O$^{17}$ Spin-lattice Relaxation
Solid State NMR Studies
of pure and doped Ices:

A Dissertation

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

by

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* * * * *

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ABSTRACT

Through a network of $\mathcal{H}$-bonds water forms a liquid that is essential to life and the environment. This formation is not fully understood or characterized. As a result, an extensive body of experimental and theoretical research has been devoted to water. In turn, ice should be an easier system than water to understand because the molecules are arranged in a rigid periodic lattice; however, this is not the case. Normal ice that we are familiar with has 13 crystalline phases all observed at different temperatures and pressures. Ice crystal structures are found to have periodic molecules, therefore, it is very interesting for there to exist a disorder in their orientations. A tremendous amount of progress has been made in understanding the physical properties of ice, but there is work yet to be carried out. Our experiments show a larger variation exists between Ice-Ih, KOH doped, and HCl doped ices. In typical laboratory samples of Ice-Ih, KOH doped or HCl doped ice there exists a detectable amount of rotational motion that is seen vividly in the NMR spectra. Also, comparative studies on pure and doped ices shows the process governing $O^{17}$ relaxation is a single proton motion.

Oxygen-17 is potentially a very effective tool for obtaining information into these systems. This is because the coupling constant for oxygen should be very sensitive
to changes in p-electron density, so that hydrogen bonding involving the lone pair electrons should be reflected in large changes in the coupling constant and analogous to the oxygen-17 spin-lattice relaxation times. By monitoring $\mathcal{O}^{17}$ as a function of temperature and dopant concentration valuable information about how the impurities affect proton rearrangements and activation energies obtained. These will give valuable information about the nature of these various defect motions in the doped ice systems.
DEDICATION

Alicia.
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INITIAL REMARKS

The rare genius with a flair for research will not benefit from instruction in the methods of research. However, most would-be researchers are not geniuses and should not rely on the wasteful methods of personal experience to enhance their productivity. Most would-be researchers require guidance in the art of research methodologies in order to help them become productive at an earlier stage in their careers.
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CHAPTER 1

Introduction

*No way of thinking, however ancient, can be trusted without proof.*

_Henry David Thoreau_

1.1 Introduction

The water molecule is the building block for ice and is one of the simplest molecules in chemistry. Using a network of $\mathcal{H}$-bonds, water forms a liquid essential to life and the environment. This formation is not fully understood or characterized. This lack of understanding results in an extensive body of experimental and theoretical research devoted to water.

Ice molecules are arranged in a rigid periodic lattice. This arrangement should allow ice to be an easier system to understand. This, however is not the case. Ice has 13 crystalline phases all observed at different temperatures and pressures[8]. A tremendous amount of progress has been made in understanding the physical properties of ice. This dissertation first gives an overview of normal ice-Ih and KOH and
HCl doped ices. Later sections will focus on the NMR techniques and semi-empirical calculations used to obtain more insight into the structure of ice-Ih.

1.2 Ice-Ih

All naturally\(^1\) occurring ice on earth is hexagonal ice, denoted ice-Ih (Fig. 1.1)[9]. Many other ice phases with unique crystalline structures exist at lower temperatures along with pressures exceeding 2 kbar (2000 atm). These other forms will not be discussed further.

The phase diagram of ice displays the conditions for which stable ice phases are formed (Fig 1.2). The lines of equilibrium between water and ice-Ih slope negatively. This indicates that the solid possesses a lower density than the liquid. The equilibrium lines extend as meta-stable phase boundaries into the area of stability of other ice phases.

The individual water molecule remains intact as the fundamental building unit in all the ice phases except ice X[9]. Since there are equal numbers of protons and lone electron pairs in the water molecule, each proton can match up with an electron pair of a neighboring molecule to form a hydrogen bond (\(\mathcal{H}\)-bond). Each water molecule forms \(\mathcal{H}\)-bonds to four nearest neighbors in a tetrahedral arrangement with one proton occupying each \(\mathcal{H}\)-bond[23] (Fig 1.3).

The tetrahedral bond geometry explains the openness and relatively low density of the ice Ih structure. The \(O\ldots O\ldots O\) angles are nearly identical to the perfect

\(^1\)This assumes STP
Figure 1.1: Ice-Ih with crystal c-axis $\parallel$ to plane of page. Open circles are oxygen atoms and closed smaller ones hydrogens. The large open circles outline the smallest unit cell[8].

tetrahedral angle (109.5°). The $H\leftrightarrow O\leftrightarrow H$ angle of the water molecule exhibits little change from the angle in the free molecule (104.4°)[8]. In the higher-pressure phases the tetrahedral bonding geometry is distorted. The $O\ldots O\ldots O$ bond angles are bent from perfect tetrahedral and the $H$-bonds are stretched. As the pressure increases the distances to non-bonded near neighbors becomes shorter. Further, $H$-bonded rings are a general feature repeated in all of the ice structures.
Figure 1.2: Ice Phase diagram showing the various phases of ice[8].

There are six different orientations possible for a water molecule in its tetrahedral bonding environment, each corresponding to a different arrangement of protons in its four H-bonds. The phase of ice becomes proton disordered if the water molecules at each lattice site samples all of its potential orientations. The phase becomes proton ordered if the molecule at each lattice site chooses a single preferred orientation. This leads to most ice phases have high and low temperature modifications, which are
Figure 1.3: Tetrahedral coordinated water molecule with hydrogen bonds denoted with dotted lines and covalent bonds denoted with solid lines. Covalent hydrogen oxygen bond \( \sim 1.0 \) \( \text{Å} \) and hydrogen bond length \( \sim 1.8 \) \( \text{Å} \).

distinguished by their degree of proton order. In most cases the existence of proton order or proton disorder affects the crystallographic symmetry of the ice phase.

Many of the physical properties of ice are unique and relate to the special features of structure, especially the \( \mathcal{H} \)-bonding. Certain physical properties arise from defects in the ideal ice structure. Three important point defects are \( \mathcal{H}_3\text{O}^+ \) ion, \( \text{OH}^- \) ion, and \( \mathcal{D} \) and \( \mathcal{L} \) bond defect sites \cite{18}\. The \( \mathcal{D} \) and \( \mathcal{L} \) bond defect sites are places where \( \mathcal{H} \)-bonds are broken by violation of the ice rule \cite{23} that there may only be one proton

\footnote{These are called Bjerrum Defects}
along each $\cdots\cdots$ bond line. The violation is caused when a water molecule undergoes rotation from one of its six possible orientations to another and the adjacent molecule to which it is hydrogen bonded fails to compensate by adjusting. Such a rotation interchanges some of the molecule's protons and electron pairs. The result is, some of the $\mathcal{H}$-bonds are converted to non-bonded $\cdots\cdots$ contacts with no protons ($\mathcal{L}$ defect) or with two associated protons ($\mathcal{D}$ defect). Also important are crystal dislocations (line defects) and sub-grain or grain boundaries (surface defects), the latter in polycrystalline ice. The ions and orientation defects, together with substitution or interstitial impurity atoms or ions, have important influence on the electrical and mechanical properties of ice and in some cases completely dominate them.

The electrical conduction in ice is carried by the protons, whose motion is closely tied to the motion of ionic defects[8]. Ionic defect can move from one lattice site to the next by a small jump of a proton from one off-center (asymmetric) position to the other. The formed $\mathcal{H}$-bond then connects the two lattice sites. Since, the small proton jumps occur collectively along a favorably oriented chain of $\mathcal{H}$-bonds, the ionic defects and the effective charge carried by them have a very high mobility in the ice structure.

The surface of ice Ih shows unique properties. Near the melting point, the surface contains many dangling broken bonds that promote the existence of a liquid-like layer[9]. Consequences of the surface properties are: sintering of snow to cohesive snowballs; re-crystallization of snow to form and its transformation to glacier ice; and
the low friction of many materials on ice, which is useful for sled riding, skiing, and skating.

1.3 Doped Ices

The proton disorder in ice has led many researchers to explore the possibility of incorporating various impurities into the ice lattice in an attempt to catalyze a proton ordered material. Impurity atoms in doped ices are located at interstitial or substitutional sites. It is well understood that even though the solubility of many materials in water is very high, the solubility of the same materials in ice is much less. Generally when water is frozen with impurities a substantial amount of the impurity is expelled. The impurities left behind are incorporated as inclusions of concentrated solution as well as impurity-solid-solution in the ice[9, 8]. Often impurities are found trapped in grain boundaries. Several impurities are incorporated in substantial amounts - HF, HCl, and KOH just to name a few. Our studies use HCl and KOH as dopants.

KOH and HCl doped ice samples have gained substantial interest since the observation of proton-ordered ice-Ih by Suga and co-workers [22], termed ice-XI (Fig 1.4). The incorporation of the hydroxide or hydronium ions are assumed to promote substantial proton rearrangements so to catalyze the formation of proton-ordered ice. The HCl molecule enters the ice lattice intact (Fig. 1.5) and introduces Bjerrum L/D defects[18] (Fig. 1.6). In HCl doped ice L-defects are primary formed[19].
Figure 1.4: Proposed structure of Ice-\(X\) with crystal c-axis \(\parallel\) to page[12, 30].

\[
H_2O + HCl \longrightarrow H_3O^+ + Cl^-
\]

Figure 1.5: HCl incorporated into ice lattice.
Figure 1.6: Bjerrum defects[8].

For KOH doped ices, the impurity separates into its substrates, K$^+$ and OH$^-$, (Fig. 1.7). The hydroxide ion promotes mainly OH$^-$ and D-defects. The potassium however, incorporates into the oxygen framework and is more or less inert[8].

1.3.1 KOH Doped Ices

When ice is doped with KOH a phase transition from proton - disordered ice-Ih to proton - ordered ice-\( \alpha \)I occurs at 72K[32]. The phase transition is observed in and is exclusive to alkali hydroxides doped ices. KOH is the most widely used dopant for such experiments. The doping with KOH introduces OH$^-$ ions that remain sufficiently mobile down to 72 K. The phase transition was first observed by Kawada in 1972[32]. Kawada observed evidence of a latent heat as the doped ice was warmed
Figure 1.7: KOH incorporated into Ice lattice.

through this temperature. In 1984 Tajima et. al.[31] using calorimetric experiments directly observed a peak at 72 K that represented the latent heat of disordering of the protons (Fig. 1.19). The change in entropy associated with the phase transition depends greatly on the time and temperature of the annealing below the transition temperature. In most experiments the entropy change has not exceeded 83\%[33] of the Pauling entropy of ice-Ih[23].

Like most impurities KOH has a low solubility in ice. However, the dielectric relaxation is greatly enhanced in KOH doped ice. When KOH doped ice is frozen from a concentrated solution inclusions of concentrated KOH solution (Ice pure, Solid-KOH-ice-solution and KOH-H$_2$O) form[8]. The KOH-H$_2$O[34] eutectic freezes at 210K.
Figure 1.8: Calorimetric experiment showing evidence of phase transition from ice-IIh to ice-\(\alpha\)I[31].

When compared with other dopants KOH responds the same at temperatures above 200 K. Between 200 K and 110 K[36, 35], however the relaxation is temperature independent and increases slowly at lower temperatures. This fast Debye relaxation is due to the presence of OH\(^-\) and \(\mathcal{L}\)-defects formed[35]. The relaxation remains fast enough at lower temperatures (72 K) to facilitate proton ordering to ice-\(\alpha\)I[35]. There exist two types of Debye relaxation below \(\sim 210\) K for KOH-doped ice. One relaxation is caused by \(\mathcal{L}\)-defects facilitating molecular rotations whereas the other by the relaxation of dipoles by OH\(^-\) following proton shifts on the hydrogen bond [35].

When KOH-doped ices are annealed in successive periods of a few hours at 263 K the Debye relaxation splits into two components with very different relaxation times[35]. After an annealing period of 20 hours the entire relaxation occurs at a
very slow rate. At low temperatures the rate is not fast enough to facilitate molecular rearrangements, and the phase transition to ice-$\alpha$ does not occur.

1.3.2 HCl Doped Ices

Shown in figure 1.9 is the phase diagram for the HCl - water system. HCl has a solubility at 263 K of $3 \times 10^{-6}$ mole fraction [37]. HCl in ice produces $\mathcal{L}$-defects which and responsible for the observed Debye relaxation[35]. Proton ordering depends on randomly reoriented bonds. These reorientation’s are due rotations or by Bjerrum defect motions. This is similar the process of motions in dielectric relaxation experiments. As mentioned previously the Debye relaxation time $\tau_D$ is $\sim 5 \times 10^{-5}$ s at -10 °C[8] in pure ice. However, in HCl doped ices the dielectric relaxation is reduced by a factor of 10[38] from pure ice. This decrease in the Debye relaxation is evidence of HCl’s inability to promote enough proton rearrangement to proton order ice.
Figure 1.9: H$_2$O and HCl phase diagram[37]
CHAPTER 2

The Humble Beginnings

There is nothing like desire from preventing the thing one says from bearing any resemblance to what one has in mind.

Marcel Proust

This chapter gives a brief overview of some of the salient aspects of Nuclear Magnetic Resonance (NMR), its application towards the study of ice and the information it provides.

2.1 Historical Overview

In 1902, the physicist Zeeman shared the Nobel prize for discovering that certain nuclei behaved strangely when in the presence of a strong external magnetic field. Fifty years later NMR was first shown in condensed matter physics by F. Bloch and E. Purcell[42, 43]. For this they shared the Nobel Prize in 1952. They successfully put the Nuclear Zeeman Effect to practice by using the first crude NMR spectrometer.
Since then NMR has completely revolutionized the study of chemistry, biology, biochemistry and physics. Using NMR allows molecular structures to be determined with ease. NMR has consequently become the most widely used technique for Chemist, Biochemist and Physicist.

