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Development of Nuclear Quadrupole Resonance Spectroscopic and Imaging Methods.

Youngil Lee

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DEVELOPMENT OF NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPIC AND IMAGING METHODS

A Dissertation
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirement for the degree of Doctor of Philosophy
in
The Department of Chemistry

by
Youngil Lee
B.S., Hanyang University, Seoul, Korea, 1989
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To Mother and Father
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ABSTRACT

Solution-state nuclear magnetic resonance (NMR) of $^1$H and $^{13}$C nuclei in molecular species is very common as is solid-state NMR of $^{13}$C in a wide variety of substances. Yet many nuclei remain little studied by conventional NMR techniques, for example $^2$H, $^{11}$B, $^{14}$N, $^{79}$Br, $^{81}$Br, and $^{93}$Nb. One method for their study is nuclear quadrupole resonance (NQR). Briefly, the reason that quadrupolar nuclei are difficult to study with conventional NMR techniques is the exceedingly large line widths these nuclei exhibit in high magnetic fields.

The first part of my dissertation deals with NQR spectroscopic techniques developed to obtain structural information on solids using three different line narrowing techniques: (1) The results of field swept $^{93}$Nb NMR experiments of BaNb$_x$S$_3$ ($x = 0.8, 1$) are presented with the Oxford 16/18 Tesla superconducting magnet at 4.2 K. (2) The development of a broadband NQR spectrometer having very wide spectral range from 200 to 300 MHz with automatic frequency selection and a novel automatically-tuned probe and the results of $^{79}$Br and $^{81}$Br NQR of some brominated aromatic compounds are discussed. (3) The development of a field cycling NQR spectrometer based on a conventional NMR, a high speed linear stepping motor, and an Oxford gas flow cryostat is described with some $^2$H and $^{14}$N NQR spectra.

The second part of my dissertation describes novel $^{11}$B and $^{14}$N NQR imaging techniques that use field cycling as a line narrowing technique and therefore, is a combination of both NQR spectroscopy and NMR imaging. A demonstration of two–dimensional $^1$H imaging using an unmodified solution-state NMR spectrometer is also presented.
CHAPTER 1

INTRODUCTION
1.1 General Introduction

Solution-state nuclear magnetic resonance (NMR) of $^1$H and $^{13}$C nuclei in molecular species is very common as is solid-state NMR of $^{13}$C in a wide variety of substances. Yet many nuclei remain little studied by conventional NMR techniques, for example $^2$H, $^{11}$B, $^{14}$N, $^{79}$Br, $^{81}$Br, and $^{93}$Nb. One method for their study is nuclear quadrupole resonance (NQR), which was first demonstrated by Dehmelt and Krüger in 1950 for $^{35}$Cl and $^{37}$Cl in trans-dichloroethene.[1.1] Briefly, the reason that quadrupolar nuclei are difficult to study with conventional NMR techniques is the exceedingly large line widths these nuclei exhibit in high magnetic fields.

The first part of my dissertation deals with NQR spectroscopic techniques developed to obtain structural information on solids using three different line narrowing techniques. The second part of my dissertation describes novel NQR imaging techniques that use field cycling as a line narrowing technique and therefore, is a combination of both NQR spectroscopy and NMR imaging. Lastly, two-dimensional $^1$H imaging is demonstrated using an conventional solution-state NMR spectrometer.

1.1.1 Basic Principle of Nuclear Magnetic Resonance

A nucleus with $S \neq 0$, $S$ being the quantum number of the nuclear spin angular momentum, has a nuclear spin angular momentum. The spinning charges with angular momentum generate the nuclear magnetic moment along the axis it spins. If the nucleus, such as the proton ($S = 1/2$), is placed in an external magnetic field, its magnetic moment has an energy which varies with the orientation of that field. There are two possible energy states of the proton spin depending on whether or not its magnetic moment is aligned with or against that field. The NMR absorption is a result of transitions between these two energy levels, stimulated by the applied rf field.

A single nucleus has a nuclear magnetic moment which precesses with some speed around the applied magnetic field. The frequency of precession, $\omega$, is known as
the Larmor frequency of the observed nucleus, and is its NMR frequency. The Larmor frequency is a function of \( \gamma \) and \( B_0 \).

\[
\omega = 2\pi v_0 = \gamma B_0
\]  

(1.1)

The magnetogyric ratio, \( \gamma \), is a proportionality constant that describes the spin state energies of a given nucleus. Each isotope with nonzero nuclear spin has its own unique value of \( \gamma \). Thus, each nucleus has the characteristic Larmor frequency in an external magnetic field.

Each nuclear orientation with respect to the external magnetic field corresponds to an energy level, the lowest corresponding to the orientation in which the nuclear magnetic moment is most closely aligned with the field. For any system of energy levels at thermal equilibrium, there are always more particles in the lower states than in the upper states. The ratio of population in each energy state is a function of energy separation, \( \Delta E \), in the form of the Boltzmann distribution.

\[
\frac{N_U}{N_L} = e^{-\Delta E/kT}
\]  

(1.2)

\( N_U \) is the population of the upper state, \( N_L \) is the population of the lower state, \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature. NMR is produced by inducing transitions between such energy levels by means of fluctuating magnetic fields of the correct frequency, \( v_0 \). Thus, energy separation is a function of transition frequency (Larmor frequency),

\[
\Delta E = h v_0
\]  

(1.3)

where \( h \) is Plank’s constant.
The sensitivity of NMR can be increased with changing of the ratio of population by increasing the external magnetic field strength or decreasing the temperature. When the ratio of population is equal to 1, a condition called saturation occurs which allows no NMR signal to be detected.

1.1.2 Magnetic and Electrostatic Interactions in NMR

In NMR, a nucleus has five main interactions with the magnetic field, neighboring magnetic moments, and the local electric charge distribution:

1. the Zeeman interaction with the magnetic field,
2. the dipole-dipole interaction with other nuclei,
3. the magnetic shielding interaction with the surrounding electrons giving chemical shift,
4. the scalar \( J \) or spin-spin coupling of two or more nuclei, and
5. the nuclear electric quadrupolar interaction with electric field gradients.[1.2-4]

The suppression of the effects of specific internal interactions while maintaining the effects of others is one of the main areas of research in the field of solid state NMR spectroscopy today.

A general Hamiltonian, \( H_T \), for the interactions by a nucleus in the solid state is

\[
H_T = H_Z + H_D + H_{CS} + H_J + H_Q.
\]  

Each interaction will be discussed in more detail in subsequent sections.

The Zeeman interaction describes the coupling of the magnetic moment of the nucleus to the applied magnetic field, \( B_0 \), yielding \( 2S + 1 \) energy levels. In terms of the spin angular moment, \( S_k \), of the nuclei in the sample, the Hamiltonian, in frequency unit, [rad s\(^{-1}\)], is [1.2]
The magnitude of this interaction is linear with the applied magnetic field. Larger separations of the energy levels developing at higher magnetic field correspond to an increase in the population difference between energy levels and an increase in the signal-to-noise ratio of the spectrum. The typical size of the Zeeman interaction at 4.7 Tesla is 200 MHz for $^1$H nucleus.

In NMR studies of solid samples, the direct dipole-dipole interaction is often the dominant contribution to the broad line widths between neighboring nuclei ($S = 1/2$). In the case of homonuclear dipolar coupling, the Hamiltonian is written as [1.2]

$$H_D = \frac{\gamma_S^2 \hbar}{r_{ij}^3} S \cdot D \cdot S$$  \hspace{1cm} (1.6)$$

where $r_{ij}$ is the internuclear distance, $D$ the dipolar coupling tensor, and $\gamma_S$ the magnetogyric ratio of spin magnetic moment, $S$. In the $^1$H homonuclear case, the contribution of dipolar interaction to the line widths is less than 40 kHz in typical systems.[1.5] The heteronuclear dipolar interaction between an isolated pair of unlike spins, $I$ and $S$, of magnetogyric ratio, $\gamma_I$ and $\gamma_S$, is [1.2]

$$H_D = \frac{\gamma_I \gamma_S \hbar}{r_{ij}^3} I \cdot D \cdot S. \hspace{1cm} (1.7)$$

The suppression of $^1$H-$^{13}$C heteronuclear dipolar coupling is a standard feature of the $^{13}$C cross polarization and magic angle spinning (CP/MAS) NMR experiment. Important features of the dipolar interaction are that it depends on the magnitude of the
magnetic moments, that it is independent of the applied magnetic field, $B_0$, and that it decreases very rapidly with the internuclear distance.[1.2]

The indirect coupling of nuclei to the static magnetic field by interaction with the fields produced by the surrounding electrons causes shifts in resonance frequencies. The chemical shifts are a reflection of the chemical environment of a nucleus in an atom or molecule.[1.3,6] The Hamiltonian of chemical shift for spin $S$ is [1.2]

$$H_{CS} = \gamma_S \hbar \mathbf{S} \cdot \mathbf{\sigma} \cdot \mathbf{B}_0$$

(1.8)

where $\mathbf{\sigma}$ is the chemical shift tensor. The chemical shift interaction is proportionally larger at higher magnetic field. Also, this is the most sensitive interaction to geometry and identity of the other atoms surrounding a particular nucleus.[1.2] The actual chemical shift line broadening in a solid is field and nuclear dependent and is on the order of 2.5 kHz at 4.7 T for $^1\text{H}$. [1.4]

The indirect spin-spin coupling interaction between a pair of spins $I$ and $S$ is represented as [1.2]

$$H_J = \mathbf{I} \cdot \mathbf{J} \cdot \mathbf{S}$$

(1.9)

where $\mathbf{J}$ is scalar coupling tensor. The coupling interaction is field independent and is usually ignored in the solid state because of its small size, less than 1000 Hz for most spin pairs.

The quadrupolar interaction occurs only when the spin angular moment, $S$, is greater than 1/2, and is the interaction of the nuclear electric quadrupole moment, $eQ$, with the non-spherically symmetrical electric field gradient around the nucleus.[1.2] The interaction is described by [1.2]
\[ H_Q = S \cdot Q \cdot S \]  \hspace{1cm} (1.10)

where \( Q \) is the quadrupolar coupling tensor. As shown in equation (1.10), the quadrupolar interaction is field independent. Because the magnitude of the interaction is up to several MHz, for example \(^{14}\text{N}\) nucleus has 0.6 – 3.5 MHz range, the quadrupolar interaction can easily dominate the spectrum in the solid state.[1.7]

These interactions are anisotropic and can have large effects on the spectrum in the solid state due to the relatively fixed orientations of the molecules, whereas in solution average values are obtained due to the fast and isotropic motion of the molecule. The dipolar and quadrupolar couplings are only observable in solid, because the average values of these interactions are exactly zero in solution.[1.2] The major interest of my research is the quadrupole interaction in the solid state which will be used to characterize molecules and image materials.

1.2 Solid-State Nuclear Quadrupole Resonance Spectroscopy

Solid-state NMR of quadrupolar nuclei, \( S > \frac{1}{2} \), and nuclear quadrupole resonance (NQR) spectroscopy are techniques to measure weak interactions between nuclei having nonzero quadrupole moments \((Q)\) and their local electric environment in the ground state of the solid system.[1.8] The most important NQR spectroscopic parameters are the quadrupole coupling constant and the electric field gradient asymmetry parameter. These parameters are highly sensitive to the minor changes in the local electric environment as well as to subtle structure changes. Thus, NQR provides valuable information on chemical bonding, structure of solids, and dynamics of solids.[1.9,10]
1.2.1 Definition of NQR

For a nucleus with a spin angular momentum greater than 1/2, which has a nonspherical charge distribution, the solid state NMR spectra are usually dominated by the nuclear quadrupolar interaction. A quadrupolar nucleus possesses an electric quadrupole moment, \( eQ \), which can interact with the electric field gradient produced by neighboring charges. In the presence of a magnetic field, it is more convenient to use nuclear spin functions appropriate for the coordinate system of the magnetic field. Thus, the common form of the Hamiltonian for this interaction for the case of an applied magnetic field is

\[
H_Q = \frac{eQ\hbar}{6S(2S-1)} \sum_{kj} V_{kj}^{lab} \left[ \frac{3}{2}(S_k S_j + S_j S_k) - \delta_{kj} S^2 \right]
\]  

(1.11)

where \( e \) is the electrostatic unit of charge, \( Q \) is the size of nuclear quadrupole moment, and \( \delta_{kj} \) is the kronecker delta.[1.3,11] Nuclear spin angular momentum is usually given the symbol \( S \). The electric field gradient, \( V_{kj} = e\delta_{kj} \), can be described by a symmetric 3 x 3 traceless tensor.[1.12] The magnitude of the electric field gradient tensor is given by the quadrupolar coupling constant. The quadrupolar coupling constant, \( C_Q \), is defined as

\[
C_Q = \frac{e^2 q_{zz} Q}{\hbar} = \frac{eV_{zz} Q}{\hbar}
\]  

(1.12)

and the asymmetry parameter, \( \eta \), is as

\[
\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}
\]  

(1.13)
where the electric field gradient is defined so that $|\nu_{zz}| > |\nu_{xx}| > |\nu_{yy}|$ and $\eta$ ranges from 0 to 1. [1.8] In the principal axis system, the electric field gradient tensor can be reduced to two parameters, $\varepsilon_{zz}$ and $\eta$:

$$\nu^{\text{PA}} = -\frac{\varepsilon_{zz}}{2} \begin{bmatrix} (1 - \eta) & 0 & 0 \\ 0 & (1 + \eta) & 0 \\ 0 & 0 & -2 \end{bmatrix}$$  \hspace{1cm} (1.14)$$

The electric field gradient tensor of the molecular coordinate system, $\nu^{\text{PA}}$, can be transformed to the laboratory system (Lab), $\nu^{\text{Lab}}$, by direction cosine matrices [1.13] using the $y$-convention:[1.14]

$$\nu^{\text{Lab}} = R_N^{-1}(\theta)R_z^{-1}(\chi)\nu^{\text{PA}}R_z(\chi)R_N(\theta)$$  \hspace{1cm} (1.15)$$

where $R$ is the rotational transformation. Only two Euler angles, $\theta$ and $\chi$, are needed to orient the electric field gradient tensor relative to the applied magnetic field, $B_0$.

For the case of zero applied magnetic field, eq. (1.11) transforms to

$$\nu^{\text{Lab}} = \frac{C}{4S(2S-1)}[3S_z^2 - S^2 + \frac{\eta}{2}(S_+^2 - S_-^2)]$$  \hspace{1cm} (1.16)$$

where $q_{zz}$ is the charge distribution of the major axis. The nuclear spin angular momentum operators are $S, S_z, S_+$, and $S_-$. The quadrupolar coupling constant and asymmetric parameter provide complementary information about the quadrupole nuclei. The quadrupolar coupling constant can easily be obtained from the transition frequencies of quadrupole nuclei in
zero applied magnetic field. The frequencies depend on the electric quadrupole moment, $eQ$, with respect to the components of the electric field gradients and also the asymmetry parameter which is zero for perfect symmetry of nuclear electronic distribution. This relationship is described further in the next section. However, in an applied magnetic field the quadrupolar coupling constant is not so easily obtained from the transition frequencies of quadrupole nuclei; this is because the other perturbations, such as the Zeeman interaction, must be considered. By measuring these two parameters, $C_Q$ and $\eta$, information on the bonding of the quadrupolar nuclei, structure of solids, and dynamics of solids can be derived.

1.2.2 NQR at Various Magnetic Fields

The energy separation of spin states is increased in proportion to the transition frequency, as shown in eq. (1.3). The transition frequency of quadrupolar nuclei represent the nuclear quadrupolar resonance (NQR) which is developed by quadrupolar interaction. There are three cases of spin energy systems that take place when the quadrupolar interaction and the Zeeman interaction are considered without the perturbations of the other interactions in spin system, as shown in Figure 1-1 for $S = 1$ [1.10] and Figure 1-2 for $S = 3/2$ [1.15] under various conditions: [1.3]

1) $H_Z > H_Q$ case: When the quadrupolar coupling is weak compared to the magnetic interaction, the nuclei are polarized by the magnetic field and the quadrupolar interaction shifts the transition about the Larmor frequency of the quadrupole nucleus. Because the quadrupolar interaction is added as a perturbation to the Zeeman interaction, the energy levels are further split by the electric field gradient, the asymmetry parameter, and the angle formed by the direction of the $eq_{zz}$ with the magnetic field. Thus, the NMR line widths of quadrupolar nucleus are broadened by the quadrupole
Figure 1-1  Energy level diagram of a spin, $S = 1$, at various conditions and the relationship of transition frequencies with the quadrupolar coupling constant and the asymmetry parameter for pure NQR ($H_Z = 0$).

$\nu_+ = \frac{3}{4} C_Q \left(1 + \frac{\eta}{3}\right)$

$\nu_- = \frac{3}{4} C_Q \left(1 - \frac{\eta}{3}\right)$

$\nu_0 = \frac{1}{2} C_Q \eta$
Figure 1-2  Energy level diagram of a spin, $S = 3/2$, at various conditions and the relationship of transition frequencies with the quadrupolar coupling constant and the asymmetry parameter for pure NQR ($H_Z = 0$).
interaction in an applied magnetic field. The broad NMR line widths of quadrupole nuclei can be partially solved by using an extremely high magnetic field. Because the energy levels can be further split in higher magnetic field, the NMR line shape of quadrupolar nuclei are easier to interpret by calculations. The quadrupole perturbed $^{93}$Nb (S = 9/2) NMR of BaNb$_x$S$_3$ (x = 0.8 and 1) has been observed with a strong magnetic field (~10 Tesla) at 4.2 K, which is described in Chapter 2. However, the problem of line broadening cannot be completely solved by this kind of experiment using high magnetic field.

