhere. Spectrum (a) is the Fourier transform of one FID. The two outer peaks are at 11.5 and 12.9 kHz. To ensure that the sample had not picked up water, it was dissolved in a 60% H₂O/D₂O mixture, recrystallized, and dried. This spectrum is shown in (b), and is the sum of seven FIDs. Here the peaks are at 11.8 and 12.8 kHz. Both spectra are 1024-point Fourier transforms of 50-point FIDs taken with a 25 μ sec increment. The predicted low frequency peak is overwhelmed by the broad zero frequency peak, which arises from unpaired protons in the sample. The asymmetry of the average dipolar coupling is reflected in the splitting of the high-frequency lines.

Figure 2.5: Simulated spectra for *p*-toluic acid. (a) Computer-simulated spectrum for the static limit of the two protons with $r_1 = 2.33$ Å. (b) Computer-simulated spectrum for the uncorrelated jump model ($P_1 = P_2 = P_3 = P_4 = 0.25$) of the two protons with $\alpha = 16^\circ$, $r_1 = 2.33$ Å. (c) Computer-simulated spectrum for the correlated jump model ($P_1 = P_2 = 0.5, P_3 = P_4 = 0$) with the same α and r_1 values as in (b). Note that the asymmetry is more pronounced in the average over orientations 1 and 2 alone. In (b) the outer lines are shifted to higher frequency due to the added contributions of the larger dipolar couplings of orientations 3 and 4.

2.2 Suppression of the Zero Frequency Peak

Although the p-toluic acid spectrum was easily analyzed, it would be certainly more pleasing if all three predicted lines had been resolved. The large zero frequency peak provides little information, and if it could be deleted the low frequency lines might be resolved. Indeed, removing the zero frequency line from the spectrum may be quite desirable for a number of reasons. A more complicated spectrum with two or more asymmetric dipole couplings with different frequencies and splittings would require resolution of the low frequency lines if the higher frequency lines are to be assigned. Also, when an interproton distance becomes larger than $\sim 4 \text{ \AA}$ the ability to resolve the peaks at $\pm \frac{3}{2}\omega_D$ ($= 3\gamma^2\hbar/2r^3$) becomes increasingly difficult. We have developed, therefore, a method to 'filter out' the nonevolving magnetization.

Two possible procedures for the suppression of the zero frequency peak are schematically shown in Figure 2.6. In each case the spin system is prepolarized in a large applied magnetic field, manipulated so as to reveal the spin couplings in the absence of the field, and finally returned to the large applied field where the evolved magnetization is sampled. For concreteness we assume that the spin system consists only of a single species (such as ^1H) of dipolar coupled spins. In the field cycle schematic of Figure 2.6a, a sample that has polarized in high field is slowly brought to zero field. Zero field evolution is initiated by a dc magnetic field pulse and terminated after a time, t_1 , by the sudden application of an intermediate magnetic field. In this intermediate field, the nuclear Larmor frequency is large compared to the dipole-dipole couplings, and any dipolar magnetization that may have developed along the direction of the applied magnetic field is long lived. The sample is then slowly returned to high field where the magnetization as a function of t_1 is measured. This cycle is repeated for a number of values of t_1 . The resulting data array $S(t_1)$

Figure 2.6: Schematic field cycle for the zero frequency suppression experiment that correlates dipolar magnetization with higher-rank operators. (a) The sample is slowly removed from high field (4.2 T) to zero field. A dc magnetic field pulse of angle θ_z initiates evolution, which proceeds for a time t_1 . Sudden reapplication of an intermediate field (0.01 T) along the z-axis terminates evolution. The sample is slowly remagnetized to high field where the signal as a function of t_1 is measured. The maximum signal is achieved when θ_z is 50° . (b) Similar to (a) except the sequence in low field is reversed. The sudden transition initiates evolution which proceeds for a time t_1 . Application of a dc field pulse terminates evolution.

may then be Fourier transformed and will reveal the zero field evolution frequencies. Figure 2.6b illustrates a field cycle that differs from Figure 2.6a only in that the sequence in low field is reversed in time.

2.2.1 Theory

In isolated spin systems, and in the absence of relaxation, the signals predicted from the two variations of the experiment shown in Figure 2.6 are identical (to within a possible change of sign). As the spin temperature hypothesis is inappropriate for spin systems where the zero field spectrum consists of discrete absorption frequencies (the spin temperature hypothesis is valid for infinitely coupled spins), the initial condition achieved after slow demagnetization, or the final condition achieved after remagnetization is not generally known. A complete theoretical analysis is therefore not generally possible. Considerable insight, however, into the basic phenomenon is obtained by considering an ideal three level system, such as that represented by a single spin-1 nucleus or the triplet sublevel of two dipolar coupled spin-1/2 nuclei.

A theoretical basis for analyzing such sequences and a number of relevant calculations appears elsewhere [30,47]. For concreteness, and because of several inherent experimental advantages (commented on below), the following discussion centers on the sequence illustrated in Figure 2.6a. While the suppression experiment is primarily of use in dipolar coupled systems, calculations are most efficiently performed by using the analogy between the triplet state of two coupled homonuclear spin-1/2 nuclei and the three level system of eigenstates that characterize a spin-1 nucleus (such as ^2H), conventionally designated as $|x\rangle$, $|y\rangle$, and $|z\rangle$. Throughout we shall use the notation appropriate to pure nuclear quadrupole resonance of a spin-1 [29] nucleus which applies equally well (with minor notational differences) to pure nuclear dipole

resonance of a pair of spin-1/2 nuclei.

Computer simulations and a simple argument appealing to the adiabaticity condition [30,47,48,49,50] have shown that when an isolated three level system is adiabatically demagnetized from a large applied field to zero field, the populations are transferred (essentially completely) directly to eigenstates of the zero field Hamiltonian. Thus, given a density operator ρ consisting of only populations ρ_{ii} in a large external field, under slow demagnetization (and ignoring relaxation) the same numbers ρ_{ii} characterize ρ in zero field, where ρ is consistently defined for each crystallite in a local frame of reference.

A three level system has two constants of the motion (two diagonal operators that commute with the Hamiltonian). In high field, where the effective quadrupolar Hamiltonian is

$$H_{hf} = -\delta_\omega I_z - 0.5A_q[(3\cos^2\theta - 1) + \eta\sin^2\theta\cos 2\phi](3I_z^2 - \mathbf{I}^2) \quad (2.13)$$

the constants of the motion are Zeeman order (proportional to I_z) and quadrupolar order (proportional to $3I_z^2 - \mathbf{I}^2$). In zero field, where the effective Hamiltonian is

$$H_{hf} = A_q[(3I_x^2 - \mathbf{I}^2) + \eta(I_x^2 - I_y^2)] \quad (2.14)$$

the constants of the motion are quadrupolar order and eta order (proportional to $I_x^2 - I_y^2$). For pairs of dipolar coupled spins, the same is true if we replace "quadrupolar" with "dipole-dipole" everywhere and allow for a motionally-induced asymmetry parameter, η [32,33,34,35,44].

For the three level system, equilibrium in high field corresponds to a Zeeman ordered state (dipolar magnetization). After adiabatic demagnetization, all nuclear spin order is conserved, but no dipolar magnetization remains because ρ is diagonal in a local frame only. No observable survives averaging over all orientations. What

is important and generally true is that ρ in zero field is described by a sum of local, second rank spherical tensor operators *independent* of the demagnetization process details as long as ρ is in the steady state.

After demagnetization, evolution is initiated by a dc magnetic field pulse of angle θ along a laboratory axis. In the local frame where ρ is defined, this axis varies from orientation to orientation. In a spin-1 nucleus, the pulse converts quadrupolar and eta order (created by the demagnetization) into the other three second rank tensors ($I_x I_y + I_y I_x$, $I_x I_z + I_z I_x$, and $I_y I_z + I_z I_y$). These do not commute with the pure quadrupolar (or dipole-dipole) Hamiltonian and evolve according to the general rule

$$\begin{aligned} e^{-iHt_1}(I_j I_k + I_k I_j)e^{iHt_1} &= (I_j I_k + I_k I_j)(t_1) \\ &= (I_j I_k + I_k I_j) \cos \omega_{jk} t_1 - I_l \sin \omega_{jk} t_1 \end{aligned} \quad (2.15)$$

The latter term corresponds to dipolar magnetization.

While this dipolar magnetization is created in the local frame of reference, and from an initial condition that may depend upon orientation, it still corresponds to a macroscopically observable signal. The action of applying a magnetic field pulse has established a unique direction *in the laboratory frame*. Following evolution, a large static magnetic field, which freezes the evolution and newly developed dipolar magnetization, is applied. A signal can be observed only for freezing fields aligned parallel to the excitation pulse. This result is well known from more traditional NQR studies [51,5].

In an isolated three level system the magnetization produced after a θ pulse is always proportional to $(2 \sin 2\theta + \sin \theta)$. This holds independent of the initial condition as long as the demagnetized operator ρ is independent of orientation. For the initial condition described above (all populations uniformly carried over to the corresponding zero field spin eigenstates) we find

$$S(t_1, \theta) \propto [2 \sin 2\theta + \sin \theta][5(\sin \omega_{yz}t + \sin \omega_{zx}t) + 4 \sin \omega_{xy}t] \quad (2.16)$$

where ω_{ij} is the frequency of separation between levels i and j . This result is based upon the calculation in Zax's thesis [30]. Note that the signal grows in as the sines of the evolution frequencies, as is appropriate for an experiment that interrogates cross-correlations [52]. $S(t_1, \theta)$ is therefore most conveniently monitored with a sine Fourier transform or, alternatively, by observing the frequencies in the "dispersion" buffer of a complex Fourier transform.