2.2 Magnetic Properties of Nuclei

In developing the fundamental theory of (NMR) it is necessary to consider some of the magnetic properties of nuclei. These properties are best discussed in terms of the nuclear spin \( I \) and the angular momentum of the particles in question.

Many nuclei act much like charged spinning bodies, resulting in spin and a magnetic moment along their axis of rotation. This is found in about a third of the atoms in the periodical chart. Since the magnetic moment \( \mu \) and the angular momentum behave as parallel vectors, the magnetic properties of a nucleus can be specified in terms of the ratio \( \frac{\mu}{I} \). This ratio is further designated by \( \gamma \), the magnetogyric ratio[5, 41]. The magnetic moment \( \mu \) is also expressed in units of Bohr magneton:

\[
\mu \approx \frac{e\hbar}{2mc}. \tag{2.1}
\]

The above equation corresponds to the magnetic moment that is ascribed to a proton \((I=\frac{1}{2})\) if it were treated as a spinning sphere with all its charge uniformly distributed over the sphere and all of its mass equally distributed throughout the sphere. Due
to over simplification, this model yields only an order of magnitude for various nuclear magnetic moments. The most general expression for the magnetic moment of a nucleus of spin \( I \) is expressed in terms of the nuclear magneton by the equation[6],

\[
\mu = g \frac{e}{2mc} (I).
\]  

(2.2)

where \( g \) is a phenomenological parameter measured by experiment.

### 2.3 Spinning Nuclei under the influence of a Magnetic field

If a spinning nucleus with spin \( I \) and magnetic moment \( \mu \) is placed in a uniform magnetic field \( \mathcal{H}_0 \), it will experience a torque. The nuclear magnetic moment will then precess in a manner analogous to the precession of a spinning top (Fig. 2.1). The frequency of precession, \( \omega_0 \), commonly known as the Larmor Frequency, is given by,

\[
\omega_0 = \gamma \mathcal{H}_0.
\]  

(2.3)

The Larmor Frequency is such that a projection of the angular momentum on the direction of \( \mathcal{H}_0 \) always assumes multiples of \( \hbar \). However, not all possible precession “cones” occur, only some selected ones[7]. The number of these “alignments” that are possible for a nucleus of spin \( I \) is \( 2I+1 \). Meaning that the magnitude of the magnetic moment of any nucleus with \( I=\frac{1}{2} \), for example, in any direction has two equal yet opposite observable values. When a nucleus of \( I=\frac{1}{2} \) is placed into a uniform magnetic

\( ^1 \)The magnetic field in the \( z \) direction is typically referred as \( \mathcal{H}_0 \). This designation is used throughout this dissertation.
field ($\mathcal{H}_0$), it will align with the field ($m_I=\frac{1}{2}$) or against it ($m_I=-\frac{1}{2}$). The former energy state representing the more energetically favorable alignment. The energy splitting is referred to as a Nuclear Zeeman Splitting (Fig. 2.2). The energy of each magnetic state is given by,

$$E = -\frac{\mu}{I}\mathcal{H}_0 m_I,$$  

(2.4)

here, $m_I$, the magnetic quantum number, has possible values of $I$, $I-1$, $I-2$, $\ldots$, $-I$.

### 2.4 The NMR experiment

The basis of the NMR experiment is to induce transitions between the Nuclear Zeeman levels (Fig 2.2). This is achieved with an alternating field, $\mathcal{H}_1$, in such a fashion that its frequency can be altered[6, 41]. When the frequency of $\mathcal{H}_1$ is identical to the Larmor frequency $\omega_0$ of the nucleus under observation, an absorption
of energy becomes possible and a transition from one energy level to another occurs.

In accordance with the quantum mechanic based selection rules, only those transitions
are allowed where $\Delta m_f = \pm 1$; further limiting the number of observable transitions for
a particular nucleus. For an $I = \frac{1}{2}$ nucleus (such as a proton) the energy difference
between the two nuclear spin states is expressed by

$$\Delta E = \frac{\mu}{I} \mathcal{H}_0 \Delta m_f = \hbar \nu = \gamma \hbar \mathcal{H}_0. \quad (2.5)$$

$\Delta m_f$ is limited by the selection rules mentioned above. The classical Bohr equation
can be readily used to calculate the frequency at which absorption occurs

$$\hbar \nu = - \frac{\mu \mathcal{H}_0}{I}, \quad (2.6)$$

which, when modified to include the magnetogyric ration, $\gamma$, becomes
Until now, the focus has been on the behavior of isolated nuclei in a magnetic field. Any real experiment involves a large number of nuclei, bringing to question the populations of various energy levels when the sample is placed into a magnetic field. At ordinary temperatures and at easily attainable magnetic fields, the equilibrium populations of different nuclei in the different possible spin states are nearly equal. This occurs because the energy difference between the various levels are small compared to kT. The tiny population excess that exist can be calculated from the Boltzmann factor, $\exp \frac{2\mu H_0}{kT}$.[5]. Since the energy levels for different nuclei are separated by $\frac{\mu H_0}{kT}$, the probability that a nucleus will inhabit an energy level of eigenstate $m$ is:
\[
\frac{1}{2I + 1} (1 - \frac{\mu_0}{I k T}).
\] (2.8)

2.4.1 Detection of the NMR Signal

The detection of the NMR signal is based on Faraday’s law. A magnetic top in a magnetic field will precess about the field direction with a characteristic frequency \(\omega_0\). This frequency is determined by its gyromagnetic ratio and \(\mu_0\). Faraday’s law is utilized in the following manner. When a coil or radius \(r\) and resistance \(R\) is placed around the spinning magnetic top (Fig. 2.4) Faraday’s law shows that the Electromotive Force (EMF) induced in the coil will produce a change in magnetic flux with time[7, 40]. This is expressed in the following manner

\[
EMF = -\frac{d\Phi}{dt}.
\] (2.9)

In the example presented above the magnetic field will be time dependent and represented mathematically as

\[
\vec{B}_t(t) = B_t^0 (\cos \psi \hat{z} + \sin \psi \sin (\omega_0 t + \phi) \hat{y} + \sin \psi \cos (\omega_0 t + \phi) \hat{x}).
\] (2.10)

The magnetic flux at any point in time is further represented as

\[
\Phi(t) = \int \vec{B}_t(t) \cdot d\vec{a}.
\] (2.11)

Setting \(d\vec{a}\) equal to \(r dr \theta \hat{x}\) leaves us with the following expression
Figure 2.4: Faraday detector with sample (a) before r.f. irradiation-no emf and (b) after r.f. applied, transverse magnetization produces emf.

\[ \Phi(t) = B_0^2 \pi r^2 \sin \psi \sin (\omega_0 t + \phi) \] \hspace{1cm} (2.12)

Lastly the EMF produced will oscillate at the precession frequency.

\[ E = \omega_0 B_0^2 \pi r^2 \sin \psi \cos (\omega_0 t + \phi) \] \hspace{1cm} (2.13)

Equation 2.13 shows that the signal intensity is proportional to \( \sin \psi \), hence the closer the magnetization is to the \( \vec{z} \) axis, the smaller the signal. Since \( \omega_0 \) is proportional \( \mathcal{H}_0 \) the signal intensity will increase with increasing external magnetic fields. This is one attractive attribute of high field NMR experiments.
The previous example presents a case for a single magnetic nuclei - this is not an accurate representation of a real sample. A real sample is comprised of \(10^{16}-10^{23}\) nuclear spins in thermal equilibrium. When subjected to an external magnetic field the nuclei as in the previous example will feel a torque and precession will result. In this case there will be a net magnet polarization along the magnetic field direction. The magnetic polarization follows Boltzman’s statistics resulting in more spin pointing up than down. This leads to a non-zero vector sum along the +z axis (or, if you change the sign of the gyromagnetic ratio, the -z axis). To obtain a signal from this sample a transverse magnetization (\(\mathcal{H}_{rf}(t)\)) is applied. This is done to rotate the bulk magnetization into the x-y plane. This is when the Faraday detector is valuable. By adjusting the amplitude and time of \(\mathcal{H}_{rf}(t)\) the angle through which our magnetization rotates from \(\mathcal{H}_z\) is controlled.

Figure 2.4 illustrates the above mentioned process. The net magnetization vector begins along \(\mathcal{H}_z\). After the application of \(\mathcal{H}_{rf}(t)\) the magnetization is rotated towards the x-y plane. Now the net magnetization will precess about an effective magnetic field, \(\mathcal{B}_{eff}\). By varying the \(\mathcal{H}_{rf}(t)\) between +x and -x successive \(\mathcal{B}_{eff}\) fields are produced, along with larger and larger cones of precession until the bulk magnetization is in the x-y plane. In the end this produces a detectable voltage and is called magnetic resonance.
2.5 Relaxation Phenomena

Once the alternating magnetic field, $\mathcal{H}_{r,t}(t)$, is turned off the bulk magnetization returns to equilibrium. This process towards equilibrium randomizes the direction of the individual spins resulting in the magnetization returning to the z-axis. The time constants for this process are briefly described below.

2.5.1 Spin-Lattice Relaxation, $T_1$

The restoring of magnetization back to its equilibrium state is commonly referred to as spin-lattice relaxation. This happens as a result of the interactions of the magnetic moments of nuclei with randomly fluctuating magnetic fields, which are the results of thermal motions of the nuclei in the molecule[3]. The thermal distribution is restored when a component of the fluctuating field precesses at the Larmor frequency of a given value of the polarizing field and induces a transition among the energy levels.

The rate of approach to equilibrium is proportional to the departure from equilibrium. The time factor used in defining this statement mathematically is referred to as the spin-lattice relaxation time $T_1$, and is written as

$$T_1 = \frac{1}{2\mathcal{W}}.$$  \hspace{1cm} (2.14)

In this equation $\mathcal{W}$ is the mean of $\mathcal{W}_+$ and $\mathcal{W}_-$. Which are defined as, respectively, the probabilities of an upward and a downward transition. This relaxation is related to the population of nuclei $n$ in different spin states by
**Figure 2.5:** Vector picture of spin-lattice relaxation: a) Equilibrium magnetization, b) Rotation of equilibrium by 180°, and c) The restoring of the magnetization to equilibrium.

\[
\frac{dn}{dt} = -2\mathcal{W}(n - n_{eq})
\]  \hspace{1cm} (2.15)

and can be expressed as the difference between the excess population and its equilibrium values \((n - n_{eq})\):

\[
n - n_{eq} = (n - n_{eq})_0 \exp \left( -\frac{t}{T} \right)
\]  \hspace{1cm} (2.16)

This representation is extremely oversimplified and the reader interested in a more complete coverage should examine references [1, 2, 3]. Shown in figure 2.4 is a simple vector picture of spin-lattice relaxation.
2.5.2 Spin-Spin Relaxation, $T_2$

Shown in figure 2.5 is a simple vector picture of spin-spin relaxation. If a sample of nuclei is placed into a magnetic field and an r.f. field is applied so that the resonance condition is achieved ($\omega_0 = -\gamma H_0$) for a sufficient length of time, such that the individual magnetic moments are drawn into phase. Upon removal of the r.f. field, the nuclei will continue to precess about the magnetic field for a period of time dependent on the *spin-lattice relaxation time* $T_1$. The decay rate, however may be faster than that expected from the magnitude of $T_1$. This rate increase happens if there are neighboring magnetic moments in the sample whose moments do not move about rapidly and make only small contributions to the magnetic field. This causes inhomogeneity in the field on a microscopic scale, and consequently the individual nuclei precess in slightly different magnetic fields and will lose phase quickly due to the difference in their precessional frequencies. The time factor involved in this relaxation process (*spin-spin relaxation time* $T_2$) is written as,

$$T_2 = \frac{1}{\Delta \omega_0} = \frac{-1}{\gamma \Delta H_0}.$$  

(2.17)

$H_0$ and $\Delta \omega_0$ corresponds to the change of the precessional frequency $\omega_0$ and the magnetic field $H_0$ caused by the spin-spin relaxation process. This process is a great illustration of the Second Law of Thermodynamics: in the absence of other forces, a system will spontaneously attain an arrangement of maximum entropy.
2.6 FID and Spin Echo

This section will focus on the two NMR experiments used throughout this work. First, the Free Induction Decay (FID) and finally the Hahn Echo (Echo) is discussed.

2.6.1 FID

See figure 2.6 for an illustration of the FID. An r.f. pulse $\mathcal{H}_{rf}(t)$ of duration $t_p$ with a select pulse rotation $\beta$

$$\beta = -\gamma B_1 \tau_p, \quad (2.18)$$

rotates the bulk equilibrium magnetization about the direction of the r.f. field applied. This is assuming a strong r.f. is applied. If the angle of rotation is selected as $\frac{\pi}{2}$, then the bulk magnetization will end up in the x-y plane along the x or y axis (dependent upon if $\mathcal{H}_{rf}(t)$ is applied along x or y). After the pulse is turned off individual spins
Figure 2.7: Free Induction Decay (FID) pulse sequence.

will precess at a frequency characteristic of its local environment [4, 5]. This precession frequency is written as,

$$\omega_{pre} = \gamma_n (H_0 - \Delta H).$$  \hspace{1cm}(2.19)$$

$H_0$ denotes the external magnetic field and $\Delta H$ local field. $\Delta H$ leads to a distribution of precession frequencies and dephasing rates. This results in a decaying constant of $T_2$. This is called a Free Induction Decay (FID). This pulse sequence is good for samples with very long $T_2$, such as liquids which are on the order of milliseconds. However in the case for solids, most de-phasing rates $T_2$ are typically quite fast sometime of the order of 10’s of us. Further the problem of amplifier dead time or in some cases probe ringing can make these signals very challenging to detect [6, 7, 41].