(2) $H_Z < H_Q$ case: When the quadrupolar coupling is larger than the magnetic interaction, the energy levels of quadrupolar nuclei are determined by the quadrupolar interaction. For S = 3/2, 5/2, etc., all energy levels are doubly degenerate in the ground state as expressed by Kramer's theorem. The transition frequency detected in this case is represented by the pure NQR. Pure NQR transition frequencies are easily calculated with the quadrupolar coupling constant and the asymmetry parameter, as shown in Figure 1-1 and Figure 1-2. The pure $^{79}$Br and $^{81}$Br (S = 3/2) NQR of the brominated aromatic compounds have been observed without the magnetic field at room temperature, as described in Chapter 3. The pure $^2$H (S = 1) and $^{14}$N (S = 1) NQR of organic samples are observed using a field cycling technique, as described in Chapter 4.

(3) $H_Z = H_Q$ case: When the quadrupolar coupling is almost equal to the magnetic interaction, it is difficult to study quadrupolar nuclei in molecules. The problem using the full Zeeman plus the quadrupolar
interaction is not easy to solve. Therefore, one of interactions should be changed to solve this problem.

1.3 Solid-State Nuclear Quadrupole Resonance Imaging

Solid-state NQR imaging techniques were recently developed as a branch of NQR spectroscopy and NMR imaging (MRI). These techniques involve an inhomogeneous magnetic field which can be called a magnetic field gradient. Since the early seventies when MRI was developed by Lauterbur [1.17,18] and independently by Mansfield [1.19-21], much research effort has been invested in the development of techniques for MRI. Medical applications of solution state MRI have progressed quickly and are well developed in clinical diagnosis and medical research for studying certain soft tissues. Because the NMR line widths in the solid state are broadened considerably by the dipolar interaction, chemical shift anisotropy, and the quadrupolar interaction, as discussed in section 1.1.2, NMR imaging of solids requires a different set of techniques [1.22-29] and hence, the development of solid state NMR imaging has been much slower than that of MRI. An important feature of NMR imaging of solids is line narrowing of a selected NMR resonance; therefore, the research for effective NQR imaging is really a search for a line narrowing technique.

MRI is based on a simple principle that the NMR line shape reflects the spatial distribution of nuclear spins in a spatially inhomogeneous magnetic field. The nuclei in different magnetic fields resonate at different frequencies by

\[ \omega = \gamma B_0 + \gamma G_r \Delta r \]  

(1.17)

where \( \Delta r \) is the spatial function and \( G_r \) is the magnetic field gradient strength. Eq. (1.17) is a modification of eq. (1.1) in which the observed line shape is the sum of the
distribution of resonance frequencies (by which we mean magnetic fields) weighted by the number of nuclei at each frequency. Thus, the projection of the concentration of the nuclei in the sample along the field gradient direction is represented by the NMR line shape in a linear magnetic field gradient.[1.30,31]

In Chapter 5, NMR imaging of $^{11}$B in a boric acid, $\text{B(OH)}_3$, phantom has been done using a field cycling NMR technique for the purpose of line narrowing the $^{11}$B resonance. Field cycling NMR is used to merge the sensitivity of high field detection with the narrow resonance of a pure NQR transition. In zero magnetic field, a very small rf coil is used as the method for spatially encoding the image by saturating the $|\pm 1/2> \rightarrow |\pm 3/2>$ transition for a selected region of the sample. In successive cycles the zero-field rf coil is translated step-wise along the sample.

In Chapter 6, NQR imaging via field cycling has been used to image $^{14}$N nuclei in a sample of acetamide and salicylamide. The image obtained is spatially resolved in one dimension and is also obtained as a function of the $|0> \rightarrow |+>$ transition frequency. The imaging plane is generated by two collinear solenoids wound with opposite handedness. In the field cycling experiment, the $^{14}$N $|0> \rightarrow |+>$ transition, is saturated throughout the sample except at the imaging plane where the magnitude of the rf field, $|B|$, is near zero.

In an exploratory project to test an MRI demonstration, a two-dimensional $^1$H NMR image is acquired on an unmodified Bruker AC100 NMR spectrometer in Chapter 7. Three kinds of phantoms are imaged with a rotated magnetic field gradient. This demonstration is the same rather simple application used in many areas of non–medical NMR imaging, such as animal imaging, plant studies, and imaging of mobile liquids inside of solid porous materials.
1.4 References


CHAPTER 2

DETERMINATION OF QUADRUPOLAR COUPLING CONSTANT AND ASYMMETRY PARAMETER IN $^{93}\text{Nb}$ NMR STUDIES OF BaNb$_x$S$_3$ ($x = 0.8, 1.0$)
2.1 Introduction

The gross structure of BaNb$_2$S$_3$ ($x = 0.8, 1$) is isostructural [2.1] with BaVS$_3$, which is hexagonal and has space group $P6_3/mmc$ with two molecules per unit cell at room temperature.[2.2,3] The crystal structure of BaNbS$_3$ is such that the sulfur and barium atoms form a slightly distorted hexagonal close-packed layers with the niobium atoms occupying one quarter of the octahedral sites between layers, namely those sites formed only by sulfur atoms. These niobium sulfur octahedra share faces and form infinite one-dimensional chains parallel to the hexagonal axis. The intrachain metal–metal distances are 2.874 Å, which are short enough to form metal-metal bonds, but the interchain metal-metal distances are long, with 6.840 Å and 5.745 Å.[2.1] The isostructural BaVS$_3$ shows interesting electronic behavior from a metallic conductor to a semiconductor by a paramagnetic to antiferromagnetic transition at 77 K. The magnetic transition is similar to that of materials related to high critical temperature, $T_c$, cuprate superconductors.[2.4,5] Also, BaNbS$_3$ has a noticeable Peierls distortion along the chain axis, a feature not seen in BaVS$_3$. However, BaNbS$_3$ is a diamagnetic semiconductor at room temperature due to the distortion along the axis of the chain.[2.6,7] Because the NbS$_3$$^{2-}$ system is linear and diamagnetic at room temperature, Nb d$^1$ electrons might be metal-metal bonding like this

\[
\text{Nb} \cdots \text{Nb} \cdots \text{Nb} \cdots \text{Nb} \cdots \text{Nb} \cdots
\]

( where ‘—’ indicates longer bond length than ‘⋯’).

Thus, only one kind of magnetically inequivalent $^{93}$Nb is expected. According to X-ray photoelectron spectroscopy (XPS), only one Nb site was observed.[2.1] However, as will be shown herein, two distinct Nb sites are observed by a $^{93}$Nb NMR
technique. One interpretation of the 4.2 K $^{93}$Nb NMR results is that two different $^{93}$Nb oxidation states exist in BaNb$_x$S$_3$ ($x = 0.8, 1$) system.

The $^{93}$Nb nucleus, has a high nuclear spin number, $9/2$, and is 100% abundant in nature, has proven to be interesting to study in, for example, niobium pentahalide as reported in the early seventies to early eighties.[2.8-13] The $^{93}$Nb NQR can easily determine the quadrupolar coupling constant, $C_Q$, and the asymmetry parameter, $\eta$, of the electric field gradient tensor at the nucleus. Most observations have been done with a superregenerative spectrometer. When the $^{93}$Nb NQR transition frequency range is known, $^{93}$Nb NQR spectroscopy is a very useful technique. For example, Nb$_2$Cl$_{10}$ (a metal dimer with two bridging halides) has four observable $^{93}$Nb transitions in the range of 5 to 13 MHz and $C_Q = 78.1$ MHz and $\eta = 0.32$ at 300 K.[2.14] However, there will be some difficulties involved in using the $^{93}$Nb NQR technique via pulse methods to search for the frequency range of the unknown $^{93}$Nb resonance of BaNb$_x$S$_3$ ($x = 0.8, 1$). The low sensitivity of the samples with broad line widths will also cause a problem. The $^{93}$Nb NMR of metallic compounds and alloys has been studied at Bell Telephone Laboratories with the same spin-echo field-swept NMR technique used in the study reported herein.[2.15-21] The $C_Q$ for Nb$_3$Sn is 49 MHz at 300 K and the field swept experiment was done with a carrier frequency of 53.1 MHz.[2.15] When large single crystals are available, the $^{93}$Nb NMR line shapes have been used to characterize the stoichiometry of a melt grown crystal and thus proven useful in determining phase diagrams for crystal growth. However, this technique has one major defect, the sensitivity of the NMR is low. The $^{93}$Nb NMR experiment, with magic angle spinning (MAS) of a sample, is an interesting technique that depends upon an analyses of the spinning sideband pattern.[2.22] The MAS NMR technique makes possible narrower spectral line widths by reducing the effects of the quadrupole interaction.[2.23] For example, $^{93}$Nb MAS NMR of NaNbO$_3$,
CQ = 19.5 MHz, spun of 6 kHz at 8.5 Tesla yields a spectrum with a center band and associated side bands; the center band is broadened to about 25 kHz by second-order quadrupolar line broadening.[2.24] Given this level of performance, 93Nb MAS NMR of samples with moderate values of CQ will not be easy to study and characterize. Since the objective of this project was to acquire information about the number of niobium sites in BaNbₓS₃ (x = 0.8, 1), and only powder samples were available, field swept NMR was the method chosen. Herein, the results of field swept, along with some frequency swept, 93Nb NMR experiments are presented. The results at 4.2 K show that two niobium sites can be detected.

2.1.1 Frequency Swept 93Nb NMR Spectroscopy

The solid-state NMR spectroscopy of quadrupole nuclei usually requires very large spectral line widths. Typically, one needs extremely short, high-power rf pulses and fast digitization to cover the wide frequency range of the NMR spectrum. In addition, extensive signal averaging is required because signal sensitivity is generally poor due to the large bandwidth of the probe and the receiver. Because these contradictory demands, it is difficult to achieve uniform spectral coverage for the NMR spectroscopy of quadrupole nuclei.

A frequency swept NMR experiment with low power pulse has been used to circumvent many of the difficulties discussed above.[2.25,26] A brief description of this technique is given here for the case of the 93Nb nucleus having a large CQ. The free induction decay (FID) is acquired after a low power pulse at a fixed carrier frequency. The FID is signal averaged to improve the signal-to-noise ratio; then the FID in time domain is converted to frequency domain by the Fourier transformation. The frequency domain spectrum is integrated for the region about the carrier frequency. Then the carrier frequency is stepped to the next value and the process repeated to obtain the next point. Ideally, the probe is retuned for each carrier frequency. Thus, an
entire spectrum over extremely wide spectral widths can be obtained by acquiring successive integrated points as a function of carrier frequency. In principle, all of the transitions for the $^{93}$Nb ($S = 9/2$) spin system can be observed, although the $l+1/2 > \rightarrow l-1/2>$, $l+3/2 > \rightarrow l+1/2>$, and $l-1/2 > \rightarrow l-3/2>$ transition will dominate the spectrum. The main disadvantage with this technique is the need for constant probe retuning which makes obtaining good line shapes extremely difficult.

2.1.2 Field Swept $^{93}$Nb NMR Spectroscopy

Recently, field swept pulsed NMR has been developed in our lab to solve the problem described above namely probe retuning.[2.27,28] This technique operates by working at constant rf frequency and requires a slow sweep of the magnetic field. The Oxford 16/18 Tesla superconducting magnet can be operated in a non-persistent mode, thus providing a slow sweeping magnetic field that can be used to obtain high quality solid-state NMR, spectra over the extremely large spectral widths needed to observe nuclei with large $C_Q$.

This technique sweeps the magnetic field in the same manner as continuous-wave (CW) NMR as used in the early years of NMR, however, the NMR signal is detected with a spin echo pulse sequence. The resonant frequency of $^{93}$Nb nucleus is 110.35 MHz at $B_0 = 10.6$ Tesla based on the $\gamma(^{93}$Nb$)$, $6.54 \times 10^{-5}$ rad s$^{-1}$ T$^{-1}$. The signal averaging is done at a fixed magnetic field; the spin echo detected in the time domain, and is then converted to the frequency domain by the Fourier transformation. The frequency domain spectrum is integrated and each integral is a data point in the field swept spectrum. Then the magnetic field is stepped to obtain the next data point. The probe is tuned for a fixed carrier frequency. Thus, an entire spectrum can be obtained by acquiring successive data points (integrated spin echo) as a function of the magnetic field, thus avoiding the problem of probe retuning.
In principle, the field swept NMR spectrum will yield an accurate line shape for the $^{93}$Nb resonance.

2.2 Experiment

The $\text{BaNb}_x\text{S}_3$ ($x = 0.8, 1.0$) has been prepared and studied to characterize the structure by Kim's research group.[2.1] Herein, we have used two $^{93}$Nb NMR techniques to determine the number of inequivalent $^{93}$Nb sites that exist in the $\text{BaNb}_x\text{S}_3$ system.

2.2.1 Frequency Swept $^{93}$Nb NMR Experiment

First, ammonium hexafluoroniobate(V) ($\text{NH}_4\text{NbF}_6$ Aldrich 20391-2, 99.99%) was used as a sept-up sample to determine the relation between pulse power and tip angle by means of pulses applied exactly on resonance based on a Bruker MSL200. In the commercial broadband probe, the spin echo pulse sequence [2.29] was chosen to use; 14 $\mu$s for a 90° tip angle pulse (28 $\mu$s for a 180°) and 40 $\mu$s for ring down time (38.5 $\mu$s delay between pulses) with low power (1 W). The $^{93}$Nb $T_1$ seemed to be quite short and so a relaxation delay of 0.5 s was used.

A $^{93}$Nb conventional NMR spectrum of $\text{NH}_4\text{NbF}_6$ was obtained with 48.916 MHz rf carrier frequency (in 4.7 Tesla) at room temperature, as shown in Figure 2-1. To increase the signal-to-noise ratio of the spectrum, the signal was averaged 100 times. With successive applications of this experiment, the frequency swept $^{93}$Nb NMR spectrum of $\text{NH}_4\text{NbF}_6$ was obtained over 48.53-49.29 MHz range with a 20 kHz step size. The probe was easily retuned by the conventional way, and then the frequency was stepped to the next value. The $^{93}$Nb NMR spectrum of $\text{BaNbS}_3$ with frequency swept method was obtained by same procedure except that the frequency range was increased from 0.76 to 1.18 MHz, and signal averaging was increased from 100 to 200 times.
A $^{93}$Nb conventional NMR spectrum of NH$_4$NbF$_6$ was obtained with 48.916 MHz rf carrier frequency (in 4.7 Tesla) at room temperature. The signal was averaged 200 times.
2.2.2 Field Swept $^{93}$Nb NMR Experiment

An Oxford 16/18 Tesla (4.2/2 K operations, respectively) cold-bore superconducting magnet was used for this work. The magnet was continuously energized by the Oxford power supply. The power supply was controlled by the homemade NMR console. The solenoidal NMR probe was fixed-tuned at 110.35 and 110.86 MHz for $x = 0.8$ and 1.0, respectively, and was mounted on a 2.1 m stainless-steel transmission line.[2.30] The instrumentation of this experiment was described in detail by previous reports.[2.27,28] A homemade NMR console was used to generate a spin-echo pulse sequence ($90^\circ_x-\tau_1-180^\circ_y-\tau_2$-acquisition) with 12 $\mu$s and 24 $\mu$s pulses, respectively, and $\tau_1 = 24$ $\mu$s ($\tau_2 = 28$ $\mu$s).[2.29] The rf pulse power was set to maximize the spin echo amplitude for the $^{93}$Nb $l+1/2 \rightarrow l-1/2$ central transition of the sample.

The $^{93}$Nb NMR spectra of BaNb$_x$S$_3$ ($x = 0.8, 1.0$) was obtained with field swept experiment at 4.2 K. Each data point in the field swept NMR spectrum was obtained by signal averaging 8 times, Fourier transforming, and then integrating the spectral region near the carrier frequency. The magnetic field was then reset to the next higher value and the process repeated; the magnetic field was swept over 9.8-11.4 T range with 90 Gauss step size. Typically, spectra were acquired in about 10 hours.

2.3 Results and Discussion

$^{93}$Nb NMR spectrum of NH$_4$NbF$_6$ with a frequency swept experiment has been obtained at room temperature, as shown in Figure 2-2a. This spectrum shows that NH$_4$NbF$_6$ is a good set-up sample for $^{93}$Nb NMR. Because NH$_4$NbF$_6$ has a octahedral coordination with an unimolecular rhombohedral cell [2.31], the asymmetry parameter is zero leading to unique $^{93}$Nb power pattern. The simulation of the $^{93}$Nb spectrum for the frequency swept mode is shown in Figure 2-2b for $\eta = 0$ and
Figure 2-2  (a) The $^{93}$Nb NMR spectrum of NH$_4$NbF$_6$ with frequency swept experiment at room temperature and 4.7 Tesla. A spin echo rf pulse sequence was used with a 14 µs 90° pulse of low power (1 W). The rf carrier frequency was swept over the 48.53-49.29 MHz range with a 20 kHz step size. (b) The simulated $^{93}$Nb spectrum for frequency swept experiment. The $^{93}$Nb simulation spectrum is well matched with experimental data with $\Delta Q = 3.8$ MHz and $\eta = 0$. 
$C_Q = 3.8 \text{ MHz}$. The match between experiment and simulation indicates only one $^{93}\text{Nb}$ site in $\text{NH}_4\text{NbF}_6$ system. Also, the $^{93}\text{Nb}$ NMR spectrum of $\text{NH}_4\text{NbF}_6$ suggests that the frequency swept experiment can be very useful and successful for nuclei having a symmetric electronic environment and a large spin number, such as $9/2$.