In summary, an initial condition, which corresponds to something other than Zeeman order, has been prepared. A dc magnetic field pulse then transforms this order into a macroscopically observable magnetization, under the influence of H_Q or H_D , parallel to the direction of the applied field pulse. Only spins that support either quadrupolar and/or multispin dipole-dipole order and those whose evolution frequencies are nonzero, contribute to the macroscopic magnetization returned to high field at the end of t_1 . Spin-1/2 nuclei that have no near neighbors in the lattice cannot support these cross-correlations between single and multispin operators and thus do not contribute to the signal. Additionally, these experiments discriminate against the contribution that arises from those pairs of spins that give rise to the zero frequency peak in the conventional sudden or adiabatic demagnetization experiments. In the experiment of Figure 2.6b, the zero frequency evolution of I_z , a first rank tensor, is responsible for the zero frequency peak. By detecting second rank order this contribution is eliminated. In the experiment of Figure 2.6a just the opposite is true. Here, zero frequency evolution of second rank order gives rise to the zero frequency peak. Detection of the newly evolved first rank order, I_z , deletes the zero frequency peak. Such spins would otherwise contribute to signals, which might

obscure important spectral details, near zero frequency. Thus, this method is fundamentally different from the phase cycling method that Kreis et al have developed, which allows for suppression of ν_0 or ν_+ and ν_- lines by using low frequency pulses.

These conclusions, derived with specific reference to the three level system only, are easily generalized to other systems and Hamiltonians, H . In zero field, any arbitrary H consists of a sum of dipole-dipole and/or quadrupolar couplings. H is therefore a sum over second rank tensors, and ρ commutes with H only if it is comprised of even rank time-independent tensor operators. A short field pulse transforms populations of ρ into coherences, and time evolution under H creates some odd rank tensor operators (including magnetization, a first rank tensor operator). A trapping field then freezes that portion of the spin order that projects onto magnetization pointing along the axis of the field pulse. Nonevolving operators, or spin systems that cannot support the multispin operators characteristic of higher order tensors, cannot contribute to the observed cross correlation signal.

2.2.2 Results

Figures 2.7a and 2.7b show the zero field NMR spectra of the protons in polycrystalline $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ obtained by using the conventional sudden experiment and the suppression sequence shown in Figure 2.6a, respectively. In the latter, the zero frequency peak is effectively suppressed. A series of experiments performed by varying θ confirm the intensity dependence predicted in equation 2.16 for $S(t_1, \theta)$. These results appear in Figure 2.8. The maximum intensity is obtained when $\theta = 50^\circ$.

The system illustrated in Figure 2.9 corresponds to the two spin-1/2 ^1H atoms undergoing correlated exchange in the p-toluic acid dimer [31]. As shown previously, motion induces asymmetry in the dipole-dipole interaction. Therefore, a low fre-

Figure 2.7: (a) Experimental spectrum of polycrystalline $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ obtained by the conventional sudden experiment. Here the zero frequency peak is equal in intensity to the peaks at $\frac{3}{2}\omega_D$. (b) Phase-corrected experimental spectrum of polycrystalline $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ obtained by the suppression scheme shown in Figure 2.6a, where θ_z is between 40° and 60° .

Figure 2.8: Plot of intensity vs. dc pulse angle θ for the experiment depicted in Figure 2.6a. The solid curve is a plot of $(2 \sin 2\theta + \sin \theta)$ for $\theta = 0^\circ$ to 180° . The experimental dc pulse angles plotted are 50° , 75° , 100° , 135° , and 170° . Error in determining the precise flip angle from the coil calibration is approximately $\pm 10^\circ$. The signal intensities were normalized to scale. Error in signal intensity values is approximately 10%.

Figure 2.9: (a) Conventional sudden experiment spectrum of polycrystalline *p*-toluic acid. The splitting between the peaks at 11.8 and 12.8 kHz arises from the correlated motion of the H-bonded carboxyl protons in *p*-toluic acid dimers. The predicted difference peak at 1.0 kHz is hidden under the broad line arising from residual protons with no near neighbors in the lattice. (b) Experimental spectrum of polycrystalline *p*-toluic acid obtained with the suppression technique in Figure 2.6a. Suppression of the peak due to nonrevolving magnetization allows us to observe the weak difference frequency line.

quency peak is expected in the spectrum. Residual ^1H atoms with no near neighbors in the lattice contribute to the large zero frequency peak observed in the normal zero field NMR experiment (Figure 2.9a). Where we monitor instead the cross-correlation spectrum (Figure 2.9b), the previously masked low frequency line is clearly observed.

Although the theory here is relevant to a proton pair, the underlying idea for the suppression experiment, that is, observation of only those coherences that correspond to correlations between multispin order created in the demagnetization to zero field and trapped by the sudden reapplication of a large magnetic field, works for larger spin systems as shown in Figure 2.10. Figures 2.10a and 10b show the conventional sudden experiment and suppressed zero field NMR spectra, respectively, for an approximately isolated four proton system in 1,2,3,4-tetrachloronaphthalene bis-(hexachloropentadiene) adduct [2]. Suppression of the intense zero frequency peak (Figure 2.10b) leads to improved dynamic range for the remainder of the spectrum, which contains considerable information about the four proton system.

Experiments utilizing the sequence in Figure 2.6b were less successful in suppressing the zero frequency peak. This sequence, while functionally equivalent for the ideal three level system, is far more sensitive to distortions that may arise from either spin-spin or spin-lattice relaxation during the field cycle. The theoretical treatment of the field cycle is most difficult when externally applied fields are of the same order of magnitude as a typical quadrupolar (dipole-dipole) field. Since the demagnetization/remagnetization is less than ideal, we are at least guaranteed that the same initial condition is achieved for each value of t_1 by utilizing the sequence of Figure 2.6a. This is not the case for the sequence of Figure 2.6b where the more problematic slow field change occurs after the zero field frequencies have been imprinted during t_1 , and thus the signal measured in high field may suffer from different

Figure 2.10: (a) Sudden experiment spectrum of 1,2,3,4-tetrachloronaphthalene bis-(hexachlorocyclopentadiene) adduct, a sample that can be treated as relatively isolated four-proton groups. (b) Suppression spectrum of the adduct obtained with the field cycle in Figure 2.6a. Here, the suppression of the zero frequency peak leads to improved dynamic range in the rest of the spectrum. However, the amplitudes of the peaks are not preserved in the four-proton system.

distortions for each point in t_1 .

However, the primary reason for the failure of the field cycle in Figure 2.6a is most likely instrumental. Figure 2.11 shows an oscilloscope trace of the bucking coil switching on and off. As the trace reveals, the switching on of the bucking coil follows a path that could be considered adiabatic. The switch off, however, especially at low field is not adiabatic. This is almost certainly the problem.

This is not, however, the only problem with the field cycle. If a delay after the pulse, but prior to the remagnetization, is inserted into this field cycle shown in Figure 2.12 a, the suppression results are remarkably good. Figure 2.13 shows the suppression results as a function of the delay. Notice that the delay becomes very long in relation to the timescale normally dealt with for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ in zero field (on the order of $150 \mu\text{sec}$).

What this suggests is that some form of order, which contributes to the poor performance of the field cycle, decays during the delay time. This also suggests that this form of order is much shorter lived than the dipole-dipole order created by the pulse.

What type of order is decaying? We begin to answer this question by making a modification to the experiment as shown in Figure 2.12b; the addition of the 90°_x pulse, and the switch in phase of the final pulse to a θ_y (recall that in such an experiment, no signal is observed unless the pulse is along the axis of sudden switching, or in this case, along a newly rotated axis). In this field cycle, there is now no component of magnetization along the laboratory z -axis. Instead, it is along the laboratory y -axis. How do the results of this experiment compare to those without the 90°_x pulse? Figure 14 shows that the suppression is essentially complete.

Figure 2.11: Oscilloscope trace of the bucking coil switching on and off. The trace monitors the current flow through the bucking coil. As the trace indicates, the bucking coil follows a smooth transition to zero field from the intermediate field. Upon reapplication of the intermediate field (switching the bucking coil off) the initial field switch is abrupt, ending in a smooth transition to the intermediate field.

Figure 2.12: Schematics of three additional field cycles for suppressing the zero frequency peak. In (a) the field cycle presented in Figure 2.6b is modified by the addition of a delay, τ , following the termination pulse, prior to remagnetization. The delay allows some component of order, which degrades the performance of the field cycle 2.6b, to decay. In field cycle (b), a 90_x° pulse immediately following the sudden transition to zero field places the magnetization perpendicular to the laboratory z -axis. After t_1 , evolution is terminated with a θ_y pulse. By rotating the zero field evolution axis by 90° , the instrumental problem of the bucking coil reapplication is no longer problematic. Field cycle (c) was also shown to work for suppression by Thayer and Millar. Either θ or θ' is set at 90° , the other dc pulse is set to 50° to achieve maximum signal.