In order to obtain signals with such short $T_2$’s it is advantageous to move the signal further out in time and start acquisition then. This is obtained with a Hahn Echo sequence.
2.7 Hahn Echo

The importance of understanding the spin or Hahn echo is that it provides the building block for multi-pulse NMR experiments[45]. Under r.f. irradiation, as shown in the previous section, the equilibrium magnetization is slightly perturbed. When two r.f. pulses are applied the sequence becomes:

\[
\left(\frac{\pi}{2}\right)_x \rightarrow \frac{\tau}{2} \leftarrow \pi_x \rightarrow \frac{\tau}{2} \leftrightarrow \text{Acquire}.
\]  

(2.20)

Shown in figure 2.8 is an illustration of the Hahn-Echo. Shortly after the \((\pi/2)_x\) pulse, the inhomogeneity of the static field causes the individual nuclear spins to fan out at different rates in the x-y plane. A \(\pi_x\) pulse then rotates all the spin precessing at the same frequency together around \(x\), and leaves those precessing at other frequencies along -\(y\). What is most important here is after a time \(\tau\) due to the \(\pi_x\) pulse[4, 5], all the magnetization will have refocused along -\(y\). Described here is a simple Hahn Echo sequence. A more rigorous development is in appendix A.
2.8 Relevant NMR Hamiltonians

2.8.1 Zeeman Hamiltonian

The static magnetic field $\mathcal{H}_{\text{static}}$ is generally chosen along the z-axis and denoted $\mathcal{H}_z$. Choosing $\mathcal{H}_{\text{static}}$ as such leads to the following

$$\hbar \mathcal{H}_z = -\sum_i\mu_i^z \mathcal{H}_z = \hbar \mathcal{H}_z \sum_i \frac{\gamma_n^i I_z^i}{\omega_0} = \hbar \sum_i \omega_0 I_z^i. \quad (2.21)$$

In this equation $\mu_i^z$ and $\gamma_n^i$ are, the magnetic moment and the magnetogyric ratio of the $i^{th}$ nucleus’s respectively. The $\sum_i$ runs over all nuclei in the sample[44, 46].

2.8.2 Dipolar Hamiltonian

The dipolar Hamiltonian describes the through space coupling associated with neighboring nuclei, and given by the following expression,

$$\hbar \mathcal{H}_D = \sum_{i<k} (-\frac{\gamma_n^i \gamma_n^j \hbar^2}{r_{ik}^3}) \left[ \frac{3 (I^i \cdot r_{ik})(I^k \cdot r_{ik})}{r_{ik}^2} - I^i \cdot I^k \right]. \quad (2.22)$$

The constant $r_{ik}$ denoted the vector from nuclei $i$ and $k$.

2.8.3 Chemical Shift Hamiltonian

The chemical shift Hamiltonian characterizes the magnetic field at the nucleus produced by surrounding electrons, and has the following tensor representation,

$$\hbar \mathcal{H}_{CS} = \hbar \sum_i \frac{\gamma_n^i I^i}{\omega_0} \cdot \sigma^i \cdot \mathcal{H}. \quad (2.23)$$
In the above expression $\sigma^i$ is the chemical shielding tensor$^3$, and is of rank two. Furthermore, $\sigma^i \cdot \mathcal{H}^4$ is the magnetic field induced by the electron at the nucleus$^{[44, 46]}$.

### 2.8.4 Electric Quadrupolar Hamiltonian

The Electric Quadrupolar Hamiltonian describes the interaction between the nuclear quadrupolar moment of the $ith$ nuclei and the electric field gradient produced by surrounding electrons and nuclei. This Hamiltonian in tensor form is expressed as

$$\hbar \mathcal{H}_Q = \sum_i \frac{e Q_i^i}{6I_i(2I_i - 1)} \mathcal{I}_i \cdot \mathcal{V}_i \cdot \mathcal{I}_i.$$  \hspace{1cm} (2.24)

$e Q_i^i$ is the nuclear quadrupolar moment, and $\mathcal{V}_i$ is the electric potential at the $ith$ nucleus$^{[44, 46]}$.

### 2.8.5 Radio Frequency Hamiltonian

It is most common that the r.f. field is applied perpendicular to the static field, and is chosen along the $x$-axis. The form of $\mathcal{H}_{rf}$ used is such that both phase and amplitude are readily modulated. However, the irradiation frequency is constant $\frac{\omega}{2\pi}^{[46]}$. This Hamiltonian has the form,

$$\hbar \mathcal{H}_{rf} = -\hbar \mathcal{H}_1(t) \cos[\omega t + \phi(t)] \sum_i \gamma_i^i \mathcal{I}_x.$$ \hspace{1cm} (2.25)

$^3$Sometimes denoted chemical shift tensor.

$^4$\mathcal{H}$ is usually equal to $\mathcal{H}_{Static}$. 

---

30
2.9 Information obtained by NMR with respect to Ice

Since NMR was first introduced to condensed matter fifty years ago, relaxation measurements have become a potent tool for obtaining information about local electronic structure. Today relaxation studies are used for elucidating information about classes of materials ranging from biological to minerals. Discussed previously were the two types of relaxation processes, $T_1$ and $T_2$; the relaxation process utilized in this research is $T_1$.

2.9.1 $T_1$ relaxation and molecular dynamics

The study of molecular motions using spin-lattice relaxation measurements can offer a tremendous amount of insight. A system of interacting nuclear spin in non-thermal equilibrium with the lattice is done by a density matrix treatment. The equilibrium density matrix is written as

$$\rho_{eq} \propto e^{-\beta H}. \quad (2.26)$$

$\beta$ is equivalent to $1/kT$ and $H$ is the interaction Hamiltonian[44, 46, 2]. In the case where the density matrix is described by a single constant $\beta$ it is reasonable to assume that the interaction between the spin and lattice relaxation is, describable by a single constant, $T_1$. The rate of change of $\beta$ is then written as

$$\frac{d\beta}{dt} = -\frac{1}{T_1}(\beta - \beta_0). \quad (2.27)$$
When assuming a spin-temperature it becomes possible to calculate the spin lattice relaxation time for an arbitrary nuclear spin irrespective of the field. When motions are sudden and/or infrequent it is possible to characterize thermally activated motions in terms of a correlation time $\tau_c$ for the motion [3, 1]. When the motion is sudden\(^5\), the spin system is not allowed enough time to change, hence, its initial density matrix is unchanged. In the case of infrequent motions\(^6\), the correlation time between two successive motions happen on a time scale much greater than the spin-spin relaxation time $T_2$. As a result the system’s equilibrium is disturbed by the motion. During the time before the next disturbance the system finds another equilibrium. In the latter the Hamiltonian is time fluctuating. The evolution of the spin system is well characterized by looking at the variation of the spin temperature due to a sudden change of the spin Hamiltonian[1, 5]:

$$\beta_f = \beta_i \frac{\text{Tr}(H_i H_f)}{\text{Tr}(H_f^2)}.$$

(2.28)

In this case Zeeman, quadrupolar, and dipolar relaxations will be present. Therefore equations for these types of interactions must be developed.

**Zeeman Relaxation**

Only the case for high field experiments will be considered. The mentioned system evolved under two Hamiltonians - Zeeman and internal fields. The total Hamiltonian is expressed as the following

\(^5\tau_c \ll \text{all resonance periods.}\)

\(^6\tau_c \gg T_2\)
\[ H_T = -\omega_0 I_z - \sum_i^N \omega_i H_i. \] \hfill (2.29)

In this equation \( i \) denotes the individual spin-spin interaction, i.e. dipolar, quadrupolar etc. Because in high field \( \mathcal{H}_s \gg \mathcal{H}_i \) the total Hamiltonian is reduced to

\[ H_T = -\omega_0 I_z. \] \hfill (2.30)

Assuming the random fluctuating fields governing relaxation are stationary and symmetric upon time reversal[1]:

\[ \bar{f}_\mu(t)f^*_\nu(t) = G_\mu(|t - t'|), \] \hfill (2.31)

the ensemble average is equal to the time average. Here, \( G_\mu(t-t') \) defines the autocorrelation function and is expressed as the following[2],

\[ G_\mu(|t - t'|) = G_\mu(0) \exp\left(\frac{|t|}{\tau_{eq}}\right), \] \hfill (2.32)

\( \tau_{eq} \) is the correlation time for the function \( G_\mu \).

The discussion now returns to the high field treatment. The evolution of the Zeeman interaction is written as,

\[ \frac{dH_z}{dt} = Tr(\Im[H_z, H_0] \rho_2) - \frac{1}{T_1} (<H_z> - <H_z>_{eq}), \] \hfill (2.33)

where \( H_0 \) is the total Hamiltonian. When the non-secular term of the density matrix is much smaller than the spin-lattice relaxation rate, the rate of change of the expectation value of \( \mathcal{H}_z \) becomes[2]
\[
\frac{dH_z}{dt} = -\frac{1}{T_1} (\langle H_z \rangle - \langle H_z \rangle_{eq}).
\]  
(2.34)

Expressing the relaxation as a function of inverse spin-temperature we have the following,

\[
\frac{d\beta}{dt} = -\frac{1}{T_1}(\beta_i - \beta_f).
\]  
(2.35)

The spin-lattice relaxation the becomes

\[
\frac{1}{T_1} = \frac{1}{Tr[H_z^2]} \sum_{\mu,m} G_{\mu m}(0) \int_0^{\infty} Tr([H_z, V_\mu^{(m)}][V_\mu^{(m)*}, H_z]) e^{\frac{-t}{\tau_{\mu}}} dt
\]  
(2.36)

\[
\frac{1}{T_1} = \frac{1}{Tr[P_z^2]} \sum_{\mu,m} G_{\mu m}(0) m^2 Tr(V_\mu^{(m)} V_\mu^{(m)*}) \frac{\tau_{\mu}}{1 + 3m^2 \omega_0^2 \tau_c^{-2}}.
\]  
(2.37)

\(V_\mu^{(m)}\) is the spin operator of the individual nuclei. Finally, the expression for the spin-lattice relaxation is

\[
\frac{1}{T_1} = \frac{2\gamma^2 g^2 \tau_c}{1 + \omega_0^2 \tau_c}.
\]  
(2.38)

The above equation shows that when \(\omega_0 \tau_c > 1\) \(1/T_1\) is proportional to \(1/\tau_c\) and when \(\omega_0 \tau_c \ll 1\) \(1/T_1\) is proportional to \(\tau_c\).

Now the quadrupolar relaxation will be considered.

**Quadrupolar Relaxation**

Considering the secular quadrupolar interaction Hamiltonian
\[ H_Q = \frac{e^2 q Q}{4 I (2 I - 1)} [3 I_z^2 - I(I + 1)]. \]  

(2.39)

Since the energy levels are not equidistant, spin-couplings are unable to suddenly establish a spin temperature, thus making the definition of a spin lattice relaxation time ambiguous. In general it is not possible to define the transition relaxation back to thermal equilibrium by a single exponential. When \( I = \frac{5}{2} \) the rate of change of populations from thermal equilibrium obeys the following equations

\[
\begin{align*}
\frac{dn_{-3/2}}{dt} &= -W_1 n_{-5/2} + W_1 n_{-3/2} \\
\frac{dn_{-1/2}}{dt} &= -W_1 n_{-3/2} - W_2 n_{-3/2} + W_2 n_{-1/2} + W_1 n_{-5/2} \\
\frac{dn_{-1/2}}{dt} &= -W_2 n_{-1/2} + W_2 n_{-3/2} + W_3 n_{1/2} - W_3 n_{-1/2} \\
\frac{dn_{1/2}}{dt} &= -W_3 n_{1/2} - W_4 n_{1/2} + W_4 n_{3/2} \\
\frac{dn_{3/2}}{dt} &= -W_4 n_{3/2} - W_5 n_{5/2} + W_4 n_{1/2} + W_1 n_{5/2} \\
\frac{dn_{5/2}}{dt} &= -W_5 n_{5/2} + W_5 n_{3/2}
\end{align*}
\]

(2.40)

In these particular experiments only the central transition\(^7\) was excited and detected, so the treatment will therefore be restricted to these population changes only.

\[
\begin{align*}
\frac{dn_{-1/2}}{dt} &= -W_2 n_{-1/2} + W_2 n_{-3/2} + W_3 n_{1/2} - W_3 n_{-1/2} \\
\frac{dn_{1/2}}{dt} &= -W_3 n_{1/2} - W_4 n_{1/2} + W_3 n_{-1/2} + W_4 n_{3/2}
\end{align*}
\]

(2.41)

The result of subtracting the second equation from the first is

\[
\frac{dn_{1/2} - dn_{-1/2}}{dt} = -W_2 (n_{-3/2} + n_{-1/2}) + W_4 (n_{1/2} - n_{3/2}) + 2W_3 (n_{1/2} - n_{-1/2})
\]

(2.42)

\( ^7 \Delta m = \pm 1 \)
at all times

\[-n_{-3/2} + n_{-1/2} = n_{1/2} - n_{3/2},\]

hence:

\[
\frac{dn_{1/2} - dn_{-1/2}}{dt} = 2(W_4 - W_2)(-n_{-3/2} + n_{-1/2}) + 2W_3(n_{1/2} - n_{-1/2}).
\]