With this successful result, we have applied this technique to the $\text{BaNbS}_3$ system. The $^{93}\text{Nb}$ NMR spectrum of $\text{BaNbS}_3$ obtained with the frequency swept experiment is shown in Figure 2-3. However, only the $^{93}\text{Nb} \, l+1/2 \rightarrow l-1/2$ transition is clearly visible with a broad line width in the center of the spectrum, and all other transitions are hard to characterize due to the poor signal-to-noise ratio for this spectrum. The poor quality of the $^{93}\text{Nb}$ spectrum of $\text{BaNbS}_3$ prevents a determination of the number of $^{93}\text{Nb}$ sites in the system. Also, the $^{93}\text{Nb}$ NMR broad line widths of $\text{BaNbS}_3$ suggests that the $^{93}\text{Nb}$ may have large $C_Q$, and so the frequency swept experiment is improper technique for $\text{BaNbS}_3$.

The $^{93}\text{Nb}$ NMR spectra of $\text{BaNb}_x\text{S}_3$ ($x = 0.8, 1.0$) with field swept NMR have been obtained at 4.2 K, as shown in Figure 2-4. Basically, the $^{93}\text{Nb}$ NMR spectra are nearly the same for $x = 0.8$ and 1.0, with more clearly observed spectral features for $\text{BaNb}_{0.8}\text{S}_3$. Because we can see singularities in the spectrum of $x = 0.8$, we decided to use this spectrum for simulations. Simulated spectra of $\text{BaNb}_{0.8}\text{S}_3$ are shown in Figure 2-5 and 6 based on the solution of the quadrupolar plus Zeeman Hamiltonian at each magnetic field value in the spectrum. The simulation includes second-order quadrupolar effects.[2.32] The way we calculate a field swept spectrum will be briefly discussed. From the experiment, the rf frequency is 110.35 MHz, and the field values of all data points are 179 points in the experimental spectrum. Thus, the simulations require a calculation of a powder pattern for each of the 179 different magnetic field values. However, instead of keeping the entire powder pattern, only the intensity at the center of the powder pattern corresponding to the rf carrier frequency is
Figure 2-3  The $^{93}\text{Nb}$ NMR spectrum of BaNbS$_3$ with frequency swept experiment at room temperature and 4.7 Tesla. A spin echo rf pulse sequence was used with a 14 μs 90° pulse of low power (1 W). The rf carrier frequency was swept over the 48.3–49.5 MHz range with a 20 kHz step size.
Figure 2-4: The $^{93}$Nb NMR spectra of (a) $\text{BaNb}_{0.8}\text{S}_3$ and (a) $\text{BaNb}_{1.0}\text{S}_3$ were obtained with field swept experiment (1.6 T widths) at 4.2 K when the rf carrier frequencies were 110.35 MHz and 110.86 MHz, respectively for (a) and (b).
Figure 2-5  The simulated $^{93}$Nb spectra of field swept experiment for $^{93}$Nb site having low $C_Q$: (a) The spectra were calculated with $\eta = 0.3$ and variable $C_Q$. (b) The spectra were calculated with $\eta = 0.7$ and variable $C_Q$. (c) Spectra were calculated with $\eta = 0.9$ and variable $C_Q$. 
Figure 2-6 The simulated $^{93}\text{Nb}$ spectra of field swept experiment for $^{93}\text{Nb}$ site having high $C_Q$: (a) The spectra were calculated with $\eta = 0.3$ and variable $C_Q$. (b) The spectra were calculated with $\eta = 0.7$ and variable $C_Q$. (c) Spectra were calculated with $\eta = 0.9$ and variable $C_Q$. 
Based on a number of simulations of $^{93}$Nb field swept NMR line shapes, the experimental spectra cannot be simulated with a single $^{93}$Nb site. Also, there are no distinctive features in the spectra that indicate three or more $^{93}$Nb sites, thus we will assume the existence of two $^{93}$Nb sites. Based on the singularities in the experimental BaNb$_{0.8}$S$_3$ spectrum, especially at 10.3 and 10.53 T, approximate values of $C_Q$ and $\eta$ were obtained by the best fits as judged by eye and comparison with a set of simulations as shown in Figure 2-5 and 2-6. We find two components; one site has $C_Q = 13$ MHz and $\eta = 0.9$ while the second site has $C_Q = 73$ MHz and $\eta = 0.9$. However, the component with $C_Q = 73$ MHz has a distinctly asymmetric powder pattern that is not reproduced in a simulation based on only a quadrupolar interaction; there must also exist another interaction with a magnitude on the order of a 1.04 MHz (0.1 Tesla). Tentatively, the shift is assigned to a chemical shift or Knight shift interaction.

We now turn to the main objective of this $^{93}$Nb NMR study, the determination of the number and relative population of the $^{93}$Nb sites in BaNb$_x$S$_3$. As discussed above, two possible $^{93}$Nb sites with two different $C_Q$ values in the system were used to determine the relative population of the $^{93}$Nb sites. First, the magnitude of both simulated data and experimental data were converted into the same percent scale for further calculation. Then, the sum of the magnitude for $C_Q = 73$ MHz simulated data (say site $\alpha$) was made to equal the sum of the magnitude for $C_Q = 13$ MHz simulated data (say site $\beta$). Two simulated data were added with variable ratio of $\alpha : \beta = 1 : n$ ($n \geq 1$), as shown in Figure 2-7 and then converted to the percent scale for determining the relative population of two $^{93}$Nb sites. Then, the new data in percent scale was multiplied in the order of 1.6 times to make the magnitude of the second and third
transition sites same as that of experimental spectrum, because the central transition was not concerned but showed too large magnitude that made difficulty to simulate the second and third sides transitions; then the data subtracted from experimental data. The number of the residual data with variable ratio after subtraction were compared by the nonlinear least-squares fitting procedure.[2.33] Based on these calculations, the ratio of two sites was determined with $\alpha : \beta = 1 : 3.1 (\chi^2 = 81.85)$; a $^{93}\text{Nb}$ site having $CQ = 13 \text{ MHz}$ has three times more abundant than the other site having $CQ = 73 \text{ MHz}$. The $^{93}\text{Nb}$ spectra combined with experimental and simulated data were shown in Figure 2-8.

At a sample temperature of 4.2 K, the $^{93}\text{Nb}$ field swept NMR spectra of BaNb$_x$S$_3$ yielded an informative powder pattern and showed that NbS$_3$ has two different $^{93}\text{Nb}$ sites with two $CQ$. Most importantly, the relative population of the two sites has been measured for the first time.
Figure 2-7  A plot of the ratio of two $^{93}$Nb sites ($\alpha : \beta = 1 : n$) versus $\chi^2$; $\alpha$ site having $C_Q = 73$ MHz, $\beta$ site having $C_Q = 13$ MHz, and $\sigma = 3$. $\chi^2 = \sum (\text{experimental data} - \text{simulated data})^2/\sigma^2$.
Figure 2-8  The $^{93}\text{Nb}$ spectra combined with simulated and experimental data. (a) The $^{93}\text{Nb}$ experimental spectrum of $\text{BaNb}_{0.8}\text{S}_3$ at 4.2 K. (b) The $^{93}\text{Nb}$ simulated spectrum with adding two sites by the ratio of $\alpha : \beta = 1 : 3.1$ for $\eta = 0.9$; $\alpha$ site has $C_Q = 73$ MHz, and $\beta$ site has $C_Q = 13$ MHz. (c) The simulated spectrum of each $^{93}\text{Nb}$ sites; $C_Q = 73$ MHz and 13 MHz with $\eta = 0.9$. (d) The residual spectrum was obtained with subtracting from (a) to (b).
### 2.4 References


CHAPTER 3

BROMINE NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY OF FLAME RETARDANTS DISPERSED IN POLYMER BLENDS USING A CONCENTRIC LOOP-GAP RESONATOR
3.1 Introduction

Since their production of flame retardants dispersed in polymers, Albemarle Co. has not found an appropriate spectroscopic method to obtain structural information of the products. In an attempt to meet their needs, we have developed a broadband nuclear quadrupole resonance (NQR) spectrometer to obtain $^{79}\text{Br}$ and $^{81}\text{Br}$ NQR spectra for flame retardants dispersed in polymers. This NQR spectrometer has a very wide spectral range from 200 to 300 MHz with automatic frequency selection and a novel automatically-tuned probe. A homemade console built [3.1] in our lab has been modified for switching from field-swept mode to frequency-swept operation. A broadband NMR probe has been built based on a concentric loop-gap resonator.

NQR is one of powerful methods available in the present time for studying the sample having large quadrupole interaction, such as brominated aromatic compounds. Nuclear magnetic resonance (NMR) and NQR are closely related techniques, except that NMR uses a large magnet whereas NQR is done without a magnet. The absence of a magnet in NQR has both positive and negative aspects:

1. Positive aspects: The probe to detect NQR frequency is designed with much more freedom by the absence of the physical constraints of size and shape imposed by the magnet. The size of the probe can be large, and then the large amount of sample can be used to improve the signal-to-noise ratio. We have used about 25 g of sample for this project. Also, NQR spectrometer can be very portable without a magnet. We have moved the spectrometer from the chemistry to the physics building within 1 hour.

2. Negative aspects: It can be difficult to find the proper NQR frequency for unknown sample. In some of the $^{81}\text{Br}$ NQR data of brominated aromatic compounds presented by Bray et al.[3.2,3],
resonant frequencies range from 220 to 252 MHz. This 32 MHz spectral region can be compared with $^1$H NMR at 300 MHz where all resonances are found within a 6 kHz region (assuming a 20 ppm shift range). With the automatically-tuned probe and the broadband NMR console, frequency ranges of 2 MHz have been measured in 5 hours.

Bray et al. obtained $^{79}$Br and $^{81}$Br NQR spectra for a wide range of brominated aromatic compounds in the 1950's.[3.2,3] All spectra reported were observed using self-quenched or externally quenched superregenerative oscillators of the push-pull Lecher-wire tuned type.[3.4] There are four important observations from this early works:

1. The NQR frequencies depend on electron density at bromine and are correlated with Hammett $\sigma$ parameters. This indicates very good possibilities for spectral identifications with an accuracy comparable with $^{13}$C NMR chemical shift interpretation. Thus, the rf frequencies range to sweep has been reduced by calculation of $\sigma$ values of brominated aromatic compounds in polymer blends.

2. In some cases, multiple NQR frequencies were observed, for example, four frequencies are found for 4,4'-dibromobiphenyl and four frequencies for 4-bromophenol. This suggests good sensitivity to local crystallographic or polymer matrix environment.

3. Spectra were obtained with good signal to noise ratio (ranged from 2 to 20) at 77 K and 300 K. The fact that spectra were obtained with the superregenerative oscillators indicates spin-lattice relaxation time ($T_1$) less than 1 s and spin-spin relaxation time ($T_2$) greater than
50 μs and an excellent potential for signal averaging with modern pulsed NQR methods.

(4) The resonant frequencies of some compounds were found to be temperature dependent. This suggests a potential of modern pulsed NQR technique that can be used as a probe to detect a phase transition of the flame retardants in the polymer matrix by shifting of NQR transition frequencies depending on temperature.

There are some alternative NMR techniques to study polymer blends today. The $^{129}$Xe NMR spectra of polymers and polymer blends have been obtained with the basic solution-state NMR method and the success of $^{129}$Xe NMR based on the chemical shift of the small nonpolar xenon atom having unusual sensitivity to its environment.[3.5,6] With $^{129}$Xe NMR two phases can be distinguished by the comparison of chemical shift and peaks in pure polymer and in polymer blends. However, this technique is useless for brominated aromatic polymer blends, because the flame retardants dispersed in polymers is difficult to dissolve in a solvent. The $^{13}$C NMR spectra of polymer blends have been obtained by using $^{13}$C cross-polarization and magic angle spinning (CP/MAS) which offers an unique insight into the molecular phase structure and mobility of amorphous polymers.[3.7] The signal-to-noise ratio of the brominated aromatic compounds will be poor because of poor cross-relaxation dynamics at the Br-$^{13}$C. The chemical shift of $^{13}$C NMR will be the same for the flame retardants whether is in the pure compound or in the polymer mixtures, unless they make the chemical bonds with the polymers. Thus, this technique is also useless for the flame retardants in polymer blends. Proton spin diffusion studies of polymer blends having modest monomer size have been done by $^1$H NMR spectra using combination of rotation and multiple pulse spectroscopic techniques (CRAMPS) which offers high resolution of $^1$H spectra.[3.8,9] However, $^1$H chemical shifts of the
polymer will be very small unless the concentration of flame retardant is very high. Therefore, this technique is also not ideal for the flame retardant/polymer mixture. Thus, all these NMR techniques are not appropriate leaving $^{79}\text{Br}$ and $^{81}\text{Br}$ NQR as the best remaining spectroscopic probe.

3.2 Instrumentation

A simplified block diagram of a bromine NQR spectrometer is shown in Figure 3-1. Since a homemade 10 - 300 MHz NMR console has digital phase shifting and flexible pulse programmer with a high-speed digital I/O card (National Instruments NB-DIO-32F) [3.1], the console was added with a digital I/O card programming that selected the rf irradiation frequency. Automatic probe tuning was done by rotating a concentric loop-gap resonator; the rotation motion is provided by an Aerotech 45SMW microstepping motor on an ART304 rotary stage. Unidex 100 motion controller is connected via an RS-232C serial port to the Macintosh. All software were written in LabView, a graphical programming language.

A broadband, 200 - 500 MHz, NMR probe has been built with a concentric loop-gap resonator [3.10], as shown in Figure 3-2. The probe has also excellent rf homogeneity, a high quality factor (Q), and a filling factor equivalent to that of a solenoidal design. The stationary outer cylinder is constructed on cylindrical high-density polyethylene dielectric material having a thickness of about 1 mm. The dielectric material is obtained by cutting the ends off a Nalgene No. 2104, 125 ml, wide-mouth bottle.[3.10] Polyethylene is a standard dielectric material for this application that is used in high Q resonance circuits at high rf power level. Since the outer diameter of the inner tuning cylinder is 47.4 mm and the inner diameter of the stationary outer cylinder is 49.6 mm, the conductor separation is 1.1 mm. The length of the resonator loop (inner cylinder) is 40 mm. This volume of inner tuning cylinder
Figure 3-1  A simplified block diagram of a bromine NQR spectrometer.
Rotary motion of tuning inner cylinder by Aerotech 45SMW stepping motor

PVC rod

Coax cable to preamplifier

Linear motion of coupling loop

Coupling loop

PVC sample holder

Tuning inner cylinder

Stationary outer cylinder

40 mm

40 mm

2 mm

1 mm

47.4 mm (o.d.)

49.6 mm (i.d.)

Figure 3-2 A simplified diagram of probe body.
makes that the maximum volume of sample holder can be \(6.9 \times 10^2\) cm\(^3\) (roughly 100 g of the brominated aromatic polymer blends). The gap of inner tuning cylinder is 1 mm across. The aspect ratio of the inner tuning cylinder is nearly square, with a diameter of 47.4 mm and a length of 40 mm. The tuning range of the probe is determined by the volume, the size of gaps, and the conductor separation of two cylinders:

1. A larger volume of two cylinders shifts the entire tuning range to lower frequency.
2. As the gap in each cylinder is reduced, the total tuning range is increased.
3. As the conductor separation is reduced, the total tuning range is increased.