Figure 2.13: Experimental results on polycrystalline $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ for the field cycle depicted in Figure 2.12a with increasing delay time. The delay times, τ , are (a) 0, (b) $100 \mu\text{sec}$, (c) 1 msec , and (d) 100 msec . The termination pulse in all of the experiments was $0.6 \mu\text{sec}$ corresponding to $\sim 50^\circ$, the sampling time, t_1 , was $5 \mu\text{sec}$.

Figure 2.14: Experimental suppression spectrum of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ using the field cycle in Figure 2.12b. The 90°_z pulse was $0.9 \mu\text{sec}$, the θ_y pulse approximately 50° at $0.6 \mu\text{sec}$. Unlike the similar field cycle in Figure 2.6b, suppression results are quite good.

The experimental results seem to indicate that a component of magnetization or some other form of order was locked along the z-axis by the non-adiabatic character of the field reapplication. The modified experiment of Figure 2.12b avoids the instrumental problem by rotating the magnetization perpendicular to the laboratory z-axis. Any order that would contribute to the zero frequency peak is now in the transverse plane.

This adds further support to the theory that some shorter lived order, which gets locked by the field reapplication, is allowed to diminish in the experiment with the delay after the pulse. If the field reapplication were ideal, the z-like component, instead of getting locked by the field, would decay during the remagnetization.

It is probably no great surprise that the sequence depicted in Figure 2.12c also works for suppression of the zero frequency peak. Millar and Thayer previously performed such experiments and achieved suppression of the zero frequency peak. This was not their goal in such experiments, so the results were ignored.

2.3 Variable Temperature Experiments

While the study of motions at room temperature indicates if the sample is undergoing motion [44] (except for 180° flips), and elucidates some of the interesting features of the motion, much more information is obtainable with variable temperature experiments [32,33,34,35]. Using variable temperature zero field experiments, one could observe, for example, the transition from the static to the fast motion regime of site exchange as calculated by Jonson et al [32]. Slowing down or speeding up motions to make the T_1 more amenable to zero field experiments is also a possibility. Or perhaps some sample will be static, or moving too rapidly at room temperature to be of any interest. Also, with variable temperature techniques one could observe the

characteristics of potential wells. This last area of research was previously done in high field [31] but could be simplified by performing the experiments in zero field.

Motional studies are not the only area of research opened up by variable temperature experiments. The study of phase transitions or of interesting phases is also accessible with variable temperature. Many phases, such as liquid crystals, glasses, or polycrystalline powders would be prime candidates for these experiments. Studies of phase transitions, such as the change from a positive to a negative anisotropic magnetic susceptibility in a liquid crystal mixture [46] could in principle be performed in zero field more easily than in high field.

Much effort has been directed toward the construction of a zero field variable temperature probe, tuned for protons, and preliminary results on the freezing of motion in a polycrystalline hydrated salt were observed. Figure 2.15 shows the expected spectra for a three level spin system as calculated by Jonson et al. Figure 2.16 shows the preliminary results of indirectly detected deuterons in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ ~70% deuterated taken at two temperatures. The results show the transition away from the fast motion limit. As predicted in Figure 2.15, the ν_0 and ν_- lines coalesce into one broadened line.

Certainly, an interesting part of conducting variable temperature motion studies would be to monitor the intermediate motion regime, far from either the static or the fast motion limit [32]. Monitoring the intermediate motion regime, however, is quite difficult. For illustration purposes, the theoretical spectra of Figure 2.15 were altered so that peak heights were normalized for all regimes. Experimentally, however, since the integrated intensity is constant, in the intermediate motion regime the intensity is smeared out over the broad range of frequencies and possibly unobservable. Given a desired signal to noise ratio, an experiment performed at the fast and slow motion

Figure 2.15: Simulated spectra taken from Jonson et al. The spectra were generated using $\eta = 0.1$ in the static limit and a twofold rotation axis of 109.4° . These parameters are suitable for a water molecule in a crystalline hydrate undergoing a twofold rotation about its C_2 axis. The static limit is at the bottom of the figure.

Figure 2.16: Indirectly detected experimental zero field spectrum of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, $\sim 70\%$ deuterated, at two temperatures. (a) At room temperature, the two site jumps of the water of hydration is in the fast motion limit and $\eta = 0.96$. The three peaks appear at 56.9 kHz, 62.6 kHz, and 121.5 kHz. (b) At the temperature of -7°C , the motion is tending toward the intermediate motion regime shown in theoretical spectra of Figure 2.15. The two peaks appear at 61.2 kHz and 124.0 kHz.

limits could be done in x amount of time, while an experiment at the intermediate motion regime would require 10^6x amount of time. Granted, the T_1 in the intermediate motion regime would be appreciably shorter and therefore make a savings of time of up to two orders of magnitude. One sees, however, that such a study is beyond the realm of most experimenter's desired timescales, especially given the two-dimensional nature of the zero field experiment.

The apparatus (probe, shuttling mechanism, cooling system) are presented in Figure 2.17. The probe was designed such that the RF coil (Figure 1.18), a low field IF coil, and sample shuttling tube are housed inside a double-wall glass dewar. The wires for the coils were passed through 1/4 inch openings in the glass dewar and the holes sealed with cork and teflon tape. Shuttling of the sample was accomplished by threading the Kel-F sample holder to the end of a 3/16 inch fiberglass piston rod. The rod was fastened at the other end to a nylon piston that rides up and down in a brass tube. Positioning of the sample in low field is accomplished by sliding the piston assembly up or down. Positioning in high field is done by an adjustable stop which is situated inside the brass tube. The pressure to drive the piston was 30 psi air forced into the top or bottom of the brass tube. Switching the direction of the high pressure air is accomplished similarly to the standard room temperature method. Temperature regulated N_2 gas was brought into the dewar via a port in the bottom of the glass dewar. Nitrogen gas was forced into the shuttle tube and the space between the shuttle tube and the inner wall of the glass dewar. The N_2 gas was injected both at the bottom of the dewar, and, by a series of Teflon tubes, up near the RF coil. The gas vented out the bottom of the dewar and past the fiberglass piston rod on top. To prevent condensation in the magnet bore, the entire probe below the RF shield is enclosed in plexiglass and continuously flushed with warm

Figure 2.17: Schematic of the variable temperature probe and shuttling apparatus.

dry air.

Two thermocouples, one placed near the zero field region and the other 1 cm away from the RF coil (both between the shuttle tube and the dewar) monitored the temperature. Temperature regulation relies upon only the thermocouple placed near the RF coil. Temperature stability during sample shuttling was $\pm 1^\circ\text{C}$ to $\pm 2^\circ\text{C}$. The difference in temperature between the thermocouple at the top and at the bottom was typically 1°C . This temperature gradient was minimized by carefully adjusting the size of the flow holes, the tubes running up to high field (near the Rf coil), and by poking holes into the shuttle tube at various points to ensure a better flow of gas.

The principle problems that this method has are temperature regulation and the shuttling mechanism. Problems with the piston can possibly be overcome by using more reliable commercially available gas or hydraulic pistons. Better temperature regulation, on the other hand, probably cannot be attained with sample shuttling. One way around the temperature regulation problem is to keep the sample stationary and switch (turn on and off) the high field magnet. Another method proposed by D. Weitekamp [40] is a direct variant of the current experiment; hold the sample stationary and physically shuttle (i. e. move) the magnet. In both of these cases, temperature control could be implemented by the standard techniques employed in NMR.

Both techniques, however, require compromises in the rest of the zero field experiment. In the switched field experiment, a smaller and perhaps less homogeneous static field, than is easily attainable with a superconducting magnet, will almost certainly be required. These limitations would diminish the signal-to-noise ratio gained by polarizing and detecting in a large magnetic field. Also, the possibility of lower homogeneity could hamper any attempts at certain high field vs. zero field correla-

tion experiments. In the experiment where the sample is held stationary and the superconducting magnet moved, this undoubtedly limits the list of samples to those with a long T_1 .

Chapter 3

Liquid Crystals

3.1 Introduction

The term 'liquid crystal' encompasses a wide variety of mesophases that occur between the crystalline solid and isotropic liquid. These mesophases are unlike the crystalline solid, which possesses both positional and orientational order, or the isotropic liquid, which has neither. Instead, the liquid crystalline phases display varying degrees of order.

Although the type and number of liquid crystals seems to be ever increasing and the distinction between the various types to be ever more ambiguous, there are two principle varieties: lyotropic and thermotropic. In the lyotropics, the crystalline solid becomes liquid crystalline upon the addition of a solvent, the phase being concentration dependent. The thermotropics change from the crystalline to the various mesophases as a function of temperature.

Due to the practical importance to industry and the vast basic scientific interest in liquid crystals, much has been researched and written about them [55,56,58,59,60,64].

From the point of view of zero field NMR, with the current experimental setup,

only the thermotropics have proven to be of any experimental interest. All of the lyotropic samples tested to date were plagued with T_1 's so short that the signal would not survive the trip to and from zero field. The thermotropics, on the other hand, have been quite suitable to study by zero field NMR.

Two of the principle thermotropic phases, the nematic and smectic, are depicted in Figure 3.1. The third principle phase, the cholesteric, is similar to the nematic except the molecules are chiral and induce a helical spiral into the order parameter. Some studies of the nematic phase in zero field will be described here, while further studies of the nematic and smectic phases are found elsewhere [38,39,41,53,54].