1/T is defined as the rate of change of (n_{1/2} - n_{-1/2}) by,

\[
\frac{1}{T} = 2(W_1) + 2W_2.
\]

The transition probabilities \(W_i\) can be written in terms of the spectral density functions[2, 1]:

\[
W_1 = 3/4\omega_Q^2 J_I(\omega) \quad 2W_2 = 3/16\omega_Q^2 J_{II}(\omega),
\]

and 1/T expressed as,

\[
\frac{1}{T} = \frac{3\omega_Q^2}{8}(J_{II}(\omega) - 2J_I(\omega)).
\]

Now it is necessary to obtain some indication of the nature of the spectral density function. In most situations it is possible to attribute molecular motions as resulting from random fluctuations. The correlation function for this motion is exponentially decaying with the Fourier transform being the spectral density function \(\mathcal{J}(\omega)\). \(\mathcal{J}(\omega)\)
are functions describe the ranges of frequency motions present in the system and have the following form[16]

\[ J(\omega) = \frac{2\tau_c}{1 + \omega_0^2 \tau_c^2}. \]  \hfill (2.48)

In many case a model is selected for the description of the molecular motion. To account for the various models the quadrupolar \( T_1 \) expression is rewritten in the following manner,

\[ \frac{1}{T_1} = \frac{3\omega_0^2}{8}(J_{II}(\omega)P^1(\theta, \phi) - 2J_I(\omega)P^2(\theta, \phi)). \]  \hfill (2.49)

\( P^i(\theta, \phi) \) are pre-factors that depend on the specific model chosen for the motion[16, 47, 11]. However, the nature of the spectral densities do not change and the relationship between \( T_1 \) and \( \tau_c \) is still valid. In the case of motional narrowing due to isotropic motions (i.e. liquids) \( 1/T_1 \) can be defined by a spin temperature[2] resulting in

\[ \frac{1}{T_1} \propto \tau_c, \]  \hfill (2.50)

\[ J_I(\omega) = J_{II}(\omega) = 2\tau_c. \]  \hfill (2.51)

In the case when a spin temperature is not definable a model of the molecular motions causing relaxation is necessary[2]. Now the heteronuclear dipole relaxation will be considered.
Heteronuclear Dipolar Relaxation

The equation for the heteronuclear dipolar relaxtaion between $O_{17}$ and $H_1$ is given by Abragam (1960) as

$$
\frac{1}{T_1^{O-H}} = \frac{\hbar^2 \gamma_S^2 \gamma_I^2 I_{O^{17}}(I_{O^{17}} + 1)}{r^6} \left[ \frac{-1}{12} J^{(6)}(\omega_{O^{17}} - \omega_{H_1}) + \frac{3}{4} J^{(6)}(\omega_{O^{17}} + \omega_{H_1}) \right]. \quad (2.52)
$$

In this equation

$$
\omega_D^2 = \frac{\hbar^2 \gamma_S^2 \gamma_I^2 I_{O^{17}}(I_{O^{17}} + 1)}{r^6}. \quad (2.53)
$$

In the extreme narrowing limit $\omega_0 \tau_c \ll 1$. Now looking at equations [2.48] and [2.52] it is evident that in the extreme narrowing limit the heteronuclear dipolar relaxation is inversely proportional to one over the correlation time. At the experimental temperatures used in this work the extreme narrowing limit is not a consideration and in this case the relaxation is directly proportional to the correlation time. Equation [2.52] is then re-expressed as,

$$
\frac{1}{T_1^{O-H}} = \frac{\hbar^2 \gamma_S^2 \gamma_I^2 I_{O^{17}}(I_{O^{17}} + 1)}{r^6} \left[ \frac{-2 \tau_c P_1(\theta, \phi)}{12(1 + (\omega_{O^{17}} - \omega_{H_1})^2 \tau_c^2)} + \frac{6 \tau_c P_2(\theta, \phi)}{4(1 + (\omega_{O^{17}} + \omega_{H_1})^2 \tau_c^2)} \right]. \quad (2.54)
$$

Most useful for our case is the dipolar frequency dependence on relaxation and the importance of this is illustrated in the next section.
Spin-Lattice Relaxation and Ice

In ice, each oxygen atom has tetrahedral symmetry, is covalently bonded to two hydrogen atom, and $\mathcal{H}$-bonded to two others. Each oxygen atom is subject to a quadrupolar interaction of non-axial symmetry. Rotations corresponding to interchange of the positions of the hydrogens atoms greatly affect the electric field gradient (EFG) tensor at the oxygen nuclei. Assuming one particular rotation or proton hop at the site of the nuclei, the spin Hamiltonian before the rotation or hop would have the form

$$H_i = \frac{\omega_p}{2} \sum_{i=1}^{4} [I_i] + H_{Q01i} + H_{z01i} + \sum_{\mu} H_{\mu}$$

(2.55)

$$H_{Q01i} = \frac{\omega_p}{48} \frac{1}{2} [3 \cos^2(\theta) - 1](3I_i^2 - I)(I + 1)).$$

Here, $\theta$ is the angle of rotation. Comparing the Zeeman, dipolar and quadrupolar components of the total relaxation results in the following assumption. The Zeeman relaxation will be neglected since in our experiments the Zeeman field is not in fluctuation and should not induce relaxation back to equilibrium. The dipolar interaction depends greatly on the strength of the dipolar coupling (i.e. $\gamma$, molecular orientations and relative distances of the coupling nuclei). In ice each oxygen is coordinated by four hydrogen atoms - two covalent and two $\mathcal{H}$-bonded. The average covalent distance is $\sim 0.9572$ Å, while the average $\mathcal{H}$-bonded distance is $\sim 1.9488$ Å[8]. When compared with $\mathcal{H}\leftrightarrow\mathcal{H}$ of similar bond distance a comparison of the product $\gamma$'s show that the dipolar coupling will be reduced by a factor of $\sim 8 \times$ for the $\mathcal{H}\leftrightarrow\mathcal{O}$ from the $\mathcal{H}\leftrightarrow\mathcal{H}$ coupling. This translates to a drop from $\sim 40$ kHz for $\mathcal{H}\leftrightarrow\mathcal{H}$ dipolar coupling.

$^8\mathcal{H}$ denotes Hydrogen and $\mathcal{O}$ denotes Oxygen.
to $\sim 5$ kHz for $\mathcal{H} \leftrightarrow \mathcal{O}$ dipolar coupling in ice. Shown by equation [2.49] the relaxation is inversely dependent upon the size of the quadrupolar coupling constant $e^2 q Q$. For $\mathcal{O}^{17}$ in ice $e^2 q Q \sim 6.66$ Mhz[14]. Comparing the relative sizes of $\omega_D$ and $\omega_Q$ it is apparent that the heteronuclear dipolar relaxation does not merit consideration.

$I_{zi}$ is a spin operator of the spin $i$, quantized along the $\mathcal{O} \rightarrow \mathcal{H}$ internuclear axis. $H_\mu$ are the quadrupolar Hamiltonians of the other oxygens and will be neglected in this treatement. After a single rotation the Hamiltonian has the following form

$$H_f = \frac{\omega_0}{2} [I_{z_1-2} + I_{z_2-3} + I_{z_3-4} + I_{z_4-1}] + H_{QO1} + H_{zO1}. \quad (2.56)$$

At this time the system reaches a new equilibrium with an inverse spin temperature of $\beta_f$ given by equation 1.28 is[1].

$$\beta_f = \beta_i \frac{\omega_0^2 + \omega_0^2 Tr[H_{QO1} H_{QO1}^*]}{\omega_0^2 + \omega_0^2 Tr[H_{QO1}^2] + \omega_o^2}, \quad (2.57)$$

$$\alpha = \frac{\omega_0^2}{4} + \frac{3 \omega_0^2}{16}. \quad (2.57)$$

Since fluctuation of the quadrupolar coupling Hamiltonian will predominate relaxation, the expression is approximated as

$$\beta_f \approx \beta_i \frac{\omega_0^2 Tr[H_{QO1} H_{QO1}^*]}{\omega_0^2 Tr[H_{QO1}^2]}. \quad (2.58)$$

Now the trace is

$$Tr[H_{QO1} H_{QO1}^*] = \frac{1}{2} (3 \cos^2(\theta) - 1) Tr[I_{z01}^2 - \frac{1}{3} I(I + 1)]. \quad (2.59)$$

Using equations 1.53 and 1.54 the final expression for $\beta_f$ is
\[ \beta_f = \beta_0 \frac{1 + \frac{3}{2}(3 \cos^2 \theta - 1) + 4(N - 1)}{4N}. \]  
\hspace{1cm} (2.60)

In the above equation \( N \) denotes the total number of molecules in the crystal. The time variation of the spin temperature due to a single rotation is then expressed as

\[ \frac{\delta \beta}{\beta} = -\frac{9}{8N} \sin^2(\theta). \]  
\hspace{1cm} (2.61)

Since there exists \( N/\tau_c \) thermally activated rotations in the crystal per unit of time, the rate of change of the spin temperature tends towards the inverse lattice temperature and is further expressed as

\[ \frac{d\beta}{dt} = -\frac{9 \sin^2(\theta)}{8\tau_c} (\beta - \beta_L) = -\frac{1}{\tau_1} (\beta - \beta_L). \]  
\hspace{1cm} (2.62)

In general the correlation time for molecular motion is sensitive to temperature changes, so measurement of \( \tau_1 \) as a function of temperature can provide information about the temperature dependence of whatever process produces fluctuations. Since, below 230 K, the rates of molecular motions, characterized by a correlation time \( \tau_c \), is quite slow, the lattice rigid and \( \omega_0 \tau_c \gg 1[1, 2, 3] \). In this limit we assume \( \tau_c \) has the following form

\[ \tau_c = \tau_0 e^{U/kT}. \]  
\hspace{1cm} (2.63)

Here \( U \) is the activation energy or barrier for the molecular motion and \( k \) is Boltzmann's constant. Furthermore, since \( \tau_1 \) is proportional to \( 1/\tau_c \) the equation becomes

\[ \tau_c = \tau_0 e^{U/kT}. \]  
\hspace{1cm} (2.63)
\[
\frac{1}{T_1} \propto e^{U/kT}.
\] (2.64)

So, from measured values \( \ln 1/T_1 \) vs. \( 1/T \), a straight line is obtained where the slope gives the activation energy \( U/k \) in units of Kelvin. This method has been employed extensively to probe molecular motions in liquids as well as solids. By measuring \( T_1 \) as a function of temperature an activation energy for the molecular motion can be calculated.

### 2.9.2 Measuring \( T_1 \): Inversion Recovery Experiment

The idea of this experiment is to rotate the equilibrium magnetization from \( +z \) to \(-z\). This is achieved with a selective or non-selective \( \pi \)-pulse[4, 7]. The recovery towards equilibrium is then sampled after a delay time \( \tau \) by applying a second pulse. This second pulse is typically a \( \pi/2 \) pulse. However, in the case of this experiment a spin-echo sequence was used, a \( \pi/2 \) and then \( \pi \) pulse (illustrated in figure 2.9). The signal intensity is measured at the echo top. This is repeated for several increasing values of the delay time, \( \tau_1 \). A least squares fit of this data is fit to the following equation:

\[
M_{eq} = M_0(1 - 2M_2 \exp(-\frac{\tau}{M_3}))
\] (2.65)

When \( \tau=5\times T_1 \) the final magnetization is \( 0.993 \times M_{eq}[7] \). The large range of signal variation makes I.R. quite precise in measuring \( T_1 \). However, the disadvantage of I.R. is that a recycle delay of \( 5\times T_1 \) is necessary, and since \( T_1 \) is not known an
approximation (long) must be made. Finally, the inversion pulse is likely to excite unwanted coherences which may interfere with the signal acquired after the final pulse if \( \tau < T_1 \). This can typically be dealt with by using appropriate phase - cycling (See Appendix B).

In the above equation (2.65) \( M_0 \) equals the initial magnetization, \( M_2 \) represents the percentage which is fit to account for incomplete inversion of spins that are slightly off resonance, \( M_3 \) represents the spin-lattice relaxation time \( (T_1) \), and \( \tau \) the delay time described above. \( T_1 \) is determined by a two, three or four parameter fit. In general only isolated spins relax via a single exponential. In the case of coupled spins systems or nuclei with nuclear spin \( I > 1/2 \) a more complicated expression (multi-exponential) is necessary. In many cases when the exact nature of \( T_1 \) relaxation is unknown a stretched exponential is utilized instead of a multi-exponential. In this particular case \( \mathcal{O}^{17} \) spin-lattice relaxation recover curves were fit to the following Williams-Watt’s [17] Function (Fig. 2.10)

\[
M(\tau) = M_0 (1 + 2M_2 e^{(-\tau/M_2)^{M_4}}), \tag{2.66}
\]
Figure 2.10: Spin-lattice relaxation inversion recovery curve fit with Williams-Watt function.

\( \mathcal{M}_4 \) is a phenomenological stretching parameter. The William-Watt’s function was selected because of the multi-exponential nature of the relaxation. In the limit where \( \mathcal{M}_4 \) goes to 1 the relaxation is single exponential and values of \( \mathcal{M}_4 \) less than one more multi-exponential behavior is observed.
CHAPTER 3

Experimental Techniques Employed in this Dissestation

Things without remedy Should be without regard: what’s done is done.
Lady Macbeth. W. Shakespeare.

3.1 NMR Experiment

The subsequent sections discusses the experimental details and hardware used throughout this dissertation. A rudimentary amount of detail is given for each aspect selected. However, for greater detail curious readers are directed to the following references[6, 7, 41].