To shape the inner cylinder, 48 gauge copper sheet, is mounted on a cylindrical polyvinyl chloride (PVC) part. The cylindrical PVC part is attached to rotary stage by a PVC rod (39 cm long) with a threaded brass rod at the upper end. Matching of the probe circuit to 50 ohms is accomplished by adjusting the distance between the coupling loop and the end of the inner tuning cylinder and changing the length of coax cable between the preamplifier and the probe. Matching of the broadband probe over spectroscopic range, 200-300 MHz, is shown in Figure 3-3. The coupling loop is made with 16 gauge insulated copper wire. The outer frame of the probe body is made with PVC pipe, as shown in Figure 3-4. The probe is shielded from rf noise by two copper shields made from 24 gauge copper sheet. The rf shields, an inner cylinder and outer box are significantly larger than the probe body to reduce coupling to the probe circuit. These rf shields are very important for reducing rf noise level, especially that from the third harmonic of neighboring FM radio stations.
Figure 3-3 A plot of probe tuning performance. (a) The impedance of the probe, |Z|, is well matched to 50 ohms. (b) The phase offset of the probe is close to 0°. The matching of the probe circuit to 50 ohms is accomplished by adjusting the distance (units in mm) between the coupling loop and the end of the inner tuning cylinder as shown on top of figure and by changing the length of coax cable between the preamplifier and the probe.
Brass rod to be mounted the rotary stage
Alumina table to install rotary stage
20 gauge copper sheet to shield rf noise
Linear position holder with wing nuts
PVC pipe
PVC pipe for supporting linear motion of a coupling loop
PVC rod to mount between metal rod and inner cylinder
PVC spacer in the center
PVC inner cylinder and sample holder
A coupling loop
Outer cylinder with polyethylene
PVC spacer to hold a copper loop to outer cylinder as close as possible
PVC outer cylinder holder
48 gauge copper sheets

Figure 3-4 A simplified diagram of probe frame.
3.3 Experiment

First, 1,3,5-tribromobenzene (C₆H₃Br₃, 98% Aldrich 14006-6) was used as a standard sample to determine the duration of a 90° tip angle pulse, the probe ringdown time, and the proper phase cycle sequence for the new bromine NQR spectroscopic experiment. The 81Br NQR spectrum of 1,3,5-tribromobenzene was obtained with the spin echo pulse sequence [3.11] at room temperature; 52 µs for a 90° tip angle pulse (104 µs for a 180°) and 24 µs for the ring down time were used with ~16 W pulse power, and the phase cycling is shown in Table 3-1. The spin-lattice relaxation of 81Br spin in 1,3,5-tribromobenzene was very short at room temperature, less than 0.2 s. Typically, relaxation delay of 0.5 s, including other processing delay, was used for this experiment. To search for the 81Br NQR transitions, the rf carrier frequency was swept over the range of 230 - 232 MHz with a 20 kHz step size. The rf carrier frequency supplied by the PTS 300 was automatically set by the Macintosh using a NB-DIO-32F parallel interface card; the probe was also automatically retuned for the consecutive rf carrier frequencies by rotating the resonator loop with a rotary motor under computer control. The numerical relationship between the tuning frequencies of the probe and the number of step to rotate for the rotary motor was obtained by using polynomial expression containing the coefficients ordered by descending powers; first, a tuning frequency of the probe was set to the zero-position of the rotary motor. Then, the rotary motor was moved with a given step size, and a tuning frequency of the probe was obtained at the position of the motor. Table 3-2 was obtained with the successive these observations for a certain range of the tuning frequency. Then, a plot, the tuning frequencies of the probe versus the rotation step-size of the rotary motor, was fitted with the polynomial expression; when a rf carrier frequency was set, the rotary motor was moved to retune the probe with the calculated rotation step-size based on a function of the rf carrier frequency.
Table 3-1  The phase cycling for $^{81}\text{Br}$ NQR Spectroscopy. The $\tau_1$ and $\tau_2$ of 24 $\mu$s were used. Acquisition time was 200 $\mu$s.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$90^\circ$ pulse</th>
<th>$180^\circ$ pulse</th>
<th>Receiver</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+X$</td>
<td>$+Y$</td>
<td>$+X$</td>
<td></td>
</tr>
<tr>
<td>$-X$</td>
<td>$+Y$</td>
<td>$-X$</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-2  The tuning frequencies of the probe versus the step-size of the rotary motor for $^{81}\text{Br}$ NQR experiment of 1,3,5-tribromobenzene at room temperature. The rotary motor was moved with a given rotation step-size by the polynomial equation that depends on the tuning frequency for automatic probe tuning.

<table>
<thead>
<tr>
<th>Rotation step-size</th>
<th>Tuning frequency/MHz</th>
<th>Impedance matching/Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>229.950</td>
<td>50</td>
</tr>
<tr>
<td>200</td>
<td>290.175</td>
<td>50</td>
</tr>
<tr>
<td>400</td>
<td>230.450</td>
<td>53</td>
</tr>
<tr>
<td>600</td>
<td>230.700</td>
<td>53</td>
</tr>
<tr>
<td>800</td>
<td>230.950</td>
<td>53</td>
</tr>
<tr>
<td>1000</td>
<td>231.175</td>
<td>50</td>
</tr>
<tr>
<td>1200</td>
<td>231.450</td>
<td>52</td>
</tr>
<tr>
<td>1400</td>
<td>231.700</td>
<td>53</td>
</tr>
<tr>
<td>1600</td>
<td>231.950</td>
<td>54</td>
</tr>
<tr>
<td>1800</td>
<td>232.200</td>
<td>52</td>
</tr>
</tbody>
</table>

†Rotation step-size = $-7.7890 \times 10^{-12} \times (\text{Frequency})^2 + 800 \times \text{Frequency} - 1.8396 \times 10^5$
A $^{81}$Br NQR spectrum was obtained by performing successive pulsed NQR experiments as a function of the rf carrier frequency. At a given rf frequency, the possible $^{81}$Br NQR signal was averaged (typically 320 transients) with a phase cycling sequence; then the free induction decay (FID) in time domain was converted to frequency domain by the Fourier transformation. The largest peak in the magnitude spectra was integrated and this integral was plotted as a function of the rf carrier frequency. Thus, a plot of integrated peak intensity as a function of frequency forms the $^{81}$Br NQR spectrum. The time required to step to the next frequency is about one second. The $^{81}$Br NQR spectrum of 1,2,4,5-tetrabromobenzene ($C_6H_2Br_4$, 98% Aldrich 27834-3) was also obtained at room temperature by the same method described above.

Because the frequency range for $^{79}$Br and $^{81}$Br NQR transition is very large, it is helpful to use the relationship between $^{81}$Br NQR transition frequencies and the Hammett $\sigma$ values as reported by Bray et al. [3.2] to narrow the search range. For the per-brominated aromatics studied here, the $\sigma$ values are particularly larger leading to exceptionally high $^{79}$Br and $^{81}$Br NQR transition frequencies, as shown in Figure 3-5 and 3-6. Because the ratio of $^{79}$Br to $^{81}$Br NQR transition frequencies is 1.1970 [3.2], $^{79}$Br NQR transitions frequencies of brominated aromatic compounds can be calculated from the $^{81}$Br NQR transition frequencies.

### 3.4 Results and Discussion

The $^{81}$Br NQR spectrum of 1,3,5-tribromobenzene was obtained at room temperature, as shown in Figure 3-7. Also, $^{79}$Br NQR transition frequencies were observed at 275.76, 277.12, and 277.38 MHz. This spectrum shows that 1,3,5-tribromobenzene is a good test sample to determine the sensitivity of $^{81}$Br NQR experiment. The 1,3,5-tribromobenzene has three different bromine sites in the unit
Figure 3-5  Correlation of $^{79}$Br NQR transition frequencies of the brominated aromatic compounds with the Hammett $\sigma$ values. The observed $^{79}$Br NQR transition frequencies (●) of 4-bromophenol, 1,2,4-tribromobenzene, 1,3,5-tribromobenzene, and 1,2,4,5-tetrabromobenzene versus $\sigma$ values were reported by Bray et al. The predicted $^{79}$Br NQR transition frequencies (○) of decabromodiphenyloxide and tetrabromophthalic anhydride were based on this correlation.
Figure 3-6 Correlation of $^{81}\text{Br}$ NQR transition frequencies of the brominated aromatic compounds with the Hammett $\sigma$ values. The observed $^{81}\text{Br}$ NQR transition frequencies (●) of 4-bromophenol, 1,2,4-tribromobenzene, 1,3,5-tribromobenzene, and 1,2,4,5-tetrabromobenzene versus $\sigma$ values were reported by Bray et al. The predicted $^{81}\text{Br}$ NQR transition frequencies (○) of decabromodiphenyloxide and tetrabromophthalic anhydride were based on this correlation.
Figure 3-7  The $^{81}$Br NQR spectrum of 1,3,5-tribromobenzene at room temperature. The spin echo pulse sequence was used to obtain the spectrum; $90^\circ-\tau_1-180^\circ-\tau_2$-acquisition.
Since one has longer C–Br bond than the other two C–Br bonds, one has a lower NQR $\pm 1/2 \rightarrow \pm 3/2$ transition frequency than the other. We observed three $^{81}\text{Br}$ NQR transition frequencies that were a good agreement of Bray’s report. To increase the signal-to-noise ratio of the spectrum, signal was averaged 320 times for the entire experiment. The spectrum in Figure 3-7 shows the signal-to-noise ratio of 27 for the largest peak; the scan time was 5 hours and the sample mass was 25 g. Bray et al. reported a signal-to-noise ratio of 5-6 for unknown mass and scan times, but these are possibly some scale as in our work. The $^{81}\text{Br}$ NQR spectrum of 1,3,5-tribromobenzene represents that this experiment is very useful technique for the nuclei having the large quadrupolar coupling constant, such as halogen nuclei, and has high sensitivity of $^{81}\text{Br}$ NQR transition frequencies to local environments around bromine. The $^{81}\text{Br}$ NQR spectrum of 1,2,4,5-tetrabromobenzene [3.13] was also obtained at room temperature with this technique, as shown in Figure 3-8. This spectrum also showed a transition frequency, 239.7 MHz, good agreement with Bray’s results, 239.71 MHz.

At the very end of the time available for this project, the $^{81}\text{Br}$ NQR scans were began two flame retardants, tetrabromophthalic anhydride [3.14] and decabromodiphenyl oxide. Unfortunately, the digital oscilloscope was broken during these runs and no transition frequencies were definitively located. Some of the instrumental improvements underway at the end including conversion to more powerful rf amplifier. The logic for this was based on anticipated problems with short $T_2$ for these samples, and thus the need for a shorter spin echo pulse sequence.

One item for probe tuning improvement considered, but not implemented, was the inclusion of a directional coupler to measure reflected power from the probe. At a new frequency, the probe would be tuned according to the polynomial expression for
Figure 3-8 The $^{81}$Br NQR spectrum of 1,2,4,5-tetrabromobenzene at room temperature. The spin echo pulse sequence was used to obtain the spectrum; $90^\circ - \tau_1 - 180^\circ - \tau_2$ - acquisition.
rotation step-size/frequency; fine tuning would be accomplished by minimizing the reflected power as a function of small rotation about the set point.

We will obtain the $^{81}\text{Br}$ NQR spectra of flame retardants with the same method used above. Then, the $^{81}\text{Br}$ NQR of the polymer blends will be acquired with the narrow rf sweeping range that can be decided the result of the pure flame retardants. With comparison of two expecting spectra from pure flame retardants and polymer blends, we can deduce the physical structure of the flame retardants in the polymer blends. These experiment can be repeated at the various temperature with some modification of probe body.
3.5 References


CHAPTER 4

A FIELD CYCLING NUCLEAR QUADRUPOLE RESONANCE SPECTROMETER WITH VARIABLE POLARIZATION FIELDS AND SAMPLE TEMPERATURE
4.1 Introduction

A field cycling nuclear quadrupole resonance (NQR) spectrometer has been developed based on a Bruker MSL200, a high speed linear stepping motor, and an Oxford gas flow cryostat. The linear motor can be operated in the fringe field (up to 5 mT) of the 4.7 Tesla magnet; the linear motor has important advantages over previous sample shuttle systems based on pneumatic devices: variable position, variable speed, and easier incorporation of variable sample temperature. The variable position is frequently used to select an advantageous magnetic field for polarizing the proton spin system. The gas flow cryostat, with sample motion, has been used for temperatures between 35 K to 300 K. The gas flow cryostat is effective at controlling $^1$H spin-lattice relaxation time of the sample; the major drawback of this arrangement is air leaks that cause blockage of the helium transfer line.

The field cycling NQR spectroscopy was a dominating tool in the seventies for measuring the magnitude and symmetry of electric field gradients at a quadrupolar nuclear site in polycrystalline solids, and has since then been used extensively for works of pure NQR spectroscopy.[4.1-12] Since it detects quadrupolar transitions by monitoring the magnetization of a more abundant and more sensitive $^1$H nuclei, the NQR spectrometer, using the field cycling technique, is useful in studying less abundant and more difficult to detect quadrupolar nuclei. The major difficulties of studying the light quadrupolar nuclei, such as $^2$H, $^{10}$B, $^{11}$B, $^{14}$N, and $^{17}$O, are that they are hard to detect in a high magnetic field due to broad line widths and in a zero magnetic field due to low resonance frequencies. The basic concepts of the field cycling NQR spectrometer originate from spin temperature and level crossing that occurs between the proton and quadrupolar spin systems.[4.13,14]
4.1.1  Spin Temperature

In an externally applied magnetic field, \( B_0 \), an assembly of spins align with that field and will have a certain spin temperature, \( T_S \).\[4.14\] The relative probability of finding the spin system having an energy level splitting, \( \Delta E \), is given by the Boltzmann distribution function \( \exp(-\Delta E/kT_S) \), as shown in eq. (1.2). When the number of the spins is the same in two energy states, the spin temperature of the system is infinite. In this case, there is no NMR signal because the magnetization of the spin system is saturated. When the spin system is placed in that field for the spin-lattice relaxation time, \( T_1 \), it is in thermal equilibrium with the surroundings (lattice) so that the spin temperature is equal to the lattice temperature. In a region of zero magnetic field, the magnetization of the spin system is reduced at a rate on the order of \( T_{1d} \), which is the spin-lattice relaxation time in zero magnetic field. The typical values of \( T_1 \) and \( T_{1d} \) for field cycling NQR spectroscopy experiments should be at least 20 and 1 seconds, respectively.\[4.15\] In fact in solids, the spin-spin interaction is usually much stronger than the spin-lattice interaction. With the spin-spin interaction, that causes thermal contact between two different spin systems, it is possible to exchange magnetization (energy) when two spin systems have the same energy level splitting. Thus, an isolated spin system cannot be affected by spin-spin interaction.

4.1.2  Level Crossing

In the field cycling experiment for the case of a quadrupolar spin system dipolar coupled to an \( S = 1/2 \) spin system, such as \(^1\text{H}\) spin, the proton spin system is used to detect the presence of the less abundant quadrupolar spin system. If the externally applied magnetic field is reduced adiabatically, the energy level splitting of the proton spin system will be reduced as a function of the Larmor frequency as described in section 1.1.1. At the same time, the energy level splitting of the quadrupolar system will be characterized by the pure NQR transition frequencies which are functions of the
quadrupolar coupling constant and the asymmetric parameter, as shown in Figure 1-1. The transition frequencies of proton and quadrupole (S = 1) spin systems as a function of the applied magnetic field are illustrated in Figure 4-1. During the demagnetization process the transition frequency of proton spin system becomes equivalent pair-wise with the pure NQR transition frequencies. Whenever the transition frequency of proton spin system becomes equivalent with a pure NQR transition frequency, energy can be exchanged by the spin-spin interaction denoted in section 4.1.1. This energy exchange between two spin systems is known as level crossing.[4.14,15] The spin temperature of the quadrupole spin system is made equal to the spin temperature of the proton spin system by level crossing.

4.1.3 Basic Field Cycling Sequence

The basic field cycling experiment [4.14] can be divided into three phases, as shown in Figure 4-2.

1. Polarization phase: The sample is placed in a large magnetic field to create $^1$H spin magnetization for a time on the order of the $^1$H $T_1$. The $^1$H spin system reaches equilibrium with the lattice in region A. At the end of this phase, the spin temperature of the $^1$H system becomes equivalent with the temperature of the lattice, this being the sample temperature.

2. Irradiation phase: The sample is then adiabatically transported to a region B of zero applied magnetic field. During the demagnetization process, level crossing occurs to transfer polarization from $^1$H to a quadrupole spin system, thus yielding a polarized quadrupole spin system for the sample at zero magnetic field. Thus, both spin systems are at the same spin temperature at the first point of this region. While the sample is held in zero magnetic field for a time on
Figure 4-1 A plot of the transition frequencies versus the magnetic field for the proton and quadrupolar ($S = 1$) spin systems. Two spin systems exchange the energy when $B = B_1$, $B = B_2$, and $B = B_3$. 
Figure 4-2  Basic field cycling sequence. In region A, the proton spin system is polarized by a large magnetic field. The sample is moved to region B of zero magnetic field, and the quadrupolar spin system may be saturated by zero field rf irradiation frequency. The sample is returned to the high magnetic field, region C, and the recovered proton magnetization observed as a function of zero field rf irradiation frequency.
the order of the $^1\text{H} T_{1d}$, rf irradiation frequency is swept stepwise to saturate pure NQR transition in successive cycles of the experiment.

(3) Detection phase: The sample is transferred to region C of high magnetic field and the recovered $^1\text{H}$ magnetization measured as a function of zero field rf irradiation frequency; during the transfer, the $^1\text{H}$ spin system is repolarized from the quadrupole spin system by level crossing, and the recovered $^1\text{H}$ magnetization is measured with a solid echo pulse sequence.[4.16,17] The recovered $^1\text{H}$ magnetization is 100% in the case when there is no resonance of quadrupolar nuclei at the zero field rf irradiation frequency, and less when a resonance is present.

4.2 Instrumentation Overview

A Macintosh II with running a LabView program (see Appendix A) controls a commercial solid-state NMR, sample motion, zero field rf irradiation, and zero magnetic field, as shown in Figure 4-3. The temperature of the sample is manually controlled by the Oxford CF1200 continuous flow cryostat. The total costs of about $42,000 was required to convert from the commercial solid-state NMR to field cycling NQR spectrometer.