The nematic, the liquid crystalline phase with the least order, always occurs before any other thermotropic liquid crystalline phase becomes isotropic. This mesophase possesses no positional order. In other words, the centers of mass of the molecules are in no way correlated. These molecules do, however, possess orientational order. The elongated, rodlike or cigar shaped molecules of the nematic are preferentially ordered with the long axis along the director n (Figure 3.1). In the plane perpendicular to the long axis the molecules experience complete isotropic motion. The approximation of these liquid crystal molecules (most of them are large organic molecules containing 6 membered aromatic rings and hydrocarbon chains) as rodlike is valid considering rotations about the long axis are 10^{-10} to 10^{-12} sec.

It is important to note that the director is an average direction of alignment. The liquid crystal molecules themselves will fluctuate quite rapidly ($\sim 10^{-9}$ sec) about the director axis. That is, all ϕ where ϕ is the angle in the plane perpendicular to the long axis will be equally probable [64]. And, since the phase possesses quadrupolar symmetry, 180° rotations about the transverse axis are allowed. The degree to which the molecules are ordered along the director axis is given by the order parameter S ,

Figure 3.1: Top; the nematic liquid crystalline phase. The elongated, cigar-shaped molecules of the nematic are aligned on average with respect to the director axis indicated by the arrow. The molecules possess no positional order. Bottom; diagram of the smectic A phase. The smectic phases in general are characterized by the layered structure illustrated above. The molecules have a preferred orientation either normal to or tilted from the layer axis. Translational diffusion within the layer occurs freely, and diffusion between layers to a lesser degree. Within the layers, positional order ranges from nonexistent, as in smectic A, to highly ordered, as in smectic E.

where

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (3.1)$$

θ is the angle between the long axis of the liquid crystal molecule and the principle axis of the director in Figure 3.2. The brackets indicate a time average. In a NMR experiment the measured angle, θ , is the angle between the internuclear vector or principle axis of the nuclear quadrupole and the externally applied magnetic field.

In the presence of a large magnetic field, as will be discussed below, the sample will exist in a monodomain (n is the same for the whole sample). In the absence of a field, however, there is no reason to expect the sample to exist as a monodomain. Indeed, in the absence of an externally applied field, the sample will exist as a polydomain structure, where the dominant factor causing alignment is the walls of the container [55]. In each domain, the liquid crystal molecules will be oriented along a local director n .

Nematic liquid crystals possess an unusual magnetic property; they have both an axial and a transverse magnetic susceptibility. The two components of the anisotropic magnetic susceptibility are $\chi_{\parallel}$ and $\chi_{\perp}$. Magnetic susceptibility is a dimensionless quantity given by $\chi = \mu_0 M/B$, where M is magnetization and B is the externally applied magnetic field [55]. The two components are usually negative, that is, they are diamagnetic, and are on the order of 10^{-6} to 10^{-7} cgs units [64]. The anisotropic magnetic susceptibility, $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, is either positive or negative. A positive $\Delta\chi$ (the case discussed here) will enable a strong dc magnetic field to align the director axis along the field axis. The free energy density of alignment, g_m , for a liquid crystal molecule in an externally applied magnetic field is

$$\begin{aligned} g_m &= -\frac{1}{2} \Delta\chi B^2 \\ &\simeq -1/2(10^{-6} \text{ cgs})(10^4 \text{ G})^2 \end{aligned} \quad (3.2)$$

Figure 3.2: Schematic of a liquid crystal molecule whose long axis (dashed line) is rotated away from the director, $\mathbf{n}$, by an angle θ .

$$\simeq -10^2 \text{erg/cm}^3$$

After the sample has been placed in the magnet, the time required for the sample to align is on the order of 1 second [64].

Because the nematic aligns in a field, from the point of view of a NMR experiment, it behaves like a single crystal. However, the anisotropic nature of the liquid crystal and the rapid motion of molecules with respect to one another alter the spectrum a bit by scaling the dipolar or quadrupolar coupling and narrowing the resonance line. This scaling factor, the order parameter, modifies the high field dipolar Hamiltonian to

$$H_D^0 = -\frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} S(3I_{1z} I_{2z} - \mathbf{I}_1 \cdot \mathbf{I}_2) \quad (3.3)$$

In the study of liquid crystals by NMR, one usually wants a spin system smaller than that found in the fully protonated molecule. As Figure 3.3 shows, the high field spectrum of the nematic Eastman Kodak 11650 (p-pentylphenyl-2-chloro-4-(p-pentylbenzoxoyloxy)benzoate), is broad and for the most part featureless. One can avoid this problem and get a beautiful, resolved spectrum by selectively substituting atoms on the liquid crystal molecule itself (an expensive proposition) or by using a small solute molecule as a probe. The use of small molecules dissolved in the liquid crystal as a probe of the anisotropic environment is a well established technique [61,62,63]. Due to the anisotropic environment, the liquid crystals will align the probe molecules, and will even align spherical molecules by distorting their shape, with a measurable order parameter. The degree of ordering will depend upon the size and shape of the molecule, and will almost certainly be less ordered than the liquid crystal molecules themselves.

In the experiments discussed here, the probe molecule is CH_2Cl_2 . The resulting

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Figure 3.3: High field NMR spectrum (185 MHz ^1H) of fully protonated Eastman Kodak 11650. Due to the large number of dipole-dipole couplings, no structure in the spectrum is resolved, and little information about the sample, and the degree of order, is obtained.

high field spectrum, Figure 3.4, yields an order parameter of $S = 0.055 \pm 0.001$. The value for the order parameter is calculated from equation 3.3 using $r = 1.771 \text{ \AA}$ for the H-H bond distance in CH_2Cl_2 . The high field spectrum was obtained using a $90_x^\circ - \tau - 180_y^\circ - \tau$ echo sequence. This sequence reduces the effect of field inhomogeneity, and allows us to delete the signal from the liquid molecules themselves by making τ longer than the T_2 of the liquid crystal. This presents no problem experimentally since T_2 of the liquid crystal is 100-300 μsec whereas T_2 of the probe molecule is 20-50 msec.

3.2 Zero Field Experiments

Before discussing the zero field experiments, what do we expect? The liquid crystals, as previously described, exist in a domain structure, and application of a sufficiently large magnetic field aligns the sample in a monodomain on the order of 1 second. When the field is reduced to low or zero field, will the disordering of the domain structure take place on a time scale measureable by zero field NMR and, will the local ordering, measured by the order parameter, be identical in high and zero magnetic field [66]? See Figure 3.5. When one performs the sudden experiment (Figure 3.6a) on the $\text{CH}_2\text{Cl}_2/11650$ mixture, the resulting spectrum, shown in Figure 3.7, is a single line at zero frequency.

When considering this spectrum, recall the nature of the nematic phase whereby all ϕ are equally probable, where ϕ is the angle transverse to the director axis. Therefore, the $e^{\pm i\phi}$ and $e^{\pm i2\phi}$ terms in the dipolar alphabet (C,D,E, and F) are averaged to zero. Thus, by isotropic motion perpendicular to the director axis, the nematic phase itself has truncated the dipole-dipole coupling Hamiltonian in zero field.

Figure 3.4: High field NMR spectrum (185 MHz ¹H) of CH₂Cl₂ dissolved in Eastman Kodak 11650, taken as a function of τ with the pulse sequence shown in the upper right hand corner. From the observed splitting, the molecular order parameter of the CH₂Cl₂ is determined to be $S = 0.055 \pm 0.001$.

Figure 3.5: (a) When a liquid crystal sample is exposed to a large, external magnetic field, B , the liquid crystal molecules will align in a monodomain along one common director axis (along the arrow). When the field is removed, on the time scale of the zero field experiments, will the molecules remained ordered as in (b) or will they revert to a polydomain structure of (c).

Figure 3.6: Schematics of zero field experiment field cycles. (a) The conventional sudden experiment field cycle described in the Introduction. (b) A modification to the sudden experiment, the sudden-z/pulsed-y field cycle. In this field cycle, the initial condition at $t_1 = 0$ is rotated from I_z to I_x by a $P_y = 90_y^\circ$ pulse. After t_1 , the transverse magnetization is rotated back to the laboratory z direction by $P_{y'}$. The sudden transition locks the z -component, which is then detected in high field.

Figure 3.7: Zero field spectrum of CH₂Cl₂ in Eastman Kodak 11650 using the conventional sudden experiment depicted in Figure 3.6a. The single line at zero frequency indicates that no evolution occurred in zero field during t_1 . In the nematic sample, which aligns along the applied magnetic field, the quantization axis in zero field will be the same as in high field unless disordering occurs.