3.1.1 Magnet

In the described NMR experiments both Oxford 360 MHZ and Oxford 400 MHz 89 mm wide bore magnets were used. The details below describe both magnets. Both Oxford magnets were of the superconducting type. Superconducting magnets are required to obtain frequencies greater than 100 MHz. The central fields of the magnets used are 8.4 and 7 T. The superconducting solenoid is made from alloys based on niobium. The solenoid is immersed in a bath of Liq He. An outer jacket
is constructed to house liq \( N_2 \). \( N_2 \) is used to cool the Cu radiation shield, thus allowing for long periods between He fills. The \( N_2 \) refill volume is 68 liters and He 60 liters. Helium evaporation rates varied between the two magnets, however, both were less than 14 cc/hr. Helium refill rates are between 3-4 months. To maintain field homogeneity room temperature shims are mounted inside the bore of the magnet. The field drift is less than \( \pm 5\% \). The axial stray field at 5 Gauss is: 3.20 m (360 MHz, 7 T) and 3.80 m (400 MHz, 8.4 T). The radial distance from the magnet center lines at 5 Gauss are as follows: 2.50 m (360 MHz, 7 T) and 3.05 m (400 MHz, 8.4 T).

3.1.2 Probe Circuit and Design

The single resonance home-built probe used in this research is shown in figure 3.1a. The probe is constructed from brass. The total length of the probe from top to sample is 86 cm. The diameter is 80 mm. There are 5 baffles for convection of cryogenic gas used during low temperature experiments. The probe is constructed with an antenna to detect probe aching during pulse experiments. Another feature of the probe is a GaAlAs diode temperature sensor mounted near the sample.

An illustration of the NMR circuit is shown in Figure 3.1b. The resonance circuit is comprised of two variable capacitors. The two capacitors are high voltage non-magnetic trimmer capacitors from Voltronics Inc. Both capacitors are rated from room temperature down to 4 K. The breakdown and working D.C. voltages are \( \sim 2000 \) V \( \sim 4000 \) V at room temperature. The capacitance is from below 1 pF and above 15 pF. Finally, the dielectric is PTFE. The coil is a simple solenoid wire made
Figure 3.1: (a) Single resonance NMR probe and (b) NMR circuit.
on copper. The Q of the resonance circuit is 86 at room temperature. The Q-factor is measured in the following way

\[ Q = \frac{1/e_{\text{time}}}{\omega_0} \times 2. \]  (3.1)

The \(1/e_{\text{time}}\) is the amount of time it takes the pulse to fall to \(1/e\) of its maximum value. By looking at the pulse coming from the probe with an oscilloscope it is possible to obtain the \(1/e_{\text{time}}\) and then calculate Q. The Q-factor is expected to increase with decreasing temperature. This is observed by shorter \(T_{90}\) times - i.e. greater coil efficiency. The typical \(V_{pp}\) at 10 dB delivered to the resonance circuit was 600 V. The corresponding power is calculated in the following way[7]

\[ P = \frac{V_{pp}^2}{400} = 900 Watts. \]  (3.2)

One more calculation and the magnetic field \(B_{\text{coil}}\) produced by the coil is obtained

\[ B_{\text{coil}}^2 = \frac{2\mu_0 Q P}{2\pi \omega_0 V} = \frac{2 \times 4\pi \times 10^{-7} \times 86 \times 900}{2\pi \times \omega_0 \times 2.5 \times 2.5 \times 10 \times \pi \times 10^{-9}}. \]  (3.3)

\[ B_{\text{coil}} = \begin{cases} 371 \text{ Gauss} & \omega_0 = 40.788 MHZ (7T) \\ 442 \text{ Gauss} & \omega_0 = 48.566 MHZ (8.4T). \end{cases} \]  (3.4)

The \(^{17}\)O enriched sample is situated within the coil. An r.f. pulse is applied to the sample and circuit alike through the inductor-coil. The Faraday coil is then used not only to apply the r.f. field to our sample, but also to detect the EMF produced by our sample.
3.1.3 NMR Spectrometer

A block diagram of the NMR spectrometer is presented in Figure 3.2. The NMR spectrometer is dissected in two parts, a transmitter and receiver. A brief discussion of these two parts will follow. A more detailed discussion the reader is found in Andrew Derome's, "Modern NMR Techniques for Chemistry Research."[6]

NMR Spectrometer Transmitter

A very crude idea of a pulsed NMR experiment can be thought of as the intermittent switching on and off of the output from a continuous frequency source. The important factor in this analogy is the duration of these switches. It is very important that each event is controlled with high precision. It is for this reason that the process is under computer control. A computer can conduct most tasks within nanoseconds. The computer operation is done with the software package MacNMR. Within MacNMR an operator may set up the pulse program they want to execute. For a simple one pulse sequence without phase cycling we have the following:

\[ \frac{\pi}{2} \rightarrow \tau \leftarrow Acquire \]  \hspace{1cm} (3.5)

As indicated above, the NMR transmitter is a series of on and off switches. For the NMR experiments described herein a brief account of how the transmitter works is given. All NMR experiments are under computer control. The operator uses the computer to input the desired pulse sequence. Once MacNMR is set up to acquire data, the following occurs: the computer signals the pulse programmer (Tecmag) to
Figure 3.2: Block diagram of the NMR spectrometer used for experiments in this dissertation.
starts giving commands to the attached electronics. The Tecmag sends signal to both
the PTS and r.f. gate. Upon this signal the PTS allows radio frequency into the r.f.
gate. An r.f. gate is an intermitted switch that allows r.f. to flow in intervals (pulses).
When the r.f. leaves the gate it is amplified by the high power amplifier. To note, the
Tecmag also send TTL pulses to the high power amplifier at the same time the r.f.
goes to the amplifier$. This is done to produce high power pulses. After the amplifier
the high power pulses are sent to the diode box. Since the diodes open with voltages
greater than 1/2 V and pulse are $\gg$ 1/2 V, the pulses proceed to the NMR sample
and circuit. The spins are then excited and it is now time to detect the resulting
signal.

**NMR Spectrometer Receiver**

The following is an outline of what happens when the signal comes back for acquisi-
tion. When the signal comes back the first stage of acquisition are the cross diodes.
A plot of a typical diode is in figure 3.3a. The plot shows for a diode, current flows
forward after a voltage of greater than 1/2 V is applied. If we take two diodes and
connect them anti-parallel (Fig. 3.3b) the following voltage vs. current behavior (Fig.
3.3b) results. In this case the diode will flow in either direction for voltages greater
that +1/2 V and less than -1/2 V.

As a result this protects the receiver from seeing the high power pulses from out
of the high power amplifier. Hence a high power pulse will see a short to ground

$^9$TTL pulses are used to do pulse NMR without them the operator is conducting continuous wave
NMR.
Figure 3.3: Current vs. Voltage diagram for single and cross diode.

and not go to the receiver. This voltage constraint also stops low voltage noise from entering the probe. As mentioned before the high power pulse from the transmitter completely opens the cross diodes and goes to the probe because it see an infinite impedance in the direction of the receiver due to the λ/4 cable. However, on the return trip the low power signal is less than +1/2 V so it does not turn on the cross diodes and goes straight to the receiver. Since our NMR signal is typically less than .1 µWatt it is necessary to amplify our signal. This is done with Doty low noise per-amps. The next component the signal encounters is the mixer. The mixer is how the experimenter electronically goes into the rotating frame. The NMR signal is
mixed with the negative of the oscillator frequency so that the resulting is only the chemical shift which is typically in Hz. Hence our signal is now in Hz instead of MHz. This has a tremendous advantage, the bandwidth and acquisition time can now be reduced. The signal is amplified a final time with D.C. amplifiers and filtered with a band past filter typically set to 100 Khz. Finally, the signal is transferred along to the ADC converter in the receiver. In order for the ADC to correctly process the data, the ADC must be able to sample the voltage oscillations of the signal faster than the shortest voltage. If sampling is done too slow the signal will appear to have a smaller frequency than it actually does. In this case the frequencies are mirrored to lower frequencies. Hence it is very important to sample very fast.

3.1.4 Low Temperature System

Cryostat

A Janis Research Company’s SuperTran-VT continuous flow cryostat with a flexible transfer line was use to cool the samples (figure 3.4 and 3.5). The cryostat is placed into the bore of the magnet and the probe is inserted. Liquid helium or nitrogen are continuously transferred through the transfer line into the sample area. Nitrogen and helium gases are transferred at a rate of 3 L/hour. This was monitored with an Oxford N₂ and He flow meter. At the bottom of the cryostat is a vaporizer/heat exchanger. The liquid is then heated to the desired temperature set by the Lake Shore Crytronics, Inc. temperature controller. Once the gas is heated it travels upward to cool the sample. To obtain accurate temperatures and prevent the
bore of the magnet from getting cold a mechanical pump is used at the sample tube vent/pumping port.

**Temperature Controller**

A Lake Shore Cryotronics, Inc. temperature controller in conjunction with a GaAlAs diode (at the sample) is used to regulate the sample temperature. As explained previously, the Lake Shore controller operates the heater and thermostat inside the Janis cryostat. The sensor used by the Janis cryostat is a calibrated CX-1030-SD Diode. The temperature calibration curve came pre-installed in the Lakeshore temperature controller. The secondary temperature sensor used was a GaAlAs diode purchased from Lakeshore Inc. The GaAlAs diode has a temperature range rating of 1.49 K to 325 K. The temperature sensor was calibrated by Lake Shore Cryotronics, Inc. The calibrated voltages for room temperature and liquid nitrogen were 0.885 V and 1.42 V. These calibrated voltages are in agreement with voltages measured at room temperature and liquid nitrogen temperature during the experiments. The GaAlAs sensor is mounted .25 cm from the sample inside the probe. This sensor is supplied 10 μA from a home-built current source and the return voltage measured by a high precision voltmeter. The accuracy of the voltage meter was to 5 significant figures. Good agreements were also maintained between the set temperature, the voltage recorded at the sample and the GaAlAs diode calibration curve. All samples were frozen in the NMR coil with nitrogen($T > 80K$) or helium($T < 80K$) gas. Thermal equilibrium was obtained after 1 h at selected temperatures. Lastly,
Figure 3.4: Janis Cryostat all measurements in inches.
Figure 3.5: Transfer line all measurements in inches.
the doped sample concentrations are based on aqueous solution concentration and it
should not be assumed that these are the concentrations in ice.

3.1.5 Pulse Sequences Utilized

For pure absorption mode acquisition all NMR experiments were conducted with
a spin echo sequence. All spin-lattice relaxation experiments used an echo inversion
recovery sequence. Shown in figure 3.6 are both pulse sequence with the selected
cohereence transfer pathway. The echo path was selected for pure absorption mode
spectra. The $m_r=1/2 \leftrightarrow 1/2$ central transition was excited and observed. An eight
step phase cycle was used with receiver phase set to

$$\phi_r = -\phi_2 + 2\phi_3. \quad (3.6)$$

Since these pulse sequences are discussed earlier in this dissertation they are not
discussed further.

3.1.6 $^{17}O$ enriched Ice-IH Preparation

All samples are prepared initially with 40% $^{17}O$ enriched water purchased from
Isotec Inc. The KOH and HCl were purchased from Aldrich Chemicals. The pure ice
sample preparation is as follows: 0.3 cc of 40% $^{17}O$ enriched water is transferred to a
NMR sample tube of the following dimensions: 9mm in diameter and 12mm in height;
the sample is then freeze-pump-thawed over two hours to remove $O_2$ impurities. The
sample is finally vacuum seal.
3.1.7 $^{17}$O enriched KOH doped Ices Preparation

For the KOH doped ices 1 L solutions of 2 M, 0.9 M, 0.35 M, and 0.05 M are initially prepared. Afterwards 0.3 cc of each stock solution is transferred to a small Pyrex NMR tube 9mm in diameter and 12mm in height. The samples are then heated to 150 Cdeg for 1.5 h to remove the water and leave behind solid KOH. 0.3 cc of 40% $^{17}$O enriched water is then added to each NMR tube. Finally, to remove $^{16}$O impurities each sample is freeze-pump-thawed over two hours period and vacuum seal.

3.1.8 $^{17}$O enriched HCL doped Ices Preparation

The HCl samples are prepared in the following manner. 0.3 cc of 40% $^{17}$O enriched water is transferred to a Pyrex NMR tube 9 mm in diameter and 12 mm in height. The appropriate amount of HCl is added to each tube to produce 2 and 0.9 M HCl.
solutions. Again to remove $O_2$ impurities the samples are freeze-pump-thawed over two hours and vacuum sealed.

3.1.9 Experimental Conditions

$T_1$ measurements are conducted with a home-built spectrometer and Tecmag pulse programmer. All experiments were conducted at either 8.4 or 7 T. These field strengths correspond to $O^{17}$ resonance frequencies of 40.788 and 48.566 MHz. All samples were referenced to $O^{17}$ in liquid water.

All presented data is obtained without $H^1$ de-coupling. An echo-inversion recovery pulse sequence for pure adsorption mode acquisition was used. The experimental temperature range differed between samples: KOH doped samples were 230 K - 60 K, HCl doped samples were 200 - 100 K, and pure ice-Ih sample were 230 K - 80 K.

For pure ice the temperature range varies between the two fields and were as follows: 8.4 T 230 K - 145 K and 7 T 230 K - 80 K. For KOH doped ices the temperature ranges were: 230 K - 95 K for the 0.05 M KOH sample, 230 K - 85 K for the 0.35 M KOH sample, 230 K - 65 K for the 0.9 M KOH sample and 230 K-90 K for the 2 M KOH sample. Finally, HCl doped ices had the following temperature ranges: 2 M HCl-ice 190 K - 130 K and 0.9 M HCl-ice 190 K - 140 K. All the HCl doped data was obtained at a magnetic field of 8.4 T and KOH doped data obtained at 7 T.