The external trigger signal from the Macintosh is used to control the Bruker MSL200 process controller. A logical low at pin 5 of the 10-pin connector on the back of the MSL is used to cause the external trigger to be true. A TTL-compatible digital I/O signal line is connected to the MSL external trigger input, that signal is produced from a National Instruments NB-MIO-16 parallel interface card in the Macintosh II.
Figure 4-3  A schematic diagram of field cycling NQR spectrometer.
The sample is shuttled between a high magnetic field and a region of zero magnetic field by a Compumotor LX-L20-P36 microstepping linear motor, as shown in Figure 4-3. The motor has a 36" long platen which permits up to 32" motion of a sample, a microstepping resolution of ~90 μm, a lift force of 9 kg, and a maximum speed of 2.54 m/s. The sample can stay in different positions allowing for polarization in a variable external magnetic field by this convenient linear motor. The linear motor is controlled with a Compumotor LX Indexer/Drive system connected via an RS-232C serial port to the Macintosh. Two LabView programs are used, one to reset the initial position of the sample, and the other to move to a new, arbitrary position. Because the motor control system makes a high electrical noise which interrupts an external trigger signal, the dc power input line to the system is isolated to protect any electrical interruptions from other dc power input lines. The motor is mounted on a 20 kg aluminum table fixed to the lift tabs of the Oxford 4.7 Tesla superconducting magnet dewar, and does not affect the magnetic field at all. The table is designed to allow to refill magnet liquid helium with minimum obstruction.

The Oxford CF1200 continuous flow cryostat operates on the principle of a continuous and controlled transfer of liquid helium or nitrogen from a separate storage dewar to the cryostat via an Oxford CFS300 ultra low loss gas shielded transfer tube. After cooling the sample region of the cryostat, the cold exhaust gas flows back along the flexible section of the transfer tube, shielding the incoming coolant to reduce its consumption. The coolant flow rate is controlled by a needle valve in the transfer tube and an Oxford VC30 gas flow controller. The flow controller consists of a vacuum gauge, needle valve and a flow meter. The return gas from the cryostat passes through the needle valve to the GAST DOA-V192-AA gas flow pump, and through the flow meter on its way to the coolant recovery line. An Oxford ITC4 temperature controller measures the temperature of a sample of the high magnetic field region in the cryostat.
and maintains the temperature at a preset level using the heater. Because a sensor to measure the temperature is mounted below the sample space of high magnetic field, the temperature of the sample at zero magnetic field is unknown, but presumed to be somewhat above the indicated temperature of ITC4. The sample temperature is specified to operate from 2 K to 500 K; we have performed field cycling experiments down to 35 K. The major difficulty we have encounter is preventing air leaks at the sliding seal for the sample transport rod. The linear motion of the motor has worked very well even when it is operating below 273 K in humid Louisiana. The probe-to-stainless-steel tubing seal is shown in Figure 4-4.

The probe is based on a 1.35 cm (i.d.) glass tube with rf coils in high field and zero field and a gradient coil to provide a region of zero magnetic field 71 cm from the center of the magnet, as shown in Figure 4-5. The $^1$H magnetization is detected with a modified one-fold saddle-shaped coil tuned to 200 MHz.[4.18-20] The coil is constructed of a 1 μm self-adhesive copper sheet with a 1.59 cm inner diameter and 2.59 cm height. The $^1$H probe operates well from 35 K to 300 K, because it has a low quality factor (Q), a measure of the efficiency of the tank circuit.[4.21] The zero-field rf coil is assembled to irradiate the sample in a zero magnetic field for a pure NQR spectroscopic experiment. The rf irradiation in zero field is done with a 5.8 cm long solenoid mounted on the glass tube (24 gauge magnet wire, 22 μH). An external capacitor system, with series and parallel capacitors, is used to create up to 40 Gauss peak-to-peak rf radiation. A Hewlett-Packard 3314A function generator is the source of rf which is then amplified by a 100 W, 0.02-10 MHz Electronic Navigation Industries 240L amplifier. At a distance of 71 cm along the bore from the magnet center, the stray field is 22.5 mT with a gradient of 500 mT/m. The gradient coil is positioned outside the rf radiation coil as shown in Figure 4-5. Because of coil heating when energized with 4.43 A by a Hewlett-Packard 6032A system power supply, the gradient current is set to zero between field cycles.
Figure 4-4 The probe-to-stainless-steel tube sealing.
Figure 4-5  The zero-field gradient coil, rf irradiation coil, and $^1$H probe.
The time required to convert from $^{13}$C CP/MAS to $^2$H field cycling NQR at 300 K is on the order of thirty minutes. About fifteen minutes is used to remove the room temperature magnet shims.

4.3 Experiments and Results

4.3.1 $^1$H $T_1$ Variable Field and Temperature

The spin-lattice relaxation rate of a proton has been measured using the field cycling technique with a variable proton spin polarization field.\[4.22\] In our experiments, the variable sample temperature was added to determine $T_1$ of toluic acid using Oxford CFC. As shown in Figure 4-6, large magnetic field gradients between 40 and 85 MHz for a $^1$H spin system in the Bruker 4.7 Tesla superconducting magnet results in the use of a small amount of sample (25 mg) for the $T_1$ experiment. The range of magnetic fields is accomplished by polarizing in the stray field of the magnet where the field plot was determined with a Hall offset generator (F. W. Bell Inc., Model # BHA 900) mounted on the end of the sample transport rod. The field cycling sequence is described in Figure 4-7. In a low magnetic field (~ 0.3 mT), the $^1$H spin magnetization is saturated within 10 s, then the sample is repositioned by the Compumotor microstepping linear motor to allow the $^1$H spin magnetization to recover at a region of known magnetic field for variable delay times. The sample is then rapidly transported to a high magnetic field, and the repolarized $^1$H spin magnetization is measured with a solid echo pulse sequence ($90^\circ_x – \tau_1 – 90^\circ_y – \tau_2 – \text{acquisition}$) at three different temperatures, 200, 250, and 300 K. Proton 90$^\circ$ pulses are 12 $\mu$s at a frequency of 200 MHz. The first delay between pulses, $\tau_1$, is 2 $\mu$s, and the second delay before echo acquisition, $\tau_2$, is 8 $\mu$s. To increase the signal-to-noise ratio of the $T_1$ experiments, the $^1$H magnetization of up to 20 field cycles is averaged. The $^1$H $T_1$ data of toluic acid are shown in Table 4-1.
Figure 4-6  A plot of MSL200 magnet field gradient. The sample position in a low magnetic field to saturate $^1$H magnetization is at 71 cm.
Figure 4-7  Field cycling sequence of $T_1$ measurement.
Table 4-1  Spin-relaxation time of toluic acid (25 mg) at various temperatures and fields.

<table>
<thead>
<tr>
<th>Magnetic Field (Larmor Frequency of Proton)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 K</td>
</tr>
<tr>
<td>1.0372 T (44.15 MHz)</td>
<td>7.415 s</td>
</tr>
<tr>
<td>1.4328 T (60.99 MHz)</td>
<td>13.14 s</td>
</tr>
<tr>
<td>2.0023 T (85.24 MHz)</td>
<td>22.93 s</td>
</tr>
</tbody>
</table>

4.3.2 Field Cycling NQR Spectroscopy

Field cycling NQR has long been used for the spectroscopy of quadrupolar nuclei.[4.14] In fact, the pure $^2$H NQR of the benzoic acid 50% deuterated carboxylic acid were reported via field cycling NQR.[4.23,24] Because of a lack of control lines for manipulating the Bruker MSL, particularly for saturating the $^1$H magnetization, a modified field cycling sequence is used as shown in Figure 4-8. A brief description of the field cycling experiment is given for the case of an $S = 1$ spin system dipolar coupled to an abundant $S = 1/2$ spin system. First, the sample is moved to a low magnetic field from a high magnetic field to saturate the $^1$H spin magnetization for 30 s. The sample is then transported back to a known magnetic field to recover $^1$H magnetization for a time on the order of the $^1$H $T_1$ (500 s for benzoic acid at 300 K). The sample is then rapidly transported to a region of zero applied magnetic field, which is generated by a cancellation coil. The time to move the sample takes about 0.5 s. While the sample is held in a zero magnetic field, rf irradiation frequency is swept stepwise in successive cycles through the experiment for about $^1$H $T_{1d}$ (3 s). The sample is transferred to a high magnetic field and the recovered $^1$H magnetization is measured as a function of frequency; the recovered $^1$H magnetization is measured with
Figure 4-8  Modified field cycling sequence of NQR experiment.
a solid echo pulse sequence. The recovered $^1\text{H}$ magnetization is 100% in the sample
there are no resonant quadrupolar nuclei at that frequency, and less when resonances
are present. The pure $^{14}\text{N}$ NQR of quinuclidine hydrochloride at $\sim60$ K is also
measured with the same field cycling sequence. At 60 K, the $^1\text{H} T_1$ for quinuclidine
hydrochloride is 200 s and $^1\text{H} T_{1d}$ is 3 s. The time required to cool down the sample
temperature with liquid He is about 5 K/min.

The $^2\text{H}$ NQR spectrum of benzoic acid (97.8% deuterated carboxylic acid)
obtained at 300 K and the $^{14}\text{N}$ spectrum of quinuclidine hydrochloride at $\sim60$ K are
shown in Figure 4-9 and 4-10. In both cases, a polarizing field of 4.7 T was used and
the $^1\text{H}$ magnetization of 2 field cycles was averaged. The $^2\text{H}$ NQR spectrum of
benzoic acid showed the $^2\text{H} \nu_-$ and $\nu_+$ transitions at 118.5 kHz and at 132 kHz with
3 kHz line width, respectively. The $^{14}\text{N}$ spectrum of quinuclidine hydrochloride was
acquired at $\sim60$ K, because the $^1\text{H} T_1$ for quinuclidine hydrochloride was very long at
300 K. The preliminary $^{14}\text{N}$ spectrum showed the $^{14}\text{N} \nu_-$ and $\nu_+$ transitions around
1.1 MHz and 1.25 MHz with 0.1 MHz wide line width, respectively. The large
absorption below 0.4 MHz was due to direct absorption of zero field rf irradiation by
the $^1\text{H}$ spin system; the observation of direct absorption was beneficial in that it quickly
demonstrated successful spectrometer performance. For the last 7 data points, a large
drift of $^1\text{H}$ magnetization was observed as a result of the system warming up. The
increase in temperature was due to the liquid He supply being depleted. Both samples
are certainly candidates for a lower polarizing field due to the very long $^1\text{H} T_1$ found at
4.7 Tesla.

Field cycling NQR has long offered useful advantages over pure NQR
spectroscopy or high-field NMR for certain samples. This work demonstrates a novel
method whereby a commercial solid-state NMR spectrometer can be adapted to field
cycling NQR spectroscopy.
Figure 4-9  Pure $^2$H NQR spectrum of deuterated benzoic acid at room temperature. Sample is polarized at 4.7 T.
Figure 4-10  Pure $^{14}$N NQR spectrum of quinuclidine hydrochloride at 60K. Sample is polarized at 4.7 T.
4.4 References


CHAPTER 5

\textbf{\textsuperscript{11}B IMAGING WITH FIELD CYCLING NMR AS A LINE NARROWING TECHNIQUE}

(This chapter has been published as an article by Youngil Lee, Daniel, C. Miahaels, and Leslie G. Butler in \textit{Chemical Physics Letters} \textbf{1993}, \textit{206}, 464-6. A letter from the publisher granting permission to reproduce this copyrighted material is attached in Appendix D.)
5.1 Introduction

NMR imaging of quadrupolar nuclei has received less attention than the imaging of $S = 1/2$ nuclei, in part due to the difficulties associated with the quadrupolar interaction. A critical feature of NMR imaging is line narrowing of a selected NMR resonance. For $S = 1/2$ spins, line narrowing schemes have included MAS and multiple pulse techniques and a resolution of about 100 μm can be obtained.[5.1] Therefore, the quest for effective NMR imaging of quadrupolar nuclei is really a search for a line narrowing technique, and several different approaches have been used.

Images have been acquired for $^{35}\text{Cl}$ and $^{81}\text{Br}$ in samples with initially cubic site symmetry and thus a narrow NMR resonance.[5.2,3] A $^{35}\text{Cl}$ image was acquired in zero magnetic field in a Zeeman-perturbed NQR experiment; the spatial resolution was about 2 mm.[5.4] Deuterated polymers, in which the line width of the $^2\text{H}$ resonance is tractable, have been imaged with multiple quantum and MAS NMR techniques and local molecular mobility observed.[5.5,6] In a promising experiment for ceramics, the central resonance of $^{27}\text{Al}$ in an aluminum oxide was imaged with a spin echo sequence.[5.7]

Field cycling NMR has a long history for the spectroscopy of quadrupolar nuclei.[5.8-10] In fact, the $^{10}\text{B}$ and $^{11}\text{B}$ NQR spectra of boric acid were acquired via field cycling NMR.[5.11] A brief description of the field cycling experiment is given here for the case of a quadrupolar spin system dipolar coupled to an abundant $S = 1/2$ spin system, such as the proton spin system in boric acid. The sample is held in high magnetic field for the $^1\text{H}$ spin-lattice relaxation time, then transported to zero magnetic field. At an intermediate point in the demagnetization process, the evolution of the $^1\text{H}$ and $^{11}\text{B}$ spin energies allows for facile transfer of polarization from $^1\text{H}$ to $^{11}\text{B}$, thus yielding a polarized $^{11}\text{B}$ spin system for the sample at zero field. While in zero magnetic field, irradiation at the $^{11}\text{B} \pm 1/2 > \rightarrow \pm 3/2 >$ transition will destroy $^{11}\text{B}$
polarization. The sample is then returned to high magnetic field; during the transfer, the
$^1$H spin system is polarized from the $^{11}$B spin system, and the recovered $^1$H
magnetization is measured. The recovered $^1$H magnetization is measured with a solid
echo pulse sequence.[5.12,13] In the spectroscopy experiments, the zero field rf
irradiation frequency is swept stepwise in successive cycles of the experiment. In the
imaging work reported herein, the rf frequency is held constant, but the zero field
irradiation coil is designed to be spatially selective. Hence, successive cycles of the
field cycling experiment, combined with translation of the zero field rf irradiation coil,
leads to an image of a quadrupole spin system that is sensitive to the value of the
quadrupole coupling constant.

5.2 Experiment

$^1$H and $^{11}$B NMR images were obtained at room temperature by field cycling
NMR in which the sample was shuttled between a high magnetic field and a region of
zero magnetic field using the sequence shown in Figure 5-1 [5.10,11] in a homemade
spectrometer.[5.14,15] $^1$H rf pulses were typically 3 μs (90° tip angle); the $^1$H rf
solenoid coil was significantly longer than the sample, 32 mm and 26 mm,
respectively, to ensure a homogeneous $^1$H $B_1$ field. The translation of a 3-turn rf coil,
mounted on a linear positioning stage, was used to spatially encode the zero field rf
irradiation. The stage (Aerotech ATS302M) has a positioning accuracy of 5 μm and a
maximum travel of 51 mm.

The imaging experiment consists of the following steps. First, the maximum and
minimum recovered $^1$H magnetizations are measured in two separate experiments:
maximum magnetization is measured with a normal polarization time, normal residence
time in zero field, and no rf irradiation while in zero field; minimum magnetization is
measured with a short polarization time (1 s), long residence time in zero field (100 s),
Figure 5-1  Field cycling and pulse sequence of the $^1$H and $^{11}$B imaging experiments. The sample is shuttled from high magnetic field, about 0.94 T, to a region of zero magnetic field, less than 1 mT, by an air–driven piston with a transit time of about 0.5 s. (a) Field cycling sequence, and (b) zero-field rf coil geometry.
and no rf irradiation while in zero field. All recovered $^1$H magnetizations measured in the imaging experiment are reported as a percentage based on these two values. In the actual imaging run, the recovered $^1$H magnetization is measured as a function of zero field rf coil position; in successive cycles, the coil is translated across the length of the sample. The imaging resolution is a function of the size of the sample region affected by the small zero field rf coil. To increase the S/N of the image, scans were averaged up to 10 times. The time required to generate an image is a simple function of the number of image data points, number of scans, and the $^1$H $T_1$. At room temperature, the $^1$H $T_1$ for benzoic acid is 60 s and quite long for boric acid, greater than 1000 s. The samples consist of powders packed into a small glass vial separated into two layers by a layer of teflon tape. The dimensions of each sample are given in the images.

5.3 Results and Discussion

Two samples were imaged so as to illustrate two points. First, $^1$H images can be obtained by 45 kHz irradiation into the $^1$H zero field resonance; the $^1$H zero field resonance frequency is determined by homonuclear dipolar coupling. Second, images of a quadrupolar spin system can be obtained by zero field rf irradiation at a pure NQR transition, here, the $^{11}$B $\pm 1/2 > \rightarrow \pm 3/2 >$ transition at 1.335 MHz in boric acid.

The $^1$H image of the 26 mm benzoic acid phantom was acquired in 12 hours with a resolution of 6 mm, as shown in Figure 5-2. The image is shown as the recovered $^1$H magnetization plotted against the zero field rf coil position. The recovered $^1$H magnetization is near 100% when the benzoic acid sample lies completely outside of the zero field rf coil; the recovered $^1$H magnetization is reduced by zero field rf irradiation of the $^1$H resonance in benzoic acid. The experimental image clearly shows the two layers of benzoic acid. Also plotted in the image is an ideal image of the phantom; most
A $^1$H NMR image of a benzoic acid phantom. The image is acquired with a 100 s polarization period and 2 s irradiation in zero field at 45 kHz with an amplitude of $3 \times 10^{-6}$ T(peak-to-peak). Each data point represents the average of 10 acquisitions. After each data is obtained, the translation stage is advanced 1.25 mm. The dashed line represents the ideal image for the phantom (arbitrary amplitude).
of the difference between the experimental and ideal images is attributed to the finite size of the zero field rf coil and fringe effects.