This spatial truncation performed by the liquid crystals themselves is different from the spin truncation performed by a high magnetic field. Spatial truncation effects the $A_{2,m'}$ terms of the Hamiltonian while the high field spin truncation effects the $T_{2,m}$ terms. The end result of this truncation is the zero field Hamiltonian

$$H_D^0 = -\frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} S(3I_{1z} I_{2z} - \mathbf{I}_1 \cdot \mathbf{I}_2) \quad (3.4)$$

Thus, the spin system, initially prepared as I_z (magnetization along the applied magnetic field), remains I_z in zero field. Since I_z commutes with the scalar dipole-dipole Hamiltonian, there is no evolution and no signal at $\pm \frac{3}{2} \omega_D$. It is important to note that the principal axis of the zero field Hamiltonian is along the director. In other words, due to the cylindrical symmetry of the nematic, all of the local fields perpendicular to the director are averaged away leaving the local fields parallel to the director, $\mathbf{n}$. The calculated signal is

$$S(t_1) = \text{Tr}\{I_z e^{-iH_D^0 t_1} I_z e^{iH_D^0 t_1}\} = 1 \quad (3.5)$$

This spectrum goes one step further in telling us something about the liquid crystal. It says that the nematic remains as a monodomain up to the point of switching the low field (100 G) to zero. If this were not the case, signal other than the line at zero frequency would be expected. The other lines would arise as follows. If a region of the sample were to tilt such that its director were no longer along the lab z -axis, the local fields would also follow the change in director axis. The spins, however, would remain aligned, by the intermediate field, along the lab z -axis. Following the sudden transition to zero field, the local magnetic field experienced by the spins in this new domain would no longer be parallel to the spin quantization axis. This situation would be similar to an arbitrary crystallite in a polycrystalline powder.

To observe the lines at $\pm \frac{3}{2}\omega_D$ in a zero field spectrum of the $\text{CH}_2\text{Cl}_2/11650$ mixture, a modification to the experiment is required. In this experiment, we rotate the spins away from the director axis since the director axis did not rotate away from the spin quantization axis. The field cycle pictured in Figure 3.6b achieves this spin rotation. Following the sudden transition to zero field, a dc magnetic field pulse perpendicular to the laboratory z -axis is applied. After the pulse, the density operator is I_x . Since $[H_D^0, I_x] \neq 0$, evolution occurs. The calculated signal is

$$S(t_1) = \text{Tr}\{I_x e^{-i\theta' I_y} e^{-iH_D^0 t_1} e^{-i\theta I_y} I_x e^{i\theta I_y} e^{iH_D^0 t_1} e^{i\theta' I_y}\}$$

where $\theta' = 360^\circ - \theta$. If θ is set at 90° , the expression can be rearranged to

$$S(t_1) = \text{Tr}\{I_x e^{-iH_D^0 t_1} I_x e^{iH_D^0 t_1}\} \quad (3.8)$$

Complete calculation of the signal requires no powder average since the sample resembles a single crystal. For arbitrary pulse angle θ , the signal after performing the trace is

$$S(t_1) = \cos^2 \theta + \sin^2 \theta \cos\left(\frac{3}{2}\omega_D t_1\right) \quad (3.9)$$

Figure 3.8 shows the zero field spectrum of $\text{CH}_2\text{Cl}_2/11650$ mixture with the initial pulse $\theta = 90^\circ$. Measurement of the order parameter from this spectrum yields $S = 0.054 \pm 0.001$. This value is within experimental error of the high field value. Thus, not only does the monodomain structure remain upon entering low fields, the local ordering within the domain is also preserved. If the order parameter were changing, or had changed, the spectrum would be different. An order parameter in the process of changing would broaden the line. The linewidth of the spectrum, ~ 45 Hz, in Figure 3.8 is on the same order as the high field linewidth. An order parameter that had changed to a new value in the intermediate field would result in

Figure 3.8: Spectra of the $\text{CH}_2\text{Cl}_2/11650$ system obtained with the field cycle in Figure 3.6b. The dc pulses in (a) were 90°_y , 270°_y and in (b) 180°_y , 180°_y . In (a), the initial state I_x was converted to I_z following the sudden field transition. I_z is not the equilibrium state, so evolution occurs. In (b), the 180°_y pulse inverts I_x to $-I_x$, which also undergoes no evolution. These results fit the calculated signal of equation 3.9. The molecular order parameter in (a) was determined to be $S = 0.054 \pm 0.001$, a value within the experimental error of the high field order parameter. Spectral linewidth of ~ 45 Hz is attributed to residual fields.

a different order parameter in the zero field experiment as opposed to the high field experiment.

To study the effect of complete demagnetization to zero field, the field cycle in Figure 3.9a was employed. This experiment involves complete demagnetization to zero field, followed by a t_1 period initiated and terminated by dc pulses. After the initial demagnetization, the density operator remains I_z , this once again the result of the spatial truncation of the zero field Hamiltonian. With this initial condition, the dc pulses must be applied perpendicular to the laboratory z -axis. The zero field spectra obtained with this method are identical, except for differences in signal-to-noise, to the sudden- z /pulsed- x experimental spectrum of Figure 3.8. Thus, the sample remained aligned as a monodomain and preserved the order parameter even after complete demagnetization to zero field.

Attempts were made to speed up the process of returning to a polydomain sample as depicted in Figure 3.5c. As was previously stated, the walls of a sample provide the orientation in the absence of a field. What would happen then if the number of walls, that is exposed surfaces, in the sample were made artificially large? An attempt to answer this question was approached by suspending, or hopefully suspending, a large number of small glass or plastic beads in the nematic/ CH_2Cl_2 sample. The beads used were 3 μm in diameter glass beads (Atomergic Chemetals Corp.; Alufrit PS-3) and 2.5 μm in diameter plastic beads (Polysciences; hydrophilic microparticles hydroxy functionality).

The theory behind this experiment is as follows. Surfaces, due to physical features such as grooves, pits etc., will orient liquid crystal molecules preferentially in such a way that the liquid crystal is in the lowest energy state. For example, liquid crystal molecules will orient parallel to a grooved surface. The free energy of alignment with

Figure 3.9: Three additional field cycles used in the liquid crystal experiments. (a) Following adiabatic demagnetization to zero field, dc pulses initiate and terminate the zero field t_1 period. Note that the pulses must be other than z -pulses because the initial condition after demagnetization in the nematic is still I_z . (b) Similar to (a) except that a 180° refocusing pulse divides the t_1 period. This pulse removes the effect of residual fields directed along the laboratory z -axis. (c) Zero field pulse sequence for the production of dipolar order. In this zero field version of the Jeener-Broekaert experiment, the $90^\circ_x - \tau - 45^\circ_y$ creates the dipolar order. After a time Δ , which allows other orders to decay, a second 45°_y transfers the dipolar order into observable magnetization, which evolves for a time t_1 . After t_1 , a 90°_z rotates the magnetization to the z -axis where it is locked by the sudden- z transition, and observed in high field.

the surface is on the order of -10^5 erg/cm³, compared to -10^2 erg/cm³ for alignment with the magnetic field [55,64]. The results of these experiments did not indicate any disordering in low field, nor did they indicate a measureable amount of alignment away from the laboratory z -axis.

With the special symmetry of the nematic, and the resulting Hamiltonian, H_D^0 , a dc pulsed analog of the spin-echo [67] can be applied. Application of a π pulse transverse to the laboratory z -axis serves to decrease the effect of residual fields on the linewidths. The field cycle for this zero field echo experiment is shown in Figure 3.9b. A spectrum of the CH₂Cl₂/11650 sample with the echo is shown in Figure 3.10. The linewidth here is narrowed from ~ 45 Hz to ~ 15 Hz. The small lines at $1/2$ the dipolar frequency and at zero frequency arise from pulse imperfections.

Additionally, with a situation in zero field where the Hamiltonian and initial state are quite analogous to high field, the creation of dipolar order via a dc pulse version of the Jeener-Broekaert experiment [52,68] was attempted. The field cycle, shown in Figure 3.9c consists of three orthogonal dc field directions; the laboratory z -axis and x and y pulsing coils. Following the sudden switch to zero field, the pulse sequence $90_z^\circ - \tau - 45_y^\circ - \Delta - 45_y^\circ - t_1 - 90_z^\circ$ was applied.

After the first 45_y° pulse, the density operator is

$$\rho = \rho_{HD} + \rho_{DQ} \quad (3.10)$$

a sum of dipolar order and double quantum terms. As is conventional, τ is chosen to be $1/4$ of the dipolar frequency, allowing for maximum transfer to dipolar order. Δ was chosen as a time sufficient to allow single and double quantum coherence to decay. The second 45_y° pulse converts the dipolar order back into observable magnetization which evolves for a time t_1 . The terminal 90_z° rotates the magnetization back along the laboratory z -direction. The z field is suddenly reapplied, and the sample shuttled

Figure 3.10: Zero field spectrum of the CH₂Cl₂/11650 sample taken with the zero field echo sequence of Figure 3.9b. The $90_y^\circ - t_1/2 - 180_y^\circ - t_1/2 - 90_y^\circ$ sequence reduces the effect of residual fields. The linewidth in this spectrum is ~ 15 Hz. The small lines which show up at one half the dipolar frequency are the result of pulse imperfections.

to high field where the signal as a function of t_1 is measured. The signal grows in sinusoidally, as expected, and is shown in Figure 3.11. The Fourier transform appears in Figure 3.11.

3.3 Sample Preparation

Samples were composed of a 10-15 weight percent mixture of CH_2Cl_2 dissolved in the nematic. These two components were placed inside a Kel-F sample shuttle and sealed with a Kalrez O-ring. Other O-ring materials are degraded by CH_2Cl_2 . Sealed samples were heated slowly to the isotropic point, usually 60°-70° C, and mixed as thoroughly as possible. This heating and mixing procedure was repeated a few times to ensure a homogeneous mix. The temperature range for the CH_2Cl_2 /nematic mixture was typically below 20° C to 60°-70° C. Once made the samples were useable for many months.