The observed spin-lattice relaxation time for the KOH and HCl doped samples are a sum of ice-impurity solid solution: solid solution + aqueous solution and impurity solid solution + solid Impurity-nH$_2$O (n=1 for KOH and n=6 for HCl). However,
since the measurements are on $O^{17}$, it is calculated that even at 100 \% $O^{17} \rightarrow O^{16}$
exchange the signal from the impurity-solid-solution\textsuperscript{10} in ice is $10 \times$ larger than the
other expected compositions. Knowing this these other composition merit little con-
sideration in the discussion.

The precision of $T_1$ was better than 10 \%. Desired temperatures were obtained
by a constant flow of $N_2$ or $He$ and temperature was controlled with a GaAlAs diode
accurate to within 1 K.

### 3.1.10 Data Processing

**O\textsuperscript{17} enriched Ice-IH**

The recovery of the magnetization of pure ice is fit by a single stretched exponential
with stretching parameters ranging from 0.45 to 0.56. The percent inversion for each
$T_1$ point is between 70 and 80 \%. In figure 5.1 the natural log of the reciprocal spin-
lattice relaxation time (Ln $1/T_1$) is plotted versus reciprocal temperature for 8.4 and
7 T field strengths.

**O\textsuperscript{17} enriched HCL doped Ices**

The Ln $1/T_1$ is plotted versus the reciprocal temperature for the HCl doped ices
along with pure ice(Fig. 5.4). This data was obtained at a magnetic field of 8.4 T. A
single stretched exponential with stretching parameters ranging from 0.45 to 0.56 is
used to fit the $T_1$ data. The percent inversion for each $T_1$ point is between 70 and
80 \%.

\textsuperscript{10}This is the phase of interest.
$^{17}$O enriched KOH doped Ices

The recovery of the magnetization for all the KOH doped ices are fit to a single stretched exponential with stretching parameters ranging between 0.45 and 0.56. The percent inversion for each $T_1$ point is between 68 and 80 %. Shown in figure 5.5 is the plot of $\ln 1/T_1$ versus the reciprocal temperature $1/T$ for the four different KOH doped ices.
CHAPTER 4

\[ \text{O}^{17} \text{ Temperature Dependence of The Lineshapes in Ice-Ih and Doped Ices} \]

So great is the worth of Dostoevsky that to have produced him is by itself sufficient justification for the existence of the Russian people in the world; and he will bear witness for his country-men at the last judgement of the nations.

\textit{Nikolay Berdyaev (Prague, 1923).}

This chapter discusses the NMR spectra obtained and their implications on molecular motions in normal and doped ices. \textit{O}\textsuperscript{17} NMR spectra of Polycrystalline ice-Ih along with KOH and HCl doped ices are obtained. The molecular dynamics are seen as exchange broadening of the powder patterns. The temperature dependence on molecular motions is also evident throughout the NMR spectra.

4.1 Experimental Parameters

All lineshape experiments are conducted with a Hahn-Echo pulse sequence at two different fields. Spectra were obtained on 8.4 T (H\textsuperscript{1}) and 7 T (H\textsuperscript{1}) spectrometers.
previously described. \( T_{90} \) pulses varied between samples but were between either 3 or 5 \( \mu \)s. These \( T_{90} \) times corresponding to r.f. field strengths of:

\[
B_1 = \frac{1}{4T_{90}} \approx 83.3 kHz \quad T_{90} = 3\mu s \\
50.0 kHz \quad T_{90} = 5\mu s
\]  

(4.1)

Recycle delays vary between samples depending on their respective \( T_1 \) values, but all recycle delay times were selected as at least \( 10 \times T_1 \). This is to ensure that spectra obtained are at full unsaturated intensities. Sample preparation for the various samples are discussed previously and are not be discussed further.

4.2 Results and Discussion

4.2.1 Ice-Ih

Shown in figure 4.1 are a series of \( ^{17} \)O NMR spectra from a sample of polycrystalline ice-Ih over the temperature range of 260-80 K. The low temperature spectrum at the lowest temperature (80 K) shows an unexpected shape. The low temperature, though broadened by a large quadrupole coupling and noticeable asymmetry, appears to have multiple sites. The origin of these multiple sites are most likely due to magnetically non-equivalent oxygen sites. However, due to the presence of larger second order broaden of the resonance lines further interpretations are not possible at the present time. At temperatures greater than 270 K the quadrupolar coupling is reduced to zero by rapid and isotropic reorientations in the liquid state. In the high temperature region the correlation time for molecular rotations is given by the expression
\[ \omega_0 \tau_c \ll 1. \quad (4.2) \]

As a result, the nuclei of interest see an average local field of zero and its resonance line is negligibly broadened. In the low temperature case the spectrum is very much different. In this case the main Hamiltonian \( \mathcal{H}_Q \) is affected by the various motions. When the jump rate \( 1/\tau_c \) is slow, the nuclei see a time varying electric field. As a result, the evolution of the nuclear spin Hamiltonian is not simple to characterize. In this limit the correlation time for the molecular motion is much greater than \( T_2 \). A plot of the magnetic resonance line width transition as a function of temperature (Fig. 4.8), shows that in the intermediate region the line becomes excessively broadened due to infrequent motions. At low temperatures where molecular rotations are nonexistent two pairs of lines are observed. Here the inverse correlation time for molecular rotations is much smaller than the frequency difference of individual frequencies and each line is broaden by an amount of the order \( \frac{\gamma Q}{\omega_0} \). The plot of line width verses inverse temperature (Fig. 4.8), shows that the motion pertaining to motional narrowing is freezing out at approximately 145 K.

4.2.2 HCl Doped Ices

Shown in figures 4.2 and 4.3 are the \( ^{17} \) NMR line shapes for 2.0 and 0.9 M HCl-ices. Experimental temperatures are 2 M HCl-ice (190-125 K) and 0.9 M HCl-ice (190 K-130 K). In figure 4.2 and 4.3 it is apparent that in the experimental temperature region the line broadening is due to infrequent motions. There is also noticeable
Figure 4.1: $^1$H NMR line-shapes of Ice-Ih obtained at 8.4 T. The full echo is acquired, however the echo is left shifted and only the FID processed. 3000 Hz of exponential broadening is added.
Figure 4.2: $^17O$ NMR lineshapes of 0.9 M HCl-ice obtained at 8.4 T. The full echo is acquired, however the echo is left shifted and only the FID processed. 3000 Hz of exponential broadening is added.

...concentration dependence on the NMR spectra. However, for the 2 M sample the 125 K line shape starts to have spectral features resembling ice-Ih. This does not appear until 125 K and not noticed at 130 K in either sample. There is an appreciable broadening of the spectral line observed in both HCl samples. Moreover, no motional narrowing effect is observed. Hence, the relation, $\omega_0 \tau_c \gg 1$ appears valid.

4.2.3 KOH Doped Ices

KOH doped ices appear to exhibit a different behavior than ice-Ih. Shown in figure 4.4-4.7 are a series of $^17O$ NMR spectra from several samples of polycrystalline KOH doped ices over the temperature range of 260 - 80 K and between the concentrations
Figure 4.3: $^{17}O$ NMR lineshapes of 2 M HCl-ice obtained at 8.4 T. The full echo is acquired, however the echo is left shifted and only the FID processed. $3000\text{Hz}$ of exponential broadening is added.

of 0.05 M KOH and 2 M KOH. There is a noticeable concentration dependence on the NMR spectra. The smallest concentration tends toward normal ice-Ih at $\sim 145$ K. Also, as the concentration is reduced the spectral features appear more like ice-Ih. This is true for 0.5 M KOH and 0.35 M KOH. The two high concentrations spectra widths and features remain fairly constant throughout the experimental temperature range. There is no appreciable broadening for 2 M, 9 M or 0.35 M KOH samples. It is apparent that the correlation time for molecular is still quite fast leading to a condition closer to

$$\omega_0\tau_c \ll 1.$$  \hspace{1cm} (4.3)
Figure 4.4: $^{17}$O NMR line shapes of 2 M KOH-ice obtained at 7 T. The full echo is acquired, however the echo is left shifted and only the FID processed. 3000 Hz of exponential broadening is added.

The low temperature spectra at 80 K shows little broadening due to a small quadrupole coupling and non-noticeable asymmetry. Molecular rotations governing motional narrowing are still active even at low temperatures. As the temperature is lowered the spectroscopic lines exhibit evidence of an isotropically averaged coupling tensor and observable exchange effects.
Figure 4.5: $\text{O}^{17}$ NMR lineshapes of 0.9 M KOH-ice obtained at 7 T. The full echo is acquired, however the echo is left shifted and only the FID processed. 3000 Hz of exponential broadening is added.

4.3 Comments on $\text{O}^{17}$ NMR linewidths

Figure 4.8 shows the $\text{O}^{17}$ static NMR spectra FWHM as a function of dopent concentration and temperature. Normal ice in temperature range of 260 - 80 K shows increasing spectral line widths ranging from 19 kHz to 65 kHz. This is direct evidence of slowing molecular reorientation. At temperatures below 145 K it is apparent that in normal ice, molecular rearrangements are almost non-existent and another process effects the line width. The proton motion in pure ice is frozen out below 145K. The above plot illustrates the effect of KOH and HCl impurities on the nature of
Figure 4.6: O$^{17}$ NMR lineshapes of 0.35 M KOH-ice obtained at 7 T. The full echo is acquired, however the echo is left shifted and only the FID processed. 3000 Hz of exponential broadening is added.

molecular rearrangements in ice. With the addition of KOH molecular reorientation rates accelerate by introducing free OH$^{-}$ ions. At high concentration of KOH (2 M, 0.9 M and .35 M) spectral line widths reach a limit of 32 kHz at 145 K and remain the same within 5 % down to 80 K. However, the 0.05 M KOH sample departs from the other concentration after 145 K and becomes more ice - like in line width and shape. This is not surprising, one expect that at low concentrations the KOH doped samples would resemble pure ice. Both of these results give evidence that bond and
Figure 4.7: $^{17}$O NMR lineshapes of 0.05 M KOH-ice obtained at 7 Tesla. The full echo is acquired, however the echo is left shifted and only the FID processed. 3000 Hz of exponential broadening is added.

molecular reorientation still occurs at a fast rate when KOH is present. A more startling result is found in the HCl doped samples. The NMR FWHMs from the two concentrations throughout the experimental temperature range (190 - 123 K) appears to show less molecular rearrangements, and line-widths resembling pure ice in the same temperature range. It is apparent that, unlike the hydroxide ions in the KOH system, the hydronium ions introduced by the HCl impurity are unable to retain sufficient mobility at low temperatures. They fail to facilitate molecular
Figure 4.8: O\textsuperscript{17} NMR line widths (KHz) of ice-Ih, KOH-ices and HCl-ices vs. Temperature (K).

Reorientation’s and the motions effecting the line width are essentially frozen out at low temperatures.
CHAPTER 5

$^{17}O$ $T_1$ Temperature Dependence in Ice-Ih and Doped Ices

*Hatred is a tonic, it makes one live, it inspires vengeance; but pity kills, it makes our weakness weaker.*

*La Peau de Chagrin. (Honor de Balzac).*

A large amount of research has been devoted to the study of molecular motions in solids and their dependence on temperature by means of spin-lattice relaxation. However, there have been few studies on quadrupolar relaxation, namely $^{17}O$. This chapter is devoted to $^{17}O$ spin-lattice relaxation studies of ice-Ih, KOH doped, and HCl doped ices.

5.1 Possible Relaxation Mechanisms

Since this dissertation previously illustrated that fluctuations of the $^{17}O$ electric field gradient will have the greatest effect on $^{17}O$ relaxation times, it will proceed to discuss what these fluctuations mean in terms of molecular motions.

As previously mentioned little is known about the mobility of the hydronium ion through ice, however, it is most likely that the acid diffuses as an intact molecule
instead of fragments [13, 15]. This is different than what is thought to occur with KOH. The KOH molecule is thought to diffuse as the fragments K⁺ and OH⁻. The motion of the hydronium ions proceed via a self-trapping polarization well [21]. This causes nearby water molecules to reorient away from their Hydrogen ends, leading to the creation of L/D defects. These defects remain mobile at very low temperatures. It is further thought the hydronium ion would remain quite mobile even down to 0 K [21]. However, soft-landing of hydronium ions experiments conducted by Cowin and co-workers[21] and those presented here found different results.

In KOH-doped ices OH⁻ and L-defects are mostly formed. For proton ordering to occur, bonds are randomly reoriented by ion or Bjerrum defect motions, just as in the process of dielectric relaxation. This fast Debye relaxation is due to the presence of OH⁻ and D-defects formed. The relaxation remains fast enough at lower temperatures (72 K) to facilitate proton ordering into ice-XI[12, 31]. There also exist two types of Debye relaxation for KOH-doped ice below ~ 210 K. One relaxation is caused by L-defects facilitating molecular rotations, whereas the other is caused by the relaxation of dipoles by OH⁻ following proton shifts on the hydrogen bond [19].