Figure 5-3 shows the $^{11}$B NQR image of the 26 mm boric acid phantom with a resolution of at least 5 mm. Because of the much longer $^1$H $T_1$ of boric acid, this image required 46 hours. In this experiment, the $^{11}$B pure NQR transition $\pm 1/2 \rightarrow \pm 3/2$ is selectively saturated, then the $^{11}$B spin system polarization is measured via the recovered $^1$H magnetization.

In these preliminary experiments, the images do not have very good resolution. However, this work does represent a very successful method for imaging $^{11}$B and other quadrupolar nuclei, i.e., $^2$H, $^{10}$B, $^{14}$N, $^{17}$O, and $^{27}$Al. The low spatial resolution originates from the simple coil geometry and poor shielding of the zero field rf coil used in these preliminary experiments. Improved coil designs, based upon two colinear but oppositely wound solenoids, are being tested.
Figure 5-3  A $^{11}$B image of a boric acid phantom. The image is acquired with a 600 s polarization period and 20 s irradiation in zero field. The sample is irradiated to saturate the $^{11}$B quadrupolar transition of boric acid at 1.335 MHz with an amplitude of $1 \times 10^{-4}$ T (peak-to-peak). Each data point represents the average of 10 acquisitions. After each data is obtained, the translation stage is advanced 1.875 mm.
5.4 References


CHAPTER 6

FIELD CYCLING $^{14}$N NQR IMAGING WITH SPATIAL AND FREQUENCY RESOLUTION

(This chapter has been accepted and is in press as an article by Youngil Lee and Leslie G. Butler in the *Journal of Magnetic Resonance* 1995. A letter from the publisher granting permission to reproduce this copyrighted material is attached in Appendix D.)
6.1 Introduction

Relative to NMR imaging of proton-containing solids, imaging of quadrupolar nuclei is rare and made difficult by the quadrupolar interaction.[6.1] One can perform the imaging experiment based on either the pure NQR experiment [6.2-4] or the quadrupolar-perturbed NMR experiment.[6.5] Recently, we have found that magnet field cycling is a useful compromise since it provides the line narrowing of pure NQR combined with the sensitivity of NMR signal detection. This was demonstrated with a one-dimensional image based on the $^{11}$B NQR resonance of a boric acid phantom.[6.6]

In a magnetic field cycling experiment, the detected signal is a function of the spin temperature in the laboratory frame.[6.7] Therefore, the conversion of the field cycling experiment from spectroscopy to an imaging experiment is based on spatially selective saturation of a specific transition, usually a pure NQR transition. For the case of one-dimensional imaging, the design of an rf coil for selective saturation of a low frequency NQR transition is limited by relatively few constraints. An imaging plane can be defined either by a plane of large amplitude $B_1$ field or by a null in the $B_1$ field. Factors such as $B_1$ homogeneity are much less important when operating in the saturation mode as compared with the linear response mode required for most NMR observations. Imaging along a spatial dimension can be done by simple translation of the rf coil in successive field cycling experiments. Incorporating the frequency domain into the experiment can be done by acquiring successive one-dimensional images as a function of the rf frequency used for the attempted saturation of the NQR resonance.

In this work, a pseudo two-dimensional image is presented based on spatial resolution in one dimension and rf frequency in the second dimension; the combination of spatial and spectroscopic measurements has interesting advantages as described by Scheler et al.[6.8] The test sample consists of acetamide and salicylamide and the $^{14}$N $|0> \rightarrow |+>$ transitions occur between 2 to 2.5 MHz in zero magnetic field. In the course
of this work, three different rf coil designs were tested. Two coil designs create an imaging plane based on a large amplitude $B_1$ field. A third design creates an imaging plane based on a null in the $B_1$ field and consists of two collinear solenoids wound with opposite handedness. The latter design was used for most of the work presented herein. This is the first image of a quadrupolar spin system which also incorporates resolution along the NQR frequency domain in the non-motionally-narrowed limit.[6.9,10]

6.2 Experiment

Field cycling NMR has long been used for the spectroscopy of quadrupolar nuclei.[6.11] In fact, the pure $^{14}$N NQR resonance of acetamide [6.12] and salicylamide [6.13] at 77 K were reported via field cycling NMR. A brief description of the field cycling experiment is given for the case of an $S = 1$ spin system dipolar coupled to an abundant $S = 1/2$ spin system. In high magnetic field, the $^1$H spin magnetization is allowed to grow for a time on the order of the $^1$H $T_1$ as illustrated in Figure 6-1. The sample is then rapidly transported to a region of zero applied magnetic field. At some point in the demagnetization process, the evolution of the $^1$H and $^{14}$N spin states allows for facile transfer of polarization from $^1$H to $^{14}$N, thus yielding a polarized $^{14}$N spin system for the sample at zero magnetic field; for convenience, we will assume that $^1$H $T_1$ in zero magnetic field is short with respect to the zero field residence time. While the sample is held in zero magnetic field, rf irradiation is used to saturate the $^{14}$N $|0> \rightarrow |+>$ transition, and so decrease the $^{14}$N polarization. The sample is then returned to high magnetic field; during the transfer, the $^1$H spin system is repolarized from the $^{14}$N spin system, and the recovered $^1$H magnetization is measured with a solid echo pulse sequence. With this sequence, the recovered $^1$H magnetization is a function of the rf irradiation frequency and the presence or absence
Figure 6-1 Field cycling sequence.
of $^{14}$N sites in regions of high $B_1$. For $^{14}$N NQR spectroscopy, the zero field rf irradiation frequency is swept stepwise in successive cycles of the experiment and the recovered $^1$H magnetization measured as a function of frequency. We note here that the $^{14}$N resonance intensity in the field cycling experiment is a complex function of $^1$H and $^{14}$N relaxation times and the relative heat capacities of the two spin systems.[6.11] Thus, it will be difficult to acquire images that accurately show the relative abundance of multiple quadrupolar sites.

The field cycling experiment is converted into an imaging experiment by modifying the rf irradiation coil used to saturate the quadrupolar transitions. Shown in Figure 6-2 are three coils we have tested: a) small rf coil, b) second derivative rf coil, and c) two collinear, oppositely wound solenoidal rf coils. For the first two, the imaging plane corresponds to maximum $|B_1|$ while the last arrangement has an imaging plane at the null, $|B_1|=0$. A one-dimensional image is created by translation across the sample of the zero field rf irradiation coil at a fixed frequency; at each coil position, the field cycling experiment is performed. A pseudo two-dimensional image is obtained by varying the frequency in successive one-dimensional experiments. An interesting feature of the two collinear, oppositely wound solenoidal rf coils is that imaging resolution improves with increasing irradiation power, as shown qualitatively in Figure 6-2d.

The field cycling instrument has been described previously [6.6] that a homemade spectrometer connected via an IEEE-488 interface to the Macintosh has been used for all experiments, as shown in Figure 6-3. All software were written in LabView, a graphical programming language (see Appendix B). A $^{14}$N phantom consists of acetamide and salicylamide and the imaging experiments are performed at room temperature. Proton 90° pulses are typically 2.8 $\mu$s and are at a frequency of 42 MHz. The $^1$H rf solenoid coil is significantly longer, 22 mm, than the sample to
Figure 6-2  Three coil designs for irradiation of the sample while in zero applied magnetic field: small rf coil (a), a second derivative rf coil (b), and two collinear, oppositely wound solenoidal rf coils (c). For each coil, the current into and out of the plane of the figure is shown with filled and empty circles, respectively. (The second derivative coil is so named as this coil is sensitive to the curvature of a magnetic field.) In figure 6-2c, the dots indicate additional coil turns; the gap between the two solenoids is 0.8 mm. In figure 6-2d, the the nonlinear characteristics of the saturation are evident in the form of a sharper imaging plane for coil design c at higher rf power levels.
Figure 6-3  A block diagram of the homemade NQR imaging spectrometer.
ensure a homogeneous $^1\text{H} B_1$ field. The imaging coil has a 0.8 mm gap; each solenoid is 45 mm long and is made from 89 turns of 32 gauge wire. Stray static magnetic fields in the zero field region are reduced to less than 30 µT with a large Helmholtz coil. To increase the S/N of the image, the $^1\text{H}$ magnetization of up to 10 field cycles is averaged. The time required to generate an image is a simple function of the number of image data points, number of scans, irradiation time, and the $^1\text{H} T_1$. At room temperature, the $^1\text{H} T_1$ for acetamide is 100 s and is inconveniently long for salicylamide, 500 s.

The presentation of the images is different for the two coil types. For images acquired with an imaging plane based on a maximum value of $|B_1|$, the recovered $^1\text{H}$ magnetization is 100% at positions in the sample where there are no resonant quadrupolar nuclei in the imaging plane, and less when such nuclei are present. Therefore, a plot of recovered $^1\text{H}$ magnetization versus coil position is inverted with respect to the quadrupolar spin density. However, for the coil design with a $B_1 = 0$ imaging plane, the response function is reversed. Consider the case where the imaging plane lies outside the sample. Because each solenoid is longer than the sample, all on-resonance quadrupolar spins are saturated leading to a minimal recovered $^1\text{H}$ magnetization. When the imaging plane position corresponds to a region containing quadrupolar nuclei, that portion of the quadrupolar spin system will retain some polarization, thus leading to a larger recovered $^1\text{H}$ magnetization.

The pseudo two-dimensional image is assembled from one-dimensional images acquired with off-resonance and on-resonance irradiation frequencies. The 2D image is constructed by converting the recovered $^1\text{H}$ magnetization of each 1D image to a percentage scale and then plotting the change in the recovered $^1\text{H}$ magnetization of each 1D image as a function of coil position and rf irradiation frequency. By using this
procedure for the pseudo two-dimensional image construction, it is not necessary to have any advanced knowledge about the $^{14}$N transition frequencies.

6.3 Results and Discussion

In this work, imaging rf coils were designed and tested, the $^{14}$N $|0\rangle \rightarrow |+\rangle$ resonances for acetamide and salicylamide were observed at room temperature, and a pseudo two-dimensional image was acquired. Both of the coil designs based on an imaging plane of large $|B_1| \parallel$ yielded some $^{14}$N images, but it proved difficult to generate a sufficiently large $B_1$ so as to saturate the $^{14}$N $|0\rangle \rightarrow |+\rangle$ transitions with $3 \, s$ of irradiation (the upper limit on the irradiation time is determined by the $^{14}$N spin-lattice relaxation time in zero magnetic field). A larger $B_1$ field is generated in the third coil design which consists of two oppositely wound, collinear solenoids; the imaging plane is the null point, $B_1 = 0$, between the two solenoids.

The room temperature $^{14}$N resonances for acetamide and salicylamide are shown in Figure 6-4 and are unusually broad relative to most $^{14}$N resonances of amides. Spectra of acetamide were acquired at 200 K and 100 K, yielding progressively narrow resonances. In spite of the broad room temperature resonances, the $^{14}$N $|0\rangle \rightarrow |+\rangle$ transitions for acetamide and salicylamide are well resolved and thus, these samples were used to create an imaging phantom.

The pseudo two-dimensional images shown in Figures 6-5 and 6-6 were generated by translating the imaging plane across the sample in successive one-dimensional imaging experiments. The one-dimensional image at 2.15 MHz shows the acetamide portion of the phantom and the image at 2.3 MHz shows salicylamide. Images at other frequencies show much less change in the recovered $^1$H magnetization as a function of coil position; the stack plot in Figure 6-5 shows the change in recovered $^1$H magnetization. For the purpose of optimizing instrument
Figure 6-4  $^{14}\text{N}$ NQR spectra of (a) acetamide and (b) salicylamide. The acetamide spectrum is acquired with a 100 s polarization period in high magnetic field and 3 s irradiation in zero magnetic field. The zero field rf amplitude is 0.59 mT$_{pp}$ and each data point represents the average of 2 field cycling sequences. The salicylamide spectrum is acquired with a 500 s polarization period and 5 s irradiation.
Figure 6-5  A pseudo two-dimensional $^{14}$N image of a acetamide/salicylamide phantom. For the frequency range of 2.09 to 2.21 MHz, each one-dimensional image is acquired with field cycling parameters optimized for acetamide; the parameters are reset for imaging salicylamide at the higher frequencies. After each data point is obtained in the one-dimensional image, the translation stage is advanced 2.5 mm.
Figure 6-6  The data shown in Figure 6-5 is replotted as a contour map. The sample dimensions are shown, including the Teflon spacers. The spatial resolution is about 5 mm.
performance, the relaxation delay and the irradiation time were set to 100 s and 3 s, respectively, for the acetamide portion of the image and to 500 s and 5 s, respectively for the salicylamide imaging. The vertical display parameters for each one-dimensional image are normalized for the 100% and 0% recovered $^1$H magnetization. The result of the pseudo two-dimensional imaging experiment clearly shows the location of acetamide and salicylamide based on spatial and frequency resolved dimensions. The spatial resolution is about 5 mm and the frequency resolution matches that predicted from the $^{14}$N spectra. The contour plot in Figure 6-6 shows the frequency and spatial resolution.

In summary, field cycling spectroscopy of quadrupolar nuclei offers several routes by which one-dimensional images can be obtained, especially since the design of the rf coil for selective saturation of a low frequency NQR transition is limited by relatively few constraints. An imaging plane can be defined either by a plane of large amplitude $B_1$ field or by a null in the $B_1$ field and one can operate in the saturation mode as compared with the linear response mode required for most NMR observations.
6.4 References


CHAPTER 7

A DEMONSTRATION OF TWO-DIMENSIONAL IMAGING
ON A SOLUTION–STATE NMR SPECTROMETER
7.1 Introduction

In normal magnetic resonance techniques, a homogeneous static magnetic field is used to determine the properties and behavior of matter on the molecular scale. The purpose of the homogenous field is to supply a steady field within the samples that gives rise to resonance widths small compared with the interactions being studied. With the use of an inhomogeneous magnetic field, there will be a broadened signal containing information on the spatial distributions of the nuclei or electrons at resonance. This inhomogeneous field allows the study of structure above the molecular level.[7.1]

A magnetic field gradient across the sample is created by adjusting the room temperature shims, usually X- and Y-shims, about the settings corresponding to a "shimmed" magnetic field as discussed previously by Hull.[7.2] If the sample has a single resonance, like water, then a one-dimensional (1D) image (or projection) is acquired by tuning on a gradient and observing the NMR spectrum. A two-dimensional (2D) image is generated from a series of 1D projections by using a method such as filtered back-projection reconstruction algorithm.[7.3]

Back-projection was first applied to reconstruct tomograms of living patients by Kuhl and Edwards.[7.4] Back-projecting each profile across a field performs reconstruction of the object, i.e., the signal intensity corresponding to a given magnetic field is applied to all the objects that make up that field and an approximation of the original object is produced after finishing for all projections. The reconstructed density is the sum of all magnetic field-projections which pass through an object. It was very attractive because of its easy application to practice, without making use of a computer or complex mathematics. Bracewell and Riddle[7.5] first developed filtered back-projection which is similar to back-projection method, except they used profiles which were modified or filtered before being back-projected. The advantage of filtered
back-projection is that after completion of the scan the image does not take long because each profile can be fully processed as it is obtained.[7.3]

A recent article discussed acquisition of the 1D NMR images with a sequential scanning of an isolated plane of magnetization as a method of planar imaging.[7.2] Herein, we demonstrate the 2D NMR images using an unmodified solution-state NMR spectrometer. While the experiment is complex and has a number of steps, acquisition of a 2D image is relatively quick for a practised user.

7.2 Samples

The samples contained water or H$_2$O/D$_2$O mixtures which are mounted in 5 and 10 mm NMR tubes, 0.5 mm wall thickness. All samples have a mirror plane perpendicular to the tube axis; the 2D image lies in the mirror plane. The NMR probes, both 5 and 10 mm, are used without modifications of $^1$H NMR coils. The sample length is about 1 cm in order that the sample fits completely inside the sensitive region of the $^1$H NMR coil. Three different samples, shown in Figure 7−1, have been imaged. The plexiglas and paraffin used in these samples are "NMR invisible" in solution−state NMR experiments.