Figure 3.11: Experimental results for the creation of dipolar order in the CH₂Cl₂ mixture using the field cycle in Figure 3.9c. At top, the interferogram comes in as a 'sine', the phase expected for a Jeener-Broekaert experiment. The τ used in the preparation of dipolar order was 160 μ sec and the delay Δ was chosen as 20 msec to allow the decay of any other coherences. Fourier transform of the interferogram leads to a two line spectrum. The linewidths and splittings, as well as the zero frequency lined may be attributed to dc pulse imperfections and residual fields.

Chapter 4

Spin Diffusion

The term spin diffusion often conjurs up images of spin order diffusing through a lattice. This form of spin diffusion, termed **spatial spin diffusion**, was first introduced by Bloembergen [69]. He introduced this idea to account for the transport of spin order away from paramagnetic impurities. Spins adjacent to the impurity are relaxed by the paramagnetic center. The resulting spin temperature difference proximal to and distal from the paramagnetic center is the driving force behind the spatial spin diffusion.

This form of spin diffusion is not, however, considered in this section. Instead, **spectral spin diffusion**, the exchange of polarization between spins separated by differing resonance frequencies, will be considered [73,78,79,80]. Both spatial and spectral spin diffusion rely on the same interaction, the dipole-dipole coupling, to mediate the diffusion process. Where the spins are equivalent (identical energy level separation), exchange of spin order occurs via spin flip-flops. On the other hand, where the resonance lines are resolved and separated from one another, the simple flip-flop exchange of order between the spins must be modified to preserve the conservation of energy. A few mechanisms, such as cooperation of extraneous spins [80] and multiple

quantum spin flips [81], have been previously proposed to allow for energy conservation. A thorough discussion of this topic can be found in the paper of Suter and Ernst [70].

The motivation behind spectral spin diffusion experiments is structural studies [72,73,74,75,76,77]. Suter and Ernst, using spin diffusion experiments, have obtained nuclear distances and orientations of the internuclear vectors for single crystals in high field. This information is also obtainable by traditional methods, such as X-ray diffraction. For many disordered materials, however, such useful information is unobtainable by the high field spin diffusion experiments and traditional structural methods. Examples of such materials are polycrystalline powders, polymers, heterogeneous polymer blends, numerous biological molecules and systems, minerals and other disordered materials, such as glass [71,72,73,74].

Ideally, spectral spin diffusion experiments would measure distances between and orientations of nuclei in these disordered materials. Additionally, the experiment may provide information to determine folding parameters in macromolecules and binding parameters in biological systems (enzyme-substrate etc.). Further, even when orientation and accurate distance information cannot be obtained, spin diffusion measurements provide proximity information, for spins must be close spatially before spectral spin diffusion can occur. This proximity information could reveal, for example, whether a macromolecule is folded-in upon itself, or whether two components in a polymer blend or heterogeneous biological system are intimately mixed or separated into domains [74].

To illustrate the potential for zero field spin diffusion measurements, we have chosen polycrystalline diethylterephthalate- d_4 , deuteration on the CD_2 groups only. This sample is ideal due to the crystallographic inequivalence of the two methy-

lene deuterons. Figure 4.1 shows the indirectly detected, zero field spectrum of diethylterephthalate- d_4 . This spectrum was taken with a zero field sampling increment of 3 μsec and 300 points in t_1 . With a recycle time between trips to zero field of 7 seconds, this leads to 1.17 hours for a single experiment. The experimental time includes the high field phase cycling discussed in the Introduction. As will be shown below, the spin diffusion experiment requires two independently incremented time domains in zero field, resulting in a time consuming experiment. We can greatly shorten the experimental time, however, by folding-in the spectrum. The spectrum is folded-in by sampling at a rate slower than that required to obtain a full bandwidth spectrum. Folding-in allows comparable frequency resolution in a shorter period of time. Figure 4.2 shows the folded-in spectrum of the same sample. Here the zero field sampling increment is 14 μsec with 64 points in t_1 for a total experiment time of 0.25 hours.

From the one-dimensional spectrum, the high frequency lines are assigned to the two inequivalent deuterons. The ν_0 lines allow the resonances labeled *a* and *c* in Figures 4.1 and 4.2 to be assigned to one of the nonequivalent deuterons. Resonances *b* and *d* are assigned to the other. The quadrupolar coupling constants and asymmetry parameters of the two methylene deuterons are $e^2qQ/h = 114.825\text{kHz}$, $\eta = 0.017$ and $e^2qQ/h = 112.35\text{kHz}$, $\eta = 0.013$. A previous two-dimensional zero field correlation experiment using the field cycle presented in Figure 4.3b measures the cross-correlation between transitions on a single deuteron [28]. The results of that experiment show crosspeaks between resonances *a* and *c*, *b* and *d*, thus confirming the assignment of the high frequency resonances based upon the ν_0 lines.

Since the dipole-dipole interaction mediates spin diffusion, the spin diffusion rate depends upon the gyromagnetic ratios, γ_1 and γ_2 , of the two nuclei of interest and

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Figure 4.1: Indirectly detected zero field deuterium spectrum of diethylterephthalate- d_4 (DET- d_4), deuterated on the CD_2 groups. The spectrum was taken with a zero field sampling increment of $3\mu\text{sec}$ and 300 points in t_1 . High field spin-locking was averaged over 20 points with a $50\mu\text{sec}$ delay between RF pulses. The expanded region shows the high frequency resonances of the methylene deuterons, which are plotted in the two-dimensional experiments. The ν_0 lines allow assignment of those peaks labelled *a* and *c* and those *b* and *d* to the two nonequivalent deuteron sites.

Figure 4.2: Experimental (top) and computer simulated spectra of DET- d_4 . Indirectly detected deuterium spectrum of DET- d_4 taken with a zero field sampling increment of $14 \mu\text{sec}$ and 64 points in t_1 . The folded-in spectrum shortens the experimental time, thereby making two-dimensional spectroscopy more feasible. The ν_0 lines in the experimental spectrum are below the noise level. This results from an uneven polarization transfer between the protons and deuterons during the demagnetization/remagnetization.

Figure 4.3: 3a) Schematic of a two-dimensional, zero field, field cycle for direct detection of deuterons. When the intermediate field pulse between the two time dimensions is short, this field cycle measures the cross-correlation between transitions on a single deuteron. When the intermediate field pulse is long compared to the dipole-dipole coupling of inequivalent deuterons, spin diffusion may occur. b) Schematic of a field cycle comparable to a) but for indirect detection of deuterons. c) Another possible field cycle to monitor spin diffusion in zero field. In this variation, t_1 is terminated by a short dc field pulse. The field is then brought adiabatically up to the intermediate field where spin diffusion will occur. The adiabatic sweep may enhance or stimulate the spin diffusion process for a particular orientation or orientations.

upon the distance between them, r_{12} , as

$$d \propto \frac{\gamma_1 \gamma_2}{r_{12}^3} \quad (4.1)$$

where d is the dipole-dipole coupling. For the case discussed here, two coupled deuterons, the total Hamiltonian can be written

$$H = H_{Q_1} + H_{Q_2} + H_D \quad (4.2)$$

where H_{Q_i} is the quadrupolar Hamiltonian for nucleus i and H_D is the dipole-dipole coupling between the two nuclei. Both the quadrupolar and dipolar interactions are expressed in their respective principal axis system. In general, these two principal axis systems will not be the same.

For diethylterephthalate- d_4 , the quadrupolar interaction dominates the energy level scheme in Figure 4.4. The labeling of the states in Figure 4.4 follows the convention of Vega [29]. In this convention, the eigenfunctions and energies for a single nucleus are

$$\begin{aligned} E_x &= A_q(1 - \eta) \quad |x\rangle = (1/\sqrt{2})(|+1\rangle - |-1\rangle) \\ E_y &= A_q(1 + \eta) \quad |y\rangle = (i/\sqrt{2})(|+1\rangle + |-1\rangle) \\ E_z &= -2A_q \quad |z\rangle = |0\rangle \end{aligned} \quad (4.3)$$

where $|+1\rangle$, $|-1\rangle$ and $|0\rangle$ are the eigenfunctions of I_z .

The labels on the arrows in Figure 4.4 represent elements of the dipole-dipole operator. Labels indicate which product of angular momentum operators written in the principal axis system of the quadrupole tensors will induce a particular transition.

In general, spin diffusion is expected to occur between energy levels of the quadrupolar Hamiltonian that are connected by a matrix element of the dipole-dipole interaction and whose energy difference is not too large compared with the size of the corresponding matrix element. Those pathways that meet these criteria are shown

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Figure 4.4: Zero field energy level diagram for two inequivalent deuterons, subject to nuclear quadrupole interactions of similar magnitude and asymmetry parameter $\eta \ll 1$. The arrows indicate those energy levels within a particular subgroup, which are connected by elements of the dipole-dipole operator.

in Figure 4.4. Therefore, spin diffusion is expected to occur within the two groups of four energy levels. Arrows between different groups of eigenstates have thus been omitted in the figure.

According to equations 4.1 and 4.2, the size of the matrix elements connecting the energy levels depends on the distance between the nuclei as well as on the orientation of the internuclear vector, r_{12} , with respect to the principal axis system of the two quadrupole tensors. By comparing experimental results to calculated matrix elements, the distance between and orientation of the two nuclei could be calculated. To better appreciate the orientation dependence, one needs to express the dipole-dipole and quadrupole Hamiltonians in a common frame.