5.2 Experimental Parameters

All $T_1$ experiments are conducted with an inversion recovery Hahn-Echo pulse sequence at two different fields. $T_1$ values were obtained by measurements at 8.4 T (H¹) and 7 T (H¹) magnets/spectrometers previously described. $T_{90}$ pulses vary between samples but are either 3 or 5 µs. The $\tau_1$ time between $P_1$ and $P_1$ is 40 µs.
and $\tau_2$ equal to 20 $\mu$s, this is done to acquire the echo top. All $T_1$ points are taken at the top of the echo height. Delay times are selected to obtain inversion as close as possible between normalized intensities of $\pm 1$. Last delays vary between samples depending on their respective $T_1$ values, but all last delay times are selected as 10 to 20 times $T_1$.

5.3 Results and Discussion

From results presented in this section, it is appropriate to assume that a slow motion process dominates relaxation. In this region, the correlation time for a single molecular rotation is described as the following: the overall rate of molecular rotation from one equivalent position to another (that is described by a correlation time $\tau_c$) is very low and the lattice is practically rigid. In this limit, the correlation time is governed by the following

$$\tau_c = \tau_0 e^{U/RT},$$  \hspace{1cm} (5.1)

where $U$ is an activation energy corresponding to the potential barrier between the two molecular positions. In the slow passage limit the correlation time is proportional to $T_1$. From measured values of $T_1$, a plot of $\ln(1/T_1)$ vs. $1/T$ should be a straight line. Where the slope is equal to the activation barrier $U/k$ (Kelvin) of the process affecting $T_1$. 

75
5.3.1 Ice-Ih

Figure 5.1 shows the natural log of the reciprocal spin-lattice relaxation time (Ln $1/T_1$) plotted versus reciprocal temperature for 8.4 and 7 T, field strengths. The temperature range varies between the two fields and are as follows: 8.4 T, 230 K - 145 K and 7 T, 230 K - 80 K. When pure ice-Ih relaxation rates are compared at the two fields, the $O^{17}$ spin-lattice relaxation rates appear mildly field dependent.

Figure 5.2a shows this dependence on field is small and narrows as the temperature is lowered. In figure 5.2b, Ln $1/T_1$ vs. $1/T$ is plotted with the ratio of Ln $1/T_1$ at both fields. The ratio $\frac{\ln(1/T_1^{8.4})}{\ln(1/T_1^{7})}$ approaches unity as the temperature is lowered, leading to the assumption that the field dependence is not a major contribution to relaxation.

From the data obtained, it is evident that molecular reorientation in normal ice-Ih follows an Arrhenius behavior. The 7 T data being the most complete is discussed further. Shown in figure 5.3 is a plot of the Ln $1/T_1$ vs. $1/T$ at 7 T.

This plot is well characterized by two exponentials. One with a long component and the other with a short component. In the upper temperature region denoted region a, we obtain an activation energy of 3.4 kcal/mol. This value is on the order of a single proton bond strength. It is concluded that what is being observed is a single proton motion or diffusion along a single $O \leftrightarrow H$ bond. In the low temperature region denoted b, we observe a different motion occurring. This motion has a small activation energy of 0.13 kcal/mol and little effect on the $O^{17}$ spin-lattice relaxation times. The correlation time for this motion is noticeably smaller than the high temperature motion. Due to
Figure 5.1: $^{17}$O $\ln 1/T_1$ vs. $1/T$ plot for Ice-Ih at 8.4 and 7 T.
Figure 5.2: $\mathcal{O}^{17}$ Ln $1/T_1$ vs. $1/T$ plot for Ice-Ih at 8.4 and 7 T. Insert $\frac{\ln(1/T_1^{8.4T})}{\ln(1/T_1^{7T})}$ to show field dependence on spin-lattice relaxation rate as a function of inverse temperature.

the reduced correlation time of this second motion and its low activation energy, it is possible that what is being observed is a sort of structural defect motion. Possibly it is a slow interstitial motion or diffusion. Two noteworthy points are: The barrier for proton motion is greater at temperatures $T \leq 145$K ($1/145K = 0.0057K^{-1}$), and two, that another process dominated the $\mathcal{O}^{17} T_1$ relaxation. It is clear that the proton motion is reduced greatly at temperatures below 145K. However, a secondary mechanism taking over at low temperatures is not well characterized.
Figure 5.3: $\mathcal{O}^{17}$ $\ln 1/T_1$ vs. $1/T$ plot for Ice-Ih at 7 T.
5.3.2 HCl Doped Ices

In Fig. 5.4 the Ln $1/T_1$ is plotted versus the reciprocal temperature for the HCl doped ices along with pure ice. This data was obtained at a magnetic field of 8.4 T. The experimental temperature ranges are as follows: Pure ice 230 K - 145 K, 2 M HCl-ice 190 K - 130 K, and 0.9 M HCl-ice 190 K - 140 K. In the experimental temperature range Ln $1/T_1$ vs. $1/T$ is fit to a straight line. The slope corresponds to a activation energy of 4 kcal/mol for pure ice, 2 M HCl doped ice, and 0.9 M HCl doped ice. The linear nature of Ln $1/T_1$ vs. $1/T$ indicates a single relaxation process. As in the case for pure ice-$I_h$, this process is primarily molecular rotations.

For the concentration selected in these experiments it is apparent relaxation rates are greatly affected by incorporating HCl into the ice matrix. There is an upward shift in the Ln $1/T_1$ vs. $1/T$ plot for the HCl doped ices when compared to pure ice. Furthermore, in the experimental temperature range the spin-lattice relaxation times for the HCl doped ices are concentration independent. However, the ions do not seem to lower the activation barrier for proton motion. Also they appear sufficient mobility below $T \sim 175$ K($1/175$ K$^{-1}$) for proton rearrangements to occur. This agrees with the Debye relaxation experiments that suggest that the relaxation is reduced by the addition of HCl[48]. The $L$-defect motion responsible for molecular rotations around the $OH^-$-axis of the water molecule is negligible. This is due to the low number of defects in the HCl-doped ice at low temperatures[49]. The measurements suggest, the mobility of the hydronium ion is quite small and only effective at
$E_a \sim 4.6 \text{ kcal/mol}$
$2 \text{ M HCl doped Ice-Ih @ 8.4 T(☐)}$

$E_a \sim 4.4 \text{ kcal/mol}$
$0.9 \text{ M HCl doped Ice-Ih @ 8.4 T(☐)}$

$E_a \sim 4.4 \text{ kcal/mol}$
Ice-Ih @ 8.4 T(☐)

Figure 5.4: $\delta^{17}$ Ln $1/\mathcal{T}_1$ vs. $1/\mathcal{T}$ plot for HCl doped ices at 8.4 T.
high temperatures ($T \geq 175$ K ($1/175$ K = 0.0057 K$^{-1}$)). This is accompanied with very little effect on the activation barrier on proton motion.

### 5.3.3 KOH Doped Ices

Shown in figure 5.5 is the plot of $\ln 1/T_1$ versus the reciprocal temperature $1/T$ for the four different KOH doped ices. This data was obtained at a magnetic field of 7 T. However, the experimental temperature range varies between samples and is as follows: 230 K - 95 K for the 0.05 M KOH sample, 230 K - 85 K for the 0.35 M KOH sample, 230 K - 65 K for the 0.9 M KOH sample, and 230 K - 90 K for the 2 M KOH sample. In the KOH doped ices the $\ln 1/T_1$ vs. $1/T$ gives a very perplexing result. Throughout all of the samples the data is separated into two regions - a and b (Fig. 6). In region a, $\ln 1/T_1$ vs. $1/T$ behavior is Arrhenius and molecular motions appear to slow with decreasing temperatures. The correlation time for this motion is substantially faster than that seen in ice in the same temperature region.

$T_1$ is also concentration dependent. All the concentrations take a sudden upward turn indicating that the correlation time for the molecular dynamics affecting relaxation times are becoming faster. This result is only over shadowed by region b being concentration independent. Both results suggest that the hydroxide ion remains sufficiently mobile down to $T \approx 80$ K ($1/80$ K = 0.0125 K$^{-1}$). In KOH-doped ice both Bjerrum and OH$^-$ defects promote rearrangements. These defects are responsible for effective reorientation of water molecules. As seen by Kawada[19] and Whitworth[30] independently, the Debye relaxation in ice is greatly enhanced by the addition of KOH to ice[8]. The Debye relaxation is observed to be temperature independent from 200
Figure 5.5: $O^{17} \ln 1/T_1$ vs. $1/T$ plot for KOH doped ices at 7 T.
K to 100 K and then rises slowly at lower temperatures. Debye relaxation experiments show the presence of two types of relaxation. One due to molecular rotations induced by $\mathcal{L}$-defect motion and the other is the relaxation of water dipoles by OH$^-$ ions following the proton shift on a hydrogen bond[19]. At low temperatures the two processes occur in concert. The sudden upturn in the $\ln 1/T_1$ vs. $1/T$ plot is the observance of both processes. In region a of figure 5.5, we observe molecular rotations caused by $\mathcal{L}$-defect motion which are concentration dependent. In region b the process is mediated by the relaxation of dipoles by OH$^-$ as a result of a proton shift. In the high temperature region of both processes the long component dominates. At low temperatures the relaxation time for the first motion is elongated, or better yet frozen out. As a result the only component left is the fast relaxation mode. This results in a lower activation barrier for proton shift or motion, and a possible relaxation process fast enough to facilitate the ordering of ice-Ih to ice-XI.
CHAPTER 6

Final Remarks

My loss is irreparable; the source of my hatred is inexhaustible; I shall make my hate last throughout my lifetime - I want to live with it, and die with it still unquenched.

Pierre Corneille.

6.1 Conclusion

6.1.1 Line shape Conclusions

These results show that a larger variation exists between Ice-Ih, KOH doped, and HCl doped ices. In typical laboratory samples of Ice-Ih, KOH doped or HCl doped ice there exists a detectable amount of rotational motion that is seen vividly in the NMR spectra. It is further evident that the motion governing the line width are greatly dependent upon the temperature of the ice and impurities introduced into the ice framework. For the HCl samples the hydronium ions appear immobile at low temperatures and not capable of promoting molecular rotations. Contrary to this, in the KOH samples the hydroxide ions remains quite mobile down to 80 K and promotes molecular rearrangements.
6.1.2 Relaxation Conclusions

Comparative studies on pure and doped ices shows the process governing $^17$O relaxation is a single proton motion. The sensitivity of the $^17$O electric quadrupolar moment gives valuable information about the motion of Bjerrum L/D defects and ionic point defects. We find doping with HCl or KOH dramatically effects the activation barrier for proton motion. Doping with KOH greatly reduces the activation barrier for proton motion. However, HCl doping leaves the barrier practically unchanged from pure ice-Ih. We have shown $^17$O spin lattice relaxation experiments yields information valuable for understanding proton motion and molecular rearrangements in pure and doped ices. Finally, we note that in the present context emphasis placed upon observing differences between HCl and KOH doped ices. This objective was obtained.
CHAPTER 7

The effects of H-bond arrangement on the stability of ice

Every substance has a finite positive entropy, at the absolute zero of temperature the entropy may become zero and does so become in the case of perfect crystalline materials.

Gilbert Newton Lewis

This chapter outlines the results of periodic semiempirical calculations on ice-Ih with various ordered hydrogen bonding topologies.

7.1 Introduction

The first major theoretical interpretation of ice is due to Linus Pauling[23] in 1935. Pauling’s interpretation was directly based on the randomness of the hydrogen bonds in water. When considering Pauling’s arguments on the residual entropy in ice, the structure must be considered. The arrangement of the oxygen atoms is known by X-ray diffraction studies[50, 51]. Each oxygen is tetrahedrally surrounded by four other oxygen atoms; all oxygen’s are hydrogen bonded. Pauling’s assumptions are derived from the Bernal-Fowler ice rules[52]: (1) the water molecule remains intact; (2) each
hydrogen atom is covalently and hydrogen bonded to adjacent oxygen atoms; (3) one hydrogen lies on each O...O axis; (4) interactions past nearest neighbor interactions may be ignored.

From assumption 2, there are six possible tetrahedral configurations on HOH. Considering the adjacent water molecule, it is shown that the probability that one of the two more closely bonded sites is occupied is $\frac{1}{2}$. Since each oxygen in water has two associated hydrogens, the probability that both of the two more closely bonded sites if occupied is $\frac{1}{4}$. Hence the total number of configurations, $W$, for Avogadro’s number of molecules, $N$, is $W=(6\times\frac{1}{4})^N=(\frac{3}{2})^N$. Substituting in $S=R\ln W$ for one mole, $S=\frac{R}{N}\ln(\frac{3}{2})^N=R\ln(\frac{3}{2})$, which yields $S_0=3.37$ J K$^{-1}$ where $S_0$ is the entropy at absolute zero. In 1936, Giauque and Stout[62] using calorimetric measurements calculated an entropy value at absolute zero of $3.4\pm0.6$ J K$^{-1}$. Thus, the measured and theoretical values agree within the limits of experimental error.

Pauling’s estimate is accurate due to the fact that a large number of different H-bond arrangements are of similar stability. Pauling’s approach assumes they are energetically equal having equal a priori probabilities. However, these structures do not have the same energy, but spread out over a band of energies. Rigorously, the probabilities are unequal resulting in a reduction of $S_0$.

Ice-Ih can be classified as an semi-amorphous solid which contains periodicity of the oxygen network, while the hydrogen sub-lattice remains disordered[8]. With this distinction between the oxygen’s and hydrogen’s in mind, we focus attention on the hydrogen sub-lattice.
As in crystals, the atoms in ice-Ih must form extended three dimensional networks. However, from x-ray diffraction experiments it follows that the hydrogen bond network is not periodic and symmetrical as in crystals[50, 51]. The hydrogen network in ice-Ih is characterized by an infinitely large unit cell containing an infinite number of atoms. Furthermore, because of the lack of periodicity no two hydrogen atoms are structurally equivalent. Since all hydrogen atoms are structurally inequivalent, the energy required to detach an atom from the network will be different for each individual atom. This results in an increasing number of detached Atoms at high temperatures, so that the breakdown of the network becomes continuous instead of an abrupt occurrence[51].