7.3 Experiment and Results

There are two simple ways to generate a series of magnetic field gradients across the sample for making a 2D image. The first is to apply a continuous gradient in one direction, then rotate the sample about an axis perpendicular to the gradient. The second, which is the method used herein, is to rotate a magnetic field gradient around a stationary sample. The values of the X- and Y-shims are adjusted, as shown in Figure 7−2, to yield a magnetic field gradient that is rotated stepwise. The X- and Y-shims of most spectrometers should be able to generate linear magnetic field gradients on the
Figure 7-1  The three samples used: (a) A 5 mm NMR tube that contains two capillary tubes (1.5 mm o.d.) with one capillary tube containing tap water and the other a 50:50 mixture of H$_2$O/D$_2$O. (b) A 10 mm NMR tube with 21 capillary tubes with five tubes in an asymmetrical configuration containing water while the others were left empty. (c) An "L" shape is milled in a plexiglas plug and then filled with water.
a. Paraffin
Tap Water
50:50 mixture of H$_2$O/D$_2$O

b. Paraffin
Empty
Tap Water

- 10 mm NMR tube
- 4 mm Plexiglas
Figure 7-2  X- and Y-shims provide a uniform magnetic field gradient across the entire sample volume. A gradient of magnitude $R$ generates a semicircular line shape depending upon the vertical scale factor.
order of 1 Gauss cm\(^{-1}\) that are centered on the sample. In this procedure, the sample is placed in the center of the rf coil, and the magnet shims adjusted, if necessary, so as to yield a relatively narrow linewidth, about 25 Hz. We assume here that the X- and Y-shims provide a uniform magnetic field gradient across the entire sample volume. The Bruker AC100 NMR spectrometer has a 2.34 Tesla superconducting magnet with both superconducting and room temperature shim coils. The current through each room temperature shim coil is controlled by a digital-to-analog converter (DAC). Each DAC is loaded with an integer between ±9999, inclusive, where a value of zero corresponds to no applied field gradient. The DAC settings are stored on the computer hard disk.

A set of magnetic field gradients is created by setting the X- and Y-shims according to the following formula:

\[
\begin{align*}
X\text{-shim value} &= X\text{-base} + R \times \cos(n \times \text{AngleStepSize}) \\
Y\text{-shim value} &= Y\text{-base} + R \times \sin(n \times \text{AngleStepSize})
\end{align*}
\]  

(7.1)  

(7.2)

where X- and Y-base are the shim settings corresponding to a homogeneous magnetic field, the AngleStepSize is typically 6\(^{\circ}\) yielding 31 projections from 0\(^{\circ}\) to 180\(^{\circ}\), inclusive, and R is the magnitude of the magnetic field gradient, in the arbitrary units of the spectrometer.

A problem we have encountered is somewhat poor performance of the shims over large sample volumes for large values of R. This is most likely due to poor shim coil windings. A sample that was used to test the quality of the magnetic field gradients is an NMR tube with a minimal amount of water, placed so that there is no water in the region outside of the rf coil. The samples were not spun and the \(^2\)H lock system, as well as, the magnetic field sweep, was deactivated.
For the test sample, a spectrum acquired without a gradient should have a narrow resonance. However, the unusual placement of the NMR tube leads to a larger than normal line width, full width at half height (FWHH), as shown in Figure 7–3a. Whereas the instrument routinely yields narrow lines for spectroscopy, \( \Delta v(\text{FWHH}) \leq 2 \text{ Hz} \), the change in the sample placement degrades the magnetic field homogeneity in the sensitive region of the rf coil, such that \( \Delta v(\text{FWHH}) \equiv 25 \text{ Hz} \). A gradient generates a rectangular line shape for the test sample, as shown in Figure 7-3b, that is symmetric about the resonance frequency. The full width near baseline (FWNB), \( \Delta v(\text{FWNB}) \equiv 1500 \text{ Hz} \) for \( R = 6000 \), can be used to calculate the strength of the magnetic field gradient:

\[
\frac{dH(R)}{dx} = \frac{2\pi \Delta v(\text{FWNB})}{\gamma^H x \text{ (tube ID)}}
\]  

(7.3)

where \( \gamma^H = 26,751 \text{ rad s}^{-1} \text{ Gauss}^{-1} \) and tube i.d. 4 mm. For the Bruker shim system, \( dH(R = 9999)/dx \equiv 1.18 \text{ Gauss cm}^{-1} \). This can be compared with whole body magnetic resonance imaging (MRI) where gradients on the order of 1-20 Gauss cm\(^{-1}\) are used. Aside from line shape, the ratio of the line widths in the presence and absence of the gradient give an approximate indication of the possible resolution of the imaging experiment. Here \( \Delta v(\text{FWNB}, \ dH(R = 6000))/\Delta v(\text{FWHH}, \text{ no gradient}) \equiv 1500/25 \), so we expect roughly a 60 point resolution across each 1D projection. More resolution would be desirable; any less means that shimming must be done to decrease the \( \Delta v(\text{FWHH}, \text{ no gradient}) \) for the given sample geometry. For our work, no additional shimming was necessary to reduce \( \Delta v(\text{FWHH}, \text{ no gradient}) \), but this would have been the next step for improving the resolution of the images. If the line shape obtained with a gradient is not well-centered at the same resonant frequency as the center of the line shape without a gradient, the origin of the gradient is not located at the
Figure 7-3  Projections of test sample:  (a) A projection without gradient ($\Delta v (\text{FWHH}) = 25$ Hz).  (b) A projection with gradient ($\Delta v (\text{FWNB}) = 1500$ Hz) for $R = 6000$.  (c) A projection with gradient ($\Delta v (\text{FWNB}) = 2011$ Hz) for $R = 9999$.  (d) The test sample with tap water in a 5 mm NMR tube.
5 mm NMR water

25 Hz

1500 Hz

2011 Hz

5 mm NMR tube

tap water

1 cm
center of the sample. This error in shim coil construction will create distortion in the 2D image similar to a blur. For demonstration purposes, rather large errors can be tolerated. Even though our instrument shows noticeable errors, visible as asymmetric line shapes in Figure 7–3b and 3c, useful 2D imaging is still practical.

A series of shim files is prepared by manually setting X- and Y-shim to the values calculated from equations (7.1) and (7.2). The shim settings are stored on the spectrometer hard disk. The goal of the 2D imaging experiment is to obtain the line shape as a function of the gradient direction for a series of projections, typically 31 in these experiments. About 100-200 data points are obtained to define the line shape and a flat baseline on both sides of the absorption in each projection. Typically, the following parameters are used: the spectral width is 30 kHz, data size = 2 K complex data points, the \(^1\)H pulse tip angle is set near 180° to reduce the signal amplitude (pure water gives an intense NMR signal), relaxation delay = 4 s (water \(T_1\) about 3.5 s), and 4 scans are obtained. The projections are then exponentially multiplied, Fourier Transformed, and phase corrected.

The data are transferred using Kermit on the Bruker and VersaTerm Pro on the Macintosh.[7.6] Data transferring takes approximately 1/2 minute per file for 2 K data. This gives 31 projections of 1–2 K points each stored as separate binary files, still in the Bruker format. All 31 projections are reformatted using a homemade data translation program for translating from instrument specific binary-coded files to ASCII text files program. The translation program was written in LabView, a graphical programming language.[7.7,8] All other programs are written in Matlab, a vector-oriented programming language, and all programs written in-house and used herein are available from the authors.

We use a program to read these ASCII text files on Matlab.[7.9] The ASCII text files are translated into Matlab language in order that the data can be processed.
Next the essential part of each 1D projection is extracted into a new file. The extraction is accomplished by using a program that displays the 1st and 31st, flipped about its center so as to be superimposable, simultaneously. Since the data was acquired at six degrees increments these two projections are separated by 180 degrees. In Figure 7–4, a sample of the two capillaries with water and water/heavy water is represented with three projections at different degrees of field gradient as examples of extracted data. The program clips each projection identically and stores all 31 in a new Matlab file. All 31 of the new projections are displayed during the process so that one can be sure nothing of value is being lost. Then they are processed using a filtered back-projection reconstruction algorithm program which makes a 2D image from the 31 one-dimensional projections. The contour maps of the 2D filtered back-projection of the five water filled capillaries and the L–shape of the original poly (methyl methacrylate) sample can be seen in Figure 7-5 and 7-6, respectively. The shapes of the water sample can be clearly observed.

7.4 Conclusion

In this demonstration the line shape reveals a dependency on the position and the amount of the H₂O within the sample. This demonstration is the same rather simple application used in many areas of non-medical NMR imaging, such as animal imaging, plant studies, and imaging of mobile liquids inside of solid porous materials. The entire imaging experiment takes only 3 hours to do.

This procedure has been shown to be reasonably accurate and easy to implement, improvements in resolution and time cost are readily attainable through pre-scan shimming and algorithm streamlining. Hopefully, this experiment is understandable to undergraduate students and would be an excellent way to familiarize them with NMR imaging and its relationship to NMR spectroscopy.
Figure 7-4  Projections of Figure 7-1(a) sample depend on X- and Y-shims vector; (a) a projection with gradient ($\theta = 0^\circ$) which pass through center of between two tubes, (b) a projection with gradient ($\theta = 52^\circ$) which deviate from center of between two tubes, (c) a projection with gradient ($\theta = 90^\circ$) which pass through one after another tube, and (d) a contour of 2D imaging of two capillary tubes with water in 5 mm NMR test tube.
Figure 7-5  Contour map of five tubes with water among 21 and the associated grayscale empty tubes are shown almost the same position of sample after demonstration.
Figure 7-6 Contour of L shaped hole in cylinder and the associated grayscale.
7.5 References


[7.8] LabView-version-2.0, National Instruments Corp., 6504 Bridge Point Parkway, Austin, TX 78730.

CHAPTER 8

CONCLUSIONS
The major interest of my research was the quadrupole interaction in the solid state which was used to characterize the structure of molecules and to image materials. The first part of this dissertation has discussed NQR spectroscopic techniques developed to obtain structural information on solids using two direct observation methods and two different line narrowing techniques. The second part of this dissertation has described novel NQR imaging techniques that use field cycling as a line narrowing technique for imaging $^{11}$B and $^{14}$N containing solids. Lastly, two-dimensional $^1$H imaging was demonstrated using a conventional solution-state NMR spectrometer.

Frequency swept and field swept NMR have been demonstrated to observe $^{93}$Nb sites of BaNb$_x$S$_3$ ($x = 0.8, 1.0$) in Chapter 2. The results from these two techniques show that field swept NMR is the more effective technique for BaNb$_x$S$_3$. At a sample temperature of 4.2 K, the $^{93}$Nb NMR spectra of BaNb$_x$S$_3$ yield an informative powder pattern and show that NbS$_3$$^{2-}$ has two different $^{93}$Nb sites with two different quadrupolar coupling constants. Most importantly, the relative population of the two sites has been measured for the first time.

A broadband nuclear quadrupole resonance (NQR) spectrometer, having automatic frequency selection and a novel automatically-tuned probe, has been developed to obtain $^{79}$Br and $^{81}$Br NQR spectra for flame retardants dispersed in polymers, as discussed in Chapter 3. The $^{79}$Br and $^{81}$Br NQR spectra of 1,3,5-tribromobenzene and 1,2,4,5-tetradibromobenzene were obtained at room temperature. At the very end of the time available for this project, the $^{81}$Br NQR scans were began with two flame retardants. Unfortunately, no transition frequencies were definitively observed during these runs. Some of the instrumental improvements underway at the end including conversion to more powerful rf amplifier and improvement of the probe tuning. The logic for this was based on anticipated problems
with short $T_2$ for these samples, and thus the need for a shorter spin echo pulse sequence. The $\text{^{81}Br}$ NQR spectroscopy of flame retardants and the polymer blends now appears to be promising.

A field cycling nuclear quadrupole resonance (NQR) spectrometer has been developed based on a Bruker MSL200, a high speed linear stepping motor, and an Oxford gas flow cryostat, as described in Chapter 4. The $^1\text{H}$ spin-lattice relaxation rate of toluic acid has been measured using the field cycling technique with a variable proton spin polarization field and variable sample temperature. The $^2\text{H}$ NQR spectrum of benzoic acid at 300 K and the $^{14}\text{N}$ spectrum of quinuclidine hydrochloride at ~60 K were obtained with the field cycling technique. Field cycling NQR has long offered useful advantages over pure NQR spectroscopy or high-field NMR for certain samples. This work demonstrated a novel method whereby a commercial solid-state NMR spectrometer can be adapted to field cycling NQR spectroscopy.

The recently developed technique of NQR imaging via field cycling has been used to image $^{11}\text{B}$ in a boric acid phantom and $^{14}\text{N}$ nuclei in a test sample of acetamide and salicylamide, respectively, as described in Chapter 5 and Chapter 6. The field cycling spectroscopy of quadrupolar nuclei offers several routes by which one-dimensional images can be obtained, especially since the design of the rf coil for selective saturation of a low frequency NQR transition is limited by relatively few constraints. An imaging plane can be defined either by a plane of large amplitude $B_1$ field or by a null in the $B_1$ field and one can operate in the saturation mode as compared with the linear response mode required for most NMR observations. This work does represent a very successful method for imaging other quadrupolar nuclei, i.e., $^2\text{H}$, $^{10}\text{B}$, $^{17}\text{O}$, and $^{27}\text{Al}$.

A two-dimensional $^1\text{H}$ imaging using an unmodified solution-state NMR spectrometer was demonstrated in Chapter 7. In this demonstration the line shape
reveals a dependency on the position and the amount of the $\text{H}_2\text{O}$ within the sample. This demonstration is the same rather simple application used in many areas of non-medical NMR imaging, such as animal imaging, plant studies, and imaging of mobile liquids inside of solid porous materials. This procedure has been shown to be reasonably accurate and easy to implement, improvements in resolution and time cost are readily attainable through pre-scan shimming and algorithm streamlining.
APPENDICES
APPENDIX A: LabView Programs for Controlling Field Cycling NQR Spectrometer in Chapter 4

LabView Version: 3.0.1

Main Program: Field cycling NQR spectrometer control

Sub Programs:
1. Motor initialization control
2. Motor control
3. MSL pulse control
Position in hierarch

Connector Pane

Field Cycling_NQR
Field cycling NQR spectrometer control

**Front Panel**

- **Saturation time, sec**: 30.00
- **Polarization time, sec**: 500.00
- **Irradiation time, sec**: 3.00
- **Amplitude (V)**: 0.0700
- **NUMBER OF SCAN**: 2
- **NUMBER OF EXPERIMENT**: 61
- **Expecting Transition Freq, MHz**: 1.0000
- **Field Current, A**: 4.4300
- **Initial Freq, MHz**: 0.110
- **Final Freq, MHz**: 0.140
- **Step Freq, Hz**: 500.00
- **Current Freq, Hz**: 1.50

**Block Diagram**

[Diagram of Block Diagram]
Field cycling NQR spectrometer control

Motor move to zero magnetic field to saturate all proton signal of sample

Turn on power supply to make zero magnetic field

Sample is staying in high magnetic field to polarize proton spin system for about proton T1 of sample

Delay time for motor motion

Delay time for motor motion

Delay time for motor motion
Field cycling NQR spectrometer control

- Move the sample to zero magnetic field
- Delay: Time to move sample to zero magnetic field
- Turn on Frequency Synthesizer to irradiate sample in zero field
- Turn off Frequency Synthesizer
- Motor move to zero magnetic field to saturate all proton signal of sample
- Motor move to high magnetic field to detect proton signal of sample
- Delay: Time to move sample to high magnetic field
- Turn off power supply
- Maximum integration

Diagram:

[Diagram showing the flow of operations with corresponding labels for each step]
Field cycling NQR spectrometer control

Page 6

- **Delay time for motor motion**: 1000

- **Motor move to high magnetic field to polarize proton signal of sample**

- **Sample is staging in high magnetic field to polarize proton spin system for about proton T1 of sample**

- **Turn on power supply to make zero magnetic field**

- **Move the sample to zero magnetic field**

- **Delay time to move sample to zero magnetic field**

- **Turn on Frequency Synthesizer to irradiate sample in zero field**

- **Turn off Frequency Synthesizer**

- **Motor move to high magnetic field to detect proton signal of sample**

- **Delay time to move sample to high magnetic field**
Delay time for motor motion

Motor move to high magnetic field
To polarize proton signal of sample

Sample is staying in high magnetic field
To polarize proton spin system
for about proton $T_1$ of sample

Turn on power supply to make zero magnetic field

Turn on Frequency Synthesizer to eradicate
Sample in zero field

Turn off Frequency Synthesizer

Motor move to high magnetic field
To detect proton signal of sample

Delay time to move sample to high magnetic field

Delay time to move sample to zero magnetic field

Delay time to move sample to zero magnetic field
Field cycling NQR spectrometer control
Connector Pane

Motor Initialization

Front Panel

error code
0

Block Diagram

Serial Port Initialization

Baud rate select
9600
Data bits select
8 bits
Stop bits select
1 stop bit
Parity select
None

PORT NUMBER
1024 Buffer size
Motor initialization control

1. Run Motor to find limit switch with slow speed.

Error code 100
Wait for 3 sec

Set Motor to Zero-position

Motor initialization control
Motor control

Connector Pane

Motor_Run

Front Panel

Motor motion, cm

error code

Block Diagram
Connector Pane

**MSL_Pulse**

Front Panel

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</thead>
<tbody>
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<td>0</td>
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</tbody>
</table>

Block Diagram

- Wait for 100 ms
- 100
MSL pulse control
Output Low TTL Voltage

LINE

100

??
Output High TTL Voltage

TTL
APPENDIX B: LabView Programs for Controlling NQR Imager in Chapter 5 and Chapter 6

LabView Version: 2.2

Main Program: Field cycling NQR imager control

Sub Programs:

1. Field cycling NQR imager_sub control
2. Pulse programmer control
3. Trigger pulse control
4. Set-pulseProgrammer-array-zero control
5. Pulse programmer-write control
6. Linear stepping motor control
7. Linear stepping motor_sub control
8. Transiac reset control
9. Transiac set-up control
10. Transiac read-out control
11. Sample move-to-high-magnetic-field control
12. Sample move-to-zero-magnetic-field control
13. Comstron frequency synthesizer control
14. TTL switch control
Field cycling NQR imager control

Front Panel

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<td>Pulse Power</td>
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</tr>
<tr>
<td>Tau SR (ms)</td>
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<tr>
<td>DW (Dwell, us)</td>
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<tr>
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<tr>
<td>NS (* of Scan)</td>
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<td>Abs/ln (12)</td>
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<td>Integral (Max)</td>
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<td>All Integals</td>
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Graphs:
- FID after Gaussian Multiplication
- Real & Imag FID
- Spectrum after FT, Baseline correction, and Magnitude calculation
- Integration vs. motor position with rf on
Create Initial Pulse Program

Data Array

Pulse Length (us)

Pulse Power

SI (* of Point)

TV (Dwell, us)

SR_Count

to_SRI (ms)

IC (* of Scan)
Field cycling NQR imager control

Block Diagram

- Determination of Minimum Integration
  - Acquiring Minimum FID using short relaxation time in high magnetic field and long relaxation time in zero magnetic field

- rf Freq, kHz
- Relaxation time in zero field, s
- Relaxation time in high field, s
- rf amplitude in zero field, V

No. of Cycle for Max & Min
No. of Total Ex.
Integral (Max) Integral (Min)
All Integrals

Integration v
Baseline Correction sequence

Fast Fourier Transformation and Magnitude Calculation

Gaussian Multiplication

Integration by adding intensity of 200 points at biggest peak

Average value = sum of 1/4 at the end of point of 1/4
BC_10 = slot_10 - average value for 10
BC_8 = slot_8 - average value for 8

Magnitude = sqrt(real/2 + imag/2)

Half-Width
Field cycling NQR imager control

Create Gaussian Multiplication Array
\[ \exp \left( \frac{-\pi L_B (t - t^*)^2}{2 GB^2 A_Q} \right) \]

Line Broadening (LB)
Gaussian Broadening (GB)
Aquisition time (AQ)

Determination of Maximum Integration
Acquiring Maximum FID using the same relaxation time in high magnetic field and in zero magnetic field as imaging experiment without RF irradiation in zero field
Baseline Correction sequence

Average value = Sum of 1/4 at the end/ # of point of 1/4
BC_10 = slot_10 - average value for 10
BC_8 = slot_8 - average value for 8

Fast Fourier Transformation and Magnitude Calculation

Magnitude = sqrt(real^2 + imag^2)

Gaussian Multiplication

Integration by adding intensity of 200 points at biggest peak

Half-Width
Field cycling NQR imager control

Baseline Correction sequence

Average value = Sum of 1/4 at the end of point of 1/4
BC_10 = slot-10 - average value for 10
BC_8 = slot-8 - average value for 8

Gaussian Multiplication

Real & Image FD

Fast Fourier Transformation and Magnitude Calculation

Magnitude = sqrt(real*2 + image^2)

spectrum after FT, Baseline correction, and Magnitude calculation
Integration by adding intensity of 200 points at biggest peak

Move stepping motor to next position

Steps to move for a data point:
- Load(13)/Execute(12)
- Direction(4)
- Rea/Instr(12)
Field cycling NQR imager_sub control

Front Panel

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</tr>
<tr>
<td>Image</td>
<td>643.00</td>
</tr>
</tbody>
</table>

Diagram showing the connections and parameters for the NQR imager sub.
Field cycling NQR imager_sub control

Block Diagram

[Diagram of a block diagram with labeled components: Set rf synthesizer, rf Freq, COM Freq, Exit, Num. of Scan, Num. of Point, Real, Image, Current Scan, Waiting, etc.}
Field cycling NQR imager_sub control

SR_Count*(Wait for Tau and 90x Pulse)

Saturation comb

Relaxation Delay, sec

StayHigh, sec

Transac: Reset for slot 8 & slot 10
Move sample to zero magnetic field

Transit time, 0.6 sec

Turn on rf synthesizer by turning on a gate switch

Channel = 0, 1, 2, 3

Switch On = 5 V

rf amplitude
Turn off MFL sensors by turning off a gate switch.
Field cycling NQR imager_sub control

Diagram Image

Reading FID

Sit to Num.

Trans Read

Image

Real Raw

Real

Trans

Image Raw

Num.
**Pulse programmer control**

**Connector Pane**

<table>
<thead>
<tr>
<th>Pulse-90 Length</th>
<th>Pulse Program = last state</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td></td>
</tr>
<tr>
<td>PP_90x90</td>
<td></td>
</tr>
</tbody>
</table>

**Front Panel**

<table>
<thead>
<tr>
<th>State</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Pulse length x 10</td>
</tr>
<tr>
<td>1</td>
<td>Start Trigger, 0.1 us</td>
</tr>
<tr>
<td>2</td>
<td>Delay, 2us, BLANKING-BAR ON</td>
</tr>
<tr>
<td>3</td>
<td>Tau_1 (Out 1), us, BLANKING-BAR ON</td>
</tr>
<tr>
<td>4</td>
<td>Tau_2, us</td>
</tr>
<tr>
<td>5</td>
<td>Digitizer Enable, 0.5 us</td>
</tr>
<tr>
<td>6</td>
<td>Short delay, 1us x wait</td>
</tr>
<tr>
<td>7</td>
<td>Pixel Level, 0.5 us</td>
</tr>
<tr>
<td>8</td>
<td>Write down pulse</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pulse-90 Length</th>
<th>Pulse Program = last state</th>
<th>Power rf level</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP_90x90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP_90x90</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Explanation**

1. Pulse length = Pulse length x 10
2. Start Trigger = 0.1 us
3. Delay = 2us, BLANKING-BAR ON
4. Tau_1 (Out 1) = us, BLANKING-BAR ON
5. Tau_2 = us
6. Digitizer Enable = 0.5 us
7. Short delay = 1us x wait
8. Pixel Level = 0.5 us
9. Write down pulse
Create initial PP data array

<table>
<thead>
<tr>
<th>Bit</th>
<th>Function</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>RF - rf level</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>RF - *</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>RF - 4</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>90 deg phase shift</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>180 deg phase shift</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Pulse ON</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>Digitizer Enable</td>
<td>128</td>
</tr>
<tr>
<td>8</td>
<td>Some Trigger</td>
<td>256</td>
</tr>
<tr>
<td>9</td>
<td>Spin lock start</td>
<td>512</td>
</tr>
<tr>
<td>10</td>
<td>Digitizer Clock (Trigger)</td>
<td>1024</td>
</tr>
<tr>
<td>11</td>
<td>Halt</td>
<td>2048</td>
</tr>
</tbody>
</table>
Pulse programmer control
Prepare for write to pulse programmer

List of Pulse Programmer NIF commands

1. (1), (1), DH-0, DM-0, DL-0 will
   reset PP address counter to zero
2. (1), (1), DH-0, DM-0, DL-0 will
   set PP for CMRC mode, ready for
   reading or writing to CMRC bus.
3. (1), (1), DH-0, DM-data, DL-data
   uses 0-stop mode for writing data
   to PP.
4. (1), (1), DH-0, DM-data, DL-data
   uses 0-stop mode for reading data
   from PP with auto-increment on.

Note: Always reset PP address counter to
zero when finished reading or writing.
Set PP to DDRMC mode

From pin of 3006 manual:
Start sending the 16 bits of PP array.
Linear stepping motor control

Connector Pane

Front Panel

Block Diagram
Linear stepping motor control

Limit reached

Step Motor

Limit checker

if/then

Limit reached

if/then

if/then
Linear stepping motor_sub control

Connector Pane

**StepMotor_AU**

Front Panel

<table>
<thead>
<tr>
<th>Absolute Position (requested)</th>
<th>high</th>
<th>middle</th>
<th>low</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
middle byte on A: 1

position

DDCODaDCDCOUCOCd' 1  ' .^KlDaiPjOailPialOlipiqiClplpilDiD;!
Transiac Reset control

Connector Pane

TransReset

Transiac_Reset

Front Panel

Block Diagram
Transiac Set-up control

Connector Pane

Sweeps

record length

pre-trig

Digitizer

Transiac Setup_Update

Front Panel

record length

64 -
128 -
256 -
512 -
1k -
2k -
4k -
8k -

Data FORMAT
Signed

pre-trig

Digitizer

Sweeps

clock

Enter
5 -
2 -
100ns -
200 -
100 -
50ns -

Clock Pre-trig:
0 -
7/8 -
6/8 -
5/8 -
4/8 -
3/8 -
2/8 -
1/8 -
0 -

Sweeps

0-8

6000 -
4000 -
2000 -
0 -
Transiac Read-out control

Connector Pane

Trans Read

Digitizer

Trans output

Front Panel

SI (# of points)

64

128

256

512

1K

2K

4K

8K

Digitizer

Slot 10

Slot 8

FID after digitizing
Sample move-to-high-magnetic-field control

Connector Pane

Front Panel

Block Diagram

Sample move-to-zero-magnetic-field control

Connector Pane

Front Panel

Block Diagram
Comtron frequecy synthesizer control

Connector Pane

Block Diagram
Comtron frequency synthesizer control
TTL switch control

Connector Pane

Front Panel

Block Diagram
APPENDIX C: Matlab Programs for Calculations of Magnetic Field and Transition Possibilities of $^{14}$N with Variable Coil Geometries

Matlab Version: 4.1

C.1 Two collinear, oppositely wound solenoidal rf coils geometry

% Calculation of magnetic field produced by opposing coil geometry
% Calculation of transition probabilities of N14 with opposing coil geometry
% May 1, 1993

clear;clc;clf;echo off;hold off

% Primary parameters
a = 0.00011; % (intercoil spacing)/2, meter
b = 0.0004;  % thickness of coil, meter
X = a*(-177:2:177); % Coil Spacing array
Y = b*(-90 : -2);  % winding direction of coils
Z = b*(2 : 90);   % winding direction of coils
V = [Y Z];
A = X + V;
U = 4*pi*10^(-7); % Tesla meter amp-1
I = 30;           % ampere_pp
R = 0.0096;       % meter
T_1d = 5;         % seconds

% Calculation of magnetic field with infinitely long coils
B_infinite = U*I/((2*a)+b)

constant = T_1d/B_infinite

% Calculation of magnetic field with produced by opposing coil geometry
B_center = 0;
for k = 1:length(A);
    r = sqrt(R^2 + A(k)^2);
\[ B_{\text{center}} = B_{\text{center}} + \left( \frac{I \cdot U}{2} \right) \frac{(R^2)}{(r^3)}; \]

end;

\[ B_{\text{center}} \]

\[ z_{\text{axis}} = (a+(b/2)) \cdot \text{linspace}(-200,200,400); \]
\[ B_{\text{axis}} = \text{zeros}(1, \text{length}(z_{\text{axis}})); \]
for \( m = 1: \text{length}(z_{\text{axis}}); \)
for \( k = 1: \text{length}(A) \)
    \[ L = A(k) + z_{\text{axis}}(m); \]
    \[ r = \sqrt{R^2 + L^2}; \]
    \[ B_{\text{axis}}(m) = B_{\text{axis}}(m) + \text{sign}(A(k)) \cdot \left( \frac{I \cdot U}{2} \right) \frac{(R^2)}{(r^3)}; \]
end;
end;

\% Calculation of transition probabilities of N14 with opposing coil geometry
\[ \text{Mag} = \text{zeros}(10, \text{length}(z_{\text{axis}})); \]
for \( n = 2:2:20; \)
    \[ \text{Mag}(n,:) = 100 \cdot \exp((-1) \cdot n \cdot \text{constant} \cdot B_{\text{axis}}^2); \]
end;

subplot(211);
plot(z_{\text{axis}}, \text{abs}(B_{\text{axis}}), '\-'); \text{hold off};
xlabel('position, meter');
ylabel('magnetic field, Tesla');

subplot(212);
for \( q = 20:-2:2; \)
    plot(z_{\text{axis}}, \text{Mag}(q,:), '\-'); \text{hold on};
end;

x.xlabel('position, meter');
ylabel('magnetization, percent');
title('Magnetization effected by opposing coil')
C.2 Second derivative rf coil geometry

% Calculation of magnetic field produced by second derivative coil geometry
% Feb. 23, 1994

clear;clc;clf;echo on;hold off;

% Primary parameters
a = 0.00011;
b = 0.0004;
A = (a+(b/2))^[-3 -1 1 3];
U = 4*pi*10^(-7);
I = 0.594;
R = 0.0096;

% Calculation of magnetic field with produced by second derivative coil geometry
z_axis = (a+(b/2))*linspace(-200,200,400);
B_axis = zeros(1, length(z_axis));
for m = 1:length(z_axis);
    L = A(1) + z_axis(m);
    r = sqrt(R^2 + L^2);
    B_axis1(m) = B_axis(m) - (I*U/2)*(R^2)/(r^3);
end;

for m = 1:length(z_axis);
    L = A(2) + z_axis(m);
    r = sqrt(R^2 + L^2);
    B_axis2(m) = B_axis(m) + (I*U/2)*(R^2)/(r^3);
end;

for m = 1:length(z_axis);
    L = A(3) + z_axis(m);
    r = sqrt(R^2 + L^2);
    B_axis3(m) = B_axis(m) + (I*U/2)*(R^2)/(r^3);
end;

for m = 1:length(z_axis);
    L = A(4) + z_axis(m);
\[ r = \sqrt{R^2 + L^2}; \]
\[ B_{\text{axis}4}(m) = B_{\text{axis}}(m) + (-1)(I*U/2)*(R^2)/(r^3); \]
end;

\[ B_{\text{axis}} = B_{\text{axis}1} + B_{\text{axis}2} + B_{\text{axis}3} + B_{\text{axis}4}; \]

\[ z_{\text{axis}} = z_{\text{axis}}*100; \]
subplot(212);
plot(z_axis, abs(B_axis), 'r'); hold off;
xlabel('Position/cm');
ylabel('magnetic field, Tesla');
C.3 Small rf coil geometry

% Calculation of magnetic field produced by small coil geometry
% Jan 9, 1994

clc;clear;clf;echo on;hold off;

% Primary parameters
a = 0.00011; % (intercoil spacing)/2, meter
b = 0.0004;  % thickness of coil, meter
A = (a+(b/2))*[1:2:5]; % Coil spacing and winding direction
U = 4*pi*10^(-7);    % Tesla meter amp-1
I = 0.594;          % 0.294 amp_pp
R = 0.0096;         % meter
T_id = 50           % seconds

% Calculation of magnetic field with produced by second derivative coil geometry
z_axis = (a+(b/2))*linspace(-200,200,400);
B_axis = zeros(1, length(z_axis));
for m = 1:length(z_axis);
    for k = 1:length(A)
        L = A(k) + z_axis(m);
        r = sqrt(R^2 + L^2);
        B_axis(m) = B_axis(m) + sign(A(k))*(I*U/2)*(R^2)/(r^3);
    end;
end;

subplot(212);
plot(z_axis, abs(B_axis), '-', hold off;
xlabel('position, meter');
ylabel('magnetic field, Tesla');
APPENDIX D: Letters of Permission

D.1 A letter from the publisher granting permission for Chapter 5

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Thank you for your recent letter in which you request permission to reproduce the following article in your doctoral thesis.

Re: 11B Imaging with field-cycling NMR as a line narrowing technique by Y. Lee in Chemical Physics Letters 1993, 206, 464-466

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Amsterdam Publishing Division

Jan van den Heuvel
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D.2 A letter from the publisher granting permission for Chapter 6

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Office of Rights and Permissions
Journal Division, Academic Press, Inc.
525 B St., Suite 1900
San Diego, California 92101-4495
Tel: 619-699-6415
Fax: 619-699-6801

October 3, 1994

Dear Editorial Supervisor:

I am writing you in reference to the article "Field Cycling $^{14}\text{N}$ NQR Imaging with Spatial and Frequency Resolution" accepted in Journal of Magnetic Resonance (Manuscript Number 94183). I am the first author of this manuscript and I would like to use a reprint in my Ph.D dissertation.

Please, forward permission to reprint the manuscript. I will appreciate your prompt reply.

Sincerely

Youngil Lee
Box F-6, Choppin Hall
Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803
Tel: 504-388-3621
October 31, 1994

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Permissions Department
ACADEMIC PRESS, INC.
Orlando, FL 32887
VITA

Youngil Lee was born in Seoul, Korea on March 1, 1967. He graduated from Bae-Moon High School in February, 1985. He studied chemistry at Hanyang University, where he received a B.S. degree in February, 1989. He began his Ph.D. studies at Louisiana State University in August, 1989. He then began research in the development of nuclear quadrupole resonance spectroscopic and imaging methods with Professor Leslie G. Butler and received his degree of Doctor of Philosophy in December, 1994.

His research is concentrated in the quadrupole interaction in the solid state which was used to characterize the structure of molecules and to image materials. He has developed three solid-state NQR spectroscopic techniques and two NQR imaging methods. He has two publications:


After graduation Youngil Lee will return to Korea to be near his family and to pursue a career in industrial chemistry.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Youngil Lee

Major Field: Chemistry

Title of Dissertation: Development of Nuclear Quadrupole Resonance Spectroscopic and Imaging Methods

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: 10/31/94