The form of the dipole-dipole interaction and therefore the nature of the spin diffusion process is different in high field and zero field. In zero field, the dipole-dipole coupling between nonresonant neighboring spins (if they possess integer spin angular momentum) is zero in first order when the quadrupoles are asymmetric. Thus, the secular part of the dipole-dipole interaction vanishes. In high field the dipole-dipole coupling is truncated, leaving the secular interaction.

The measurement of spin diffusion in zero field requires the high field preparation period, two time dimensions in zero field separated by a mixing period during which the spin diffusion occurs, and a high field detection period. See Figure 4.5 for a schematic of the field cycle. The experiment proceeds as follows. The initial pulse converts polarization of the quadrupole system prepared by the adiabatic demagnetization into coherences. These coherences evolve for a time t_1 , when a second pulse is applied. This second pulse converts a portion of the evolved coherences back into populations. Those coherences that are not converted into populations decay in a time T_2 . During the mixing period, τ_m , the spin diffusion process, which is

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Figure 4.5: The two-dimensional exchange experiment used to monitor spin diffusion for the results presented here. The periods t_1 and t_2 are incremented systematically while the mixing time τ_m is kept constant. Fourier transformation with respect to t_1 and t_2 yields a two-dimensional exchange spectrum where the cross peaks ($\omega_1 \neq \omega_2$) indicate the occurrence of spin diffusion.

mediated by the dipole-dipole coupling, causes populations of the energy levels on the deuterons to undergo exchange. This process is striving toward an internal equilibrium. The third pulse converts these new populations back into coherences that evolve for a time t_2 , before being reconverted into populations for the return to high field.

In the spin diffusion experiment, t_1 and t_2 were incremented separately between 0 and 882 μsec , for a total of 64 points in each dimension. Thus, with the folded-in spectrum, the zero field period consists of 4096 trips to zero field (not counting phase cycling). The data were zero filled in both dimensions to 256 points and Fourier transformed. Examples of the resulting two-dimensional spectra are shown in Figure 4.6. The spectra show the results of 1 msec and 50 msec mixing periods.

In the short mixing time spectrum, no cross peaks are observed. In the 50 msec spectrum, however, cross peaks between the a and b and between the c and d resonances are observed. This is the anticipated result, indicating that spin diffusion is indeed occurring. The absence of crosspeaks at the 1 msec mixing time is not too surprising. In a methylene group, the distance between deuterons is on the order of 3.4 Å, leading to a dipole-dipole coupling on the order of 1 kHz. A coupling of that strength should give crosspeaks at mixing times greater than ~ 1 .

In this experiment, detection of the deuterons is done indirectly. The extra initiating pulse and terminating pulse of the indirect detection experiment (as opposed to the sudden transitions before t_1 and after t_2 in the direct detection experiment) leave too many variables for a complete calculation. As previously stated in the Introduction, the initial condition after adiabatic demagnetization is unknown, and even if the form for the initial condition were known, the populations after the level crossings would remain unknown. Such ambiguities make an explicit calculation of

Figure 4.6: Experimental spin-diffusion spectra of diethylterephthalate- d_4 . Only the ν_+ and ν_- lines shown in the expanded plot of Figure 4.2 are shown. The two spectra were recorded with different mixing times and show that spin diffusion occurs on a time scale of a few milliseconds.

the spin diffusion rate as a function of distance and orientation of the deuterons, as well as a function of the second and third pulse angles impossible. Thus, direct detection of the deuterium signal is desirable because calculation of the signal is easier.

The field cycle in Figure 4.5 is not the only way to perform the spin diffusion experiment. A modification to the cross-correlation field cycles of Figure 4.3a and 4.3b, where the pulse between t_1 and t_2 is long (long enough for spin diffusion to occur) will also work. Additionally, the field cycle presented in Figure 4.3c was previously introduced by Zax [30] as a possible spin diffusion measuring field cycle. Zax reports that a possible advantage of this field cycle is that it sweeps through a large range of low fields that may stimulate or enhance the spin diffusion process for a particular orientation or orientations. These field cycles also present the possible advantage of relying on the intermediate field T_1 , as opposed to the zero field T_1 , during the mixing period. This may allow for a longer mixing period and therefore more opportunity for spin diffusion to occur.

Chapter 5

Pulses in Zero Field

5.1 Introduction

In high field NMR of solids, spin echoes [82,83] and multiple spin echoes [84,85,86] reveal that the broad lines found in solid state NMR can be narrowed. In zero field NMR, an analog of the Hahn echo was previously shown to narrow the line in a nematic liquid crystal where the line broadening is the result of residual fields [87]. This Chapter describes the application of single echo pulses and pulse trains to solids.

The linewidth in a dipole-dipole coupled system such as $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ in zero field is on the order of 7 kHz. This linewidth is really quite broad when compared with the linewidth in high resolution experiments of solids performed in high field. Previous computer simulations [30] and experimental evidence [2,30,47] indicate that the linewidth in a hydrated salt, such as $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, is not the result of residual fields. In the limit of a poorly shimmed zero field, for example ~ 100 mG residual field, the contribution to the linewidth is only on the order of a few hundred Hz. Instead, the linewidth is the result of dipolar broadening. In $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ the two hydrogen atoms of the water molecule are coupled not only to themselves, but

are also weakly coupled to the nearest neighbor water molecules, and to the next removed nearest neighbors, and so on.

Experiments on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, where the concentration of protons is diluted with deuterons, indicate that the linewidth does decrease as the proton concentration, and therefore interpair dipolar coupling, decreases [30,37,38,36]. Upon dilution, fine structure caused by the libration of the water molecule is observed. The line is actually the superposition of two lines, each line approximately 2 kHz wide. Thus, when the interpair dipole-dipole couplings are diluted, the linewidth in the proton spectra tends to the linewidth in the deuteron spectra (100-200 Hz linewidths). This seems reasonable, since in deuterons the dipole-dipole coupling is quenched by the quadrupolar interaction in zero field, and as a result, dipolar broadening is minimal in the deuterium spectra.

In the four spin system of 1,2,3,4-tetrachloronaphthalene bis-(hexachlorocyclopentadiene) adduct, the situation is fundamentally different from the two coupled spin system of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. The linewidth of the zero field spectrum results primarily from the allowed transitions within the four spin system itself [2,30,47]. An additional contribution to the linewidth arises from the intermolecular dipolar coupling, and from the large number of chlorine atoms situated about the hydrogen atoms. The contribution from the chlorine atoms is small, however, due to the quenching of the dipolar coupling because of the quadrupolar interaction, and by the small gyromagnetic ratio of the chlorine atoms.

5.2 Experimental Results

Figure 5.1 shows three pulse sequences used in the echo experiments. The field cycle in 1a is used to apply a single pulse, separated by two $t_1/2$ periods. As shown

Figure 5.1: Schematic field cycles for the echo experiments. (a) Field cycle to monitor the effect of the pulses on the zero field spectrum. After the $t_{1/2}$ period, a θ_i pulse is applied, where $i = z$ or x . A second $t_{1/2}$ period occurs before the intermediate field is suddenly reapplied and the magnetization sampled in high field. (b) In this field cycle a single θ_i pulse is applied after a time τ . This is followed by a t_1 period. With this field cycle, the effect of the pulse on the FID can be monitored. (c) An extension of the field cycle in (b) for delivering multiple dc magnetic field pulses in zero field. Following the τ and initial θ_i pulse, the sequence $[\Delta - \theta_i]_n$, where $n = 0, 1, 2, \dots$, is applied and the t_1 sequence is initiated. t_1 is incremented up to Δ , at which time a θ_i pulse is applied and the process repeated for increasing values of n . From this one can monitor the effect of a multiple pulse train on the zero field signal.

previously in Chapter 3, the application of a Hahn echo in zero field works well in a nematic liquid crystal where the zero field Hamiltonian is identical to the high field Hamiltonian. With this field cycle we can monitor what effect the Hahn echo has on a solid in zero field where the Hamiltonian is H_D , not H_D^0 . Calculation of the signal for the field cycle in Figure 1a is done as follows.

$$S(t_1) = \text{Tr}\{I_{x,L} R e^{-iH_z t_1/2} R^{-1} e^{-i\theta_i I_z} R e^{-iH_z t_1/2} R^{-1} I_{x,L} R e^{iH_z t_1/2} R^{-1} e^{i\theta_i I_z} R e^{iH_z t_1/2} R^{-1}\} \quad (5.1)$$

After powder averaging the signal, where θ_i is a x -pulse,

$$S(t_1) = \frac{1}{9}[3 + 4 \cos(\frac{3}{2}\omega_D t_1/2) + 2 \cos(\frac{3}{2}\omega_D t_1)] + \frac{1}{15}[1 + 2 \cos \theta_x + 2 \cos 2\theta_x][\cos(\frac{3}{2}\omega_D t_1) - 1] \quad (5.2)$$

Where θ_i is a x -pulse the signal is

$$S(t_1) = \frac{1}{9} \cos \theta_x [3 + 4 \cos(\frac{3}{2}\omega_D t_1/2) + 2 \cos(\frac{3}{2}\omega_D t_1)] + \frac{1}{15} [1 + 2 \cos \theta_x + \frac{9}{4} \cos 2\theta_x][\cos(\frac{3}{2}\omega_D t_1) - 1] \quad (5.3)$$

When the zero field spin echo analog, a 180° or 180° dc pulse, is applied to polycrystalline $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, the result is shown in Figure 5.2. Aside from the line at zero frequency, lines appear at the dipolar frequency ± 42 kHz, as in the conventional sudden experiment, and at one-half the dipolar frequency, ± 21 kHz. This confirms the calculated signal of equations 5.2 and 5.3. The signal arising from those spins that have evolved for one-half the full evolution period, $t_1/2$, produces the inner lines at one-half the dipolar frequency. These lines should not be compared to the small lines at one-half the dipolar frequency resulting from the application of the Hahn echo to a nematic liquid crystal. In that case the lines arise from imperfections in the pulses. In the solid the lines are not an experimental artifact, instead they arise

Figure 5.2: Zero field spectra of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ with the field cycle in Figure 5.1a where (a) $\theta_i = 180^\circ$ and (b) $\theta_i = 180^\circ$. The 100 point FID's with t_1 increments of $10 \mu\text{sec}$, $5 \mu\text{sec}$ on either side of the pulse were zero filled to 1024 points and Fourier transformed. In (a) the peaks appear at $\pm 42 \text{ kHz}$ (5.6 kHz wide) and $\pm 21 \text{ kHz}$ (2.8 kHz wide). (b) The peaks appear at $\pm 42 \text{ kHz}$ and $\pm 21 \text{ kHz}$, both are 4.4 kHz wide.

because the full dipolar Hamiltonian, H_D , is effective. In the conventional sudden experimental spectrum of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, the linewidth is 7 kHz. In the 180° echo spectrum the outer lines are 5.6 kHz wide and the inner lines 2.8 kHz wide. In the 180°_x spectrum both lines are 4.4 kHz wide. The narrowing of the lines compared to the sudden experiment indicates that some of the dipolar broadening is averaged away. The reason for the difference in the linewidths between the two experiments is not known.

A field cycle that demonstrates the effect of the solid echo analog, $\theta_i = 90^\circ$, in zero field appears in Figure 5.1b. This field cycle demonstrates how well the solid echo performs under the untruncated dipolar Hamiltonian in zero field. As the calculations reveal, in zero field the Hamiltonian prevents the echoes from being perfect as they are in high field. Calculation of the signal for the field cycle in Figure 5.1b is quite similar to the calculation for Figure 5.1a. The only difference is in replacing the $t_1/2$ in the first evolution period by τ and the $t_1/2$ in the second evolution period by t_1 . The signal for the z -pulse is

$$S(t_1) = \frac{1}{9} [1 + 2 \cos(\frac{3}{2} \omega_D \tau)] [1 + 2 \cos(\frac{3}{2} \omega_D t_1)] \quad (5.4)$$

$$- \frac{2}{15} [1 + 2 \cos \theta_z + 2 \cos 2\theta_z] [\sin(\frac{3}{2} \omega_D \tau) \sin(\frac{3}{2} \omega_D t_1)]$$

The maximum in the signal is at $\theta_z = 104.5^\circ$, so the choice of $\theta_z = 90^\circ$ is near the maximum echo amplitude. Experimental examples on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ for four values of τ are presented in Figure 5.3 along with the conventional sudden experiment. These results show that application of the pulses does elicit some refocusing of the magnetization and does cause the signal to last longer before becoming comparable to the noise.

Echo formation in the two coupled spin system is not an exception, the echo also works in the four proton system of 1,2,3,4-tetrachloronaphthalene bis-(hexachloro-

Figure 5.3: (a) Conventional sudden experiment performed on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. Experimental results for the zero field analog of the solid echo, $\theta_x = 90^\circ$, with the field cycle in Figure 5.1b performed on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ where (b) $\tau = 30\mu\text{sec}$, (c) $\tau = 52\mu\text{sec}$, (d) $\tau = 92\mu\text{sec}$ and, (e) $\tau = 132\mu\text{sec}$. The arrow points to the time of the pulse. As the experimental results indicate, the echo does have a positive effect on the duration of the signal before the signal is within the noise. As indicated by (e), however, the effect diminishes after a long τ . All experiments were performed with a $1\mu\text{sec}$ increment in t_1 .

cyclopentadiene) adduct. Figure 5.4 shows results of the sudden experiment and two examples with different values of τ for this four spin system. With this sample, the echo clearly forms, but distinguishing whether or not the echo prolonged the signal is difficult to determine given the more complicated FID.

To find out if multiple echos will further prolong the signal, in analogy to high field spin-locking, one can apply the field cycle in Figure 5.1c. After the sudden transition to zero field, the magnetization is allowed to evolve in zero field for a time τ . This time is chosen to correspond to some specific point in the FID, such as a maximum or null point. At this point a θ_i pulse, where $i = z$ or x , is applied and the magnetization allowed to evolve for t_1 . The intermediate magnetic field is suddenly reapplied and the magnetization as $S(t_1)$ is sampled. After t_1 has been incremented up to $t_1 = \Delta$, an additional θ_i pulse is applied, followed by a t_1 period. This $(\Delta - \theta_i)_n$ segment is repeated and the echo train mapped out point by point. Calculation of the signal for the field cycle in Figure 5.1c is complicated. The calculation is set up similar to the calculation for Figure 5.1b, but with the evolution periods of length Δ added.

Figure 5.5 shows the initial portion of the zero field FID for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. As the plot indicates, the period is approximately 24 μsec . This figure is referred to later to indicate where multiple pulses are applied. Experimental examples for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ with $\theta_i = 90^\circ$ multiple pulses appear in Figure 5.6 and Figure 5.7. The pulses applied in Figure 5.6 are applied 'on-resonance', that is, they are applied consistently at multiples or fractions of 24 μsec (either 12 or 24 μsec). The data shown in Figure 5.7 are for pulses applied 'off-resonance'. As the two figures show, pulsing 'on-resonance' or 'off-resonance' makes little or no difference in the long time behavior of the signal. Figure 5.6a shows that pulses applied too early on in the

Figure 5.4: (a) Conventional sudden experiment on 1,2,3,4-tetrachloronaphthalene bis-(hexachlorocyclopentadiene) adduct. 90° solid echo of Figure 5.1b applied at (b) $\tau = 10\mu\text{sec}$ and (c) $\tau = 20\mu\text{sec}$. All the experiments were performed with a $5\mu\text{sec}$ increment in t_1 . In this four-proton system the echo pulse clearly has an effect on the FID. The ability to determine if the signal lasts longer in time is thwarted by the signal-to-noise ratio and complex FID.

Figure 5.5: Initial portion of the $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ zero field FID. The zero field frequency of 42 kHz corresponds roughly to a complete cycle every 24 μsec .

Figure 5.6: Field cycle in Figure 5.1c applied to $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. (a) Multiple 90° pulses applied every 12 μsec . (b) Multiple 90° pulses applied every 24 μsec . (c) Multiple 90° pulses applied every 12 μsec , after the initial pulse is applied at 18 μsec .

Figure 5.7: Field cycle in Figure 5.1c applied to $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. (a) Multiple 90°_z applied every 18 μsec . (b) First 90°_z pulse applied at 24 μsec , and multiple 90°_z pulses applied every 22 μsec .

FID cause a disruption in the signal. Also, we see from the figures that following an initial period of fast decay, the signal stabilizes into a slow decay. An experimental example of the application of multiple $\theta_i = 90^\circ$ pulses to the four proton system in 1,2,3,4-tetrachloronaphthalene bis-(hexachlorocyclopentadiene) adduct is shown in Figure 5.8. The figure indicates that the signal is clearly prolonged by multiple pulses in the four proton system.

Multiple 180° pulses on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ are shown in Figure 5.9 with two different Δ delays. As the plots show, the signal is inverted after each pulse. A calculation of the signal up to the point of one pulse (that is, $\Delta = 0$) shows that the inversion is expected

$$\begin{aligned}
 S(t_1) = & \frac{1}{9} \cos \theta_x [1 + 2 \cos(\frac{3}{2} \omega_D \tau)] [1 + 2 \cos(\frac{3}{2} \omega_D t_1)] \\
 & - \frac{2}{15} [1 + 2 \cos \theta_x + \frac{9}{4} \cos 2\theta_x] [\sin(\frac{3}{2} \omega_D \tau) \sin(\frac{3}{2} \omega_D t_1)]
 \end{aligned} \quad (5.5)$$

The inversion of the signal can be seen by setting $\theta_x = 180$ and $\tau = 0$.

Unfortunately, pulse programmer hardware limitations prevented the echo trains from being applied for even longer periods of time. Thus, we are unable to find out how much the linewidth of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and 1,2,3,4-tetrachloronaphthalene bis-(hexachloro-cyclopentadiene) adduct could be narrowed, and how much different the narrowing is in the two different samples, the two and four proton systems.

Figure 5.8: Multiple 90° as in Figure 1c performed on 1,2,3,4-tetrachloronaphthalene bis-(hexachlorocyclopentadiene) adduct. Here, the multiple pulses, which are applied every $10\mu\text{sec}$, clearly elicit multiple echos.

Figure 5.9: (a) Multiple 180°_x pulses as in Figure 5.1c on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. The pulses are applied every $12 \mu\text{sec}$. (b) The echo 180°_x pulses are applied every $24 \mu\text{sec}$, with the first pulse applied at $12 \mu\text{sec}$.

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