When further compared to crystals, we take a look at the unit cell structure. Each unit cell in a crystal must contain an integral number of stoichiometric molecules since all unit cells are alike. In ice-Ih the unit cell is defined by the symmetry of the oxygen network, with random arrangements of hydrogen atoms. This makes the unit cell infinitely large and consequently there will be no restriction with regard to the relative numbers of chemically different hydrogen atoms.

7.2 Previous Theoretical Work on Ice-Ih

Considering the above statements, the arrangement of protons in ice-Ih has been of interest for many years. In particular the identification of low energy structures that are most stable at 0 K. When modeling ice it is important to consider the entire assembly of molecules and not just to sum the individual bonds. This is clearly
indicated when comparing the binding energy of ice and H₂O dimer. The electronic energy of the hydrogen bond in H₂O dimer is 0.24 ev with an O-O distance of 2.976Å, compared with the inter-site distance of 2.750Å in ice-Ih at 0 K[8]. The first attempt at modeling the structure and binding energy in terms of individual atoms in ice-Ih was carried out by Bernal and Fowler[52]. In 1951, Bjerrum[18] argued the dipole-dipole interaction between water molecules would favor the dimer configuration. However, later Pitzer and Polissar[53] showed the dipole-dipole effect will become negligible with increasing number of molecules. All lattice energy calculations present a number of difficult problems, the first of these arise from the disorder in ice-Ih. In the water dimer the hydrogen bond interaction contains a substantial electrostatic component, represented on the empirical pair potentials by placing fixed charged on the H₂O molecule. Since, these charges have long range interaction the summation must be taken out to sufficiently large number, this is difficult due to the disordered nature of ice-Ih.

In 1982 Morse and Rice calculated the lattice energy and corresponding density[59] of an ordered ice-Ih structure by the use of pair potentials, and some years later Kozack and Jordan (1992)[60] would use different potentials for a 96 molecule unit cell. Here the molecules were disordered with zero total dipole moment. But, between the two results there is a 10 % difference in energy or density. One notable consideration with these results is that the potential is parameterized to fit experimental data for liquid water. To understand the stability of various ice structures, ab initio calculations have been carried out by several researchers[63, 64]. The determination
of energy in these methods is relative to separated molecules, with an accuracy of 0.04 eV. As mentioned in the above passage, most works have been dedicated to deciphering the hydrogen network atomic arrangements, however, following the discovery of ice-XI (proton ordered ice-Ih) [22] several researchers have turned their attention to the enumeration of possible zero entropy structures.

Work by Howe [54] cleverly illustrates a systematic analysis of the possible ordered structures of ice-Ih, by the use of 4, 8, and 12 molecule unit cell clusters. Howe identifies 17 total structures with low residual entropy. However, in this work no attempt to separate the structure by energy was mentioned. More recently Singer and co-workers enumerated 19 symmetry inequivalent ice structures based on an eight water cell.

As stated earlier it is not possible to treat the total energy of a cluster of ice as a sum of the energies of individual hydrogen bonds, since one must account for some form of many body interaction. Using symmetry allowed structures obtained from the Singer group, calculations on all 19 structures were conducted and a range of energies was obtained and the lowest energy structures were identified.

For this work we use the 19 hydrogen bonding topology structures provided by the Singer group. Shown in figure 7.1 are several one unit cell illustrations of the various structures. The oxygen network is a slight distortion from hexagonal symmetry, better characterized as orthorhombic. The protons are arranged either anti-ferroelectric or ferroelectric with respect to the c-axis. Initial lattice parameters (a, b, and c taken
from Leadbetter[12] with structure number 18) are optimized in our calculations along with all bond distances and angles.

7.3 Method used in this work: Periodic PM3 calculations

PM3[68] is the third parameterization based on the MNDO[69] (MNDO = moderate neglects differential overlap) method. The PM3 method characterizes structure with experimental enthalpies of formations at 298 K (see figure 7.4); whereas ab initio methods characterize structures with equilibrium electronic energies (see figure 7.4). Since in ice the zero point energy (ZPE) effects are so large it is not easy to directly compare the two results. So, we have used ideal gas law statistical thermodynamic expressions[58] to convert the enthalpies at 298 K down to values at 0 K and then with ZPE corrections to electronic equilibrium values. This is automated in the Gaussian 98W program when one performs a vibration normal mode analysis. With this conversion, it is possible to make legitimate comparisons between PM3 and ab initio.

The ability of any method to accurately account for the hydrogen bonding nature in HOH is vital to its success as a tool for characterizing the water framework. For calculations on water, the extended network is vital to accurately predicting molecular properties. This makes cluster methods limited unless extrapolated to bulk. Ab initio methods of sufficiently high level and size of basis set (like MP2/AUG-cc-pVDZ) well characterize water clusters, but are computationally impractical for clusters larger than 10 Å. Semi-empirical methods are less computational intensive, thus making
Table 7.1: **Hydrogen bonding energy per water (kcal/mol)** $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}($cluster$)^{12}$

<table>
<thead>
<tr>
<th>Cluster</th>
<th>MP2-DZP</th>
<th>MP2-aug-cc-pVDZ</th>
<th>MP2-DZP (BSSE corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{H}_2\text{O})_2$ (linear HB)</td>
<td>-3.18</td>
<td>-2.67</td>
<td>-2.52</td>
</tr>
<tr>
<td>$(\text{H}_2\text{O})_3$ (Ring)</td>
<td>-6.58</td>
<td>-5.52</td>
<td>-5.10</td>
</tr>
<tr>
<td>$(\text{H}_2\text{O})_4$ (Ring)</td>
<td>-8.63</td>
<td>-7.28</td>
<td>-6.89</td>
</tr>
<tr>
<td>$(\text{H}_2\text{O})_6$ (Prism)</td>
<td>ND</td>
<td>-7.82</td>
<td>ND</td>
</tr>
<tr>
<td>$(\text{H}_2\text{O})_6$ (Cage)</td>
<td>ND</td>
<td>-7.79</td>
<td>ND</td>
</tr>
<tr>
<td>$(\text{H}_2\text{O})_6$ (Book)</td>
<td>ND</td>
<td>-7.77</td>
<td>ND</td>
</tr>
<tr>
<td>$(\text{H}_2\text{O})_6$ (Ring)</td>
<td>-9.33</td>
<td>-7.69</td>
<td>-7.59</td>
</tr>
</tbody>
</table>

Table 7.2: Cont **Hydrogen bonding energy per water (kcal/mol)** $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}($cluster$)$

extended network calculation more feasible. Most importantly semi-empirical calculations are optimized to experimental values for water monomer and dimer in the PM3 training set. This allows a good starting point for these types of calculations. MOPAC 2000 is the first computational package capable of doing periodic PM3 calculations. In tables 7.1, 7.2, and 7.3 we illustrate various ab initio results and PM3 results for water dimer, trimer, tetramer, and hexamer.
<table>
<thead>
<tr>
<th>Cluster</th>
<th>MP2-CBS</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₂O)₂ (linear HB)</td>
<td>ND</td>
<td>-2.76</td>
</tr>
<tr>
<td>(H₂O)₃ (Ring)</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>(H₂O)₄ (Ring)</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>(H₂O)₆ (Prism)</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>(H₂O)₆ (Cage)</td>
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<td>(H₂O)₆ (Book)</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>(H₂O)₆ (Ring)</td>
<td>-6.62</td>
<td>ND</td>
</tr>
</tbody>
</table>

Table 7.3: Con’t Hydrogen bonding energy per water (kcal/mol) H₂O(g) → H₂O(cluster)

Tsai and Jordan’s[73] manuscript on water six gives a good starting point for direct comparison of semi-empirical calculations and various ab initio methods. The water six cluster has a great variety of hydrogen bonding structures of which the prism is identified as the lowest equilibrium electronic energy configuration[73].

It is well accepted that for complete characterization of hydrogen bonding in water by computational methods flexible basis sets and the inclusion of electron correlation is necessary. Several methods have proven suitable for handeling these constraints, namely Mollet-Plessset (MP2)[74] with a large basis set. Jordan’s calculations included the augmented correlation - consistent (aug-cc-pVDZ) basis set for the MP2 level geometry optimizations. These results are shown in table 7.1. At the selected levels of theory without basis set superposition error corrections(BSSEC) the electronic energy for H₂O to (H₂O)₆ (prism) varies from -7.69 to -7.82 kcal/mol/water.

When BSSEC is added the values are reduced to between -6.64 to -6.60 kcal/mol. Comparing these results to those obtained by semi-empirical (PM3) calculation, we
see good agreement between the two. As mentioned previously to directly compare
the two methods, the PM3 heats of formations are corrected for zero point (ZPE) and
thermal corrections (PM3 to 0 K to equilibrium), see figure 7.2. Along with these
results figure 7.3 shows calculations of 2, 3 and 4 water clusters and good agreement
is found between the BSSEC and semi-empirical results.

Because ZPE corrections are bigger than thermal corrections in water clusters,
the PM3 energies are closer to 0 K energetics then ab initio equilibrium electronic
energies. When PM3 energies are thermally and ZPE corrected, the energetics are
excellent compared to MP2-CBS results. The most stringent test are presented in
table 7.3. A complete basis calculation eliminates the need for BSSEC[60] is in and
is in excellent agreement with PM3. Also, experimental values are available at dimer
where agreement is also good. The MOPAC 2000 is now discussed.

7.4 Using MOPAC 2000 to do Periodic Calculations

The computational package used in this research is MOPAC[67]. The MOPAC
package is based on semiempirical theory, in particular NDDO[66]. By extending
this method and allowing for a simple approximation, MOPAC allows for periodic
calculation on structurally extended systems in particular solids. MOPAC[56, 67]
actually uses a cluster technique that is valid when the chosen cell is sufficiently large
(2x2x2 i.e. eight water cell) (\sim 10 \text{Å}). MOPAC is used in conjunction with MAKPOL.
MAKPOL is responsible for extending a given unit cell into multiple cells. In our
case each unit cell was comprised of eight waters. The MAKPOL program extended
our eight water cells to 2×2×2 systems, along the, a, b, and c-axis (Fig. 7.3). This gives a multicell of eight fundamental unit cells in each case. Lastly, calculated heat of formations, ΔH_{\text{29sk}}^\text{f}, were obtained and analyzed.

The input files for the MOPAC 2000 program were obtained in the following manner. All structures were viewed using Hyperchem[57]. The Hyperchem file is given in figure 7.4 and has an *.hin extension.

The water eight unit cell is supplemented with three F- atoms, one along each axis (figure 7.5). These ghost (F) atoms are used to identify translations along the a, b, and c axes which are defined once geometries are converted to Z-matrix format. The Hyperchem program can convert its files to MPOAC’s Z-matrix format where it uses the *.zmt extension. The F- atoms are now replaced by generic ghost atoms denoted xx (figure 7.6) in MOPAC. Translation parameters are now input into the *.zmt file uses Tv in place of the atom’s designation (figure 7.7). These translation parameters are equivalent to the lattice a, b, and c constants.

The input MAKPOL file is made by adding the following line; MERS=(2,2,2) (figure 7.8) as the first line and changing the file name to Make-filename.dat. Once this file is run through MAKPOL, a new file is generated with the name filename.dat. This new file is our input 2x2x2 unit cell for MOPAC’s periodic calculation (figure 7.9). The line, ”PM3 charge=0 singlet MERS=(2,2,2) LET” is added to the top of the MOPAC input file (figure 7.10), flags for the ghosts are set to 0, and the periodic calculation is started. These calculations took approximately 24 hours on a 1.2 GHz,
768 Mb RAM PC. Finally, the output file (figure 7.11) is generated and the following parameters are obtained.

### 7.5 Results

Section 7.3.1 gives the 19 crystal structures used in this work. In these structures we enforced no symmetry, hence the geometric optimization is not trivial and is time consuming. For this reason all angles and intermolecular distances are optimized. The optimized structures consisted of a cluster of 192 atoms (Fig. 7.3): 64 oxygen’s atoms and 128 hydrogen atoms. Internal consistency is obtained by varying the gradient such that it was approximately 1 in MOPAC’s reduced units. The $\Delta H_{298K}^f$ values for our semiempirical PM3 calculations for each structure are shown in table 7.4\textsuperscript{13}. Along with heats of formation, we present and discuss the obtained lattice constants(Table 7.2).

Experiments support structure number 18 for proton ordered ice.\textsuperscript{14} This structure is identified as space group Cmc21. The Pna21(anti-ferroelectric) structure is identified as number two. Our results find Cmc21 and Pna21 as among the lowest energy structures, but numbers 2, 11, 12 and 15 are all more stable by enthalpies. When comparing all 19 structures it is apparent that the energy differences are very small but not negligible compared to kT at 70 K. In most case the difference is of the order of a few percent. Caution must be take when assigning a low temperature

\textsuperscript{13}F=ferroelectric and A=anti-ferroelectric

\textsuperscript{14}The structures are separate into ferroelectric and anti-ferroelectric arrangement by comparing their dipole moment values.
<table>
<thead>
<tr>
<th>Ice Structure</th>
<th>Proton Ordering</th>
<th>Lattice Parameters(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F</td>
<td>a=4.5670, b=7.4430, c=7.3650</td>
</tr>
<tr>
<td>2 (Pna21)</td>
<td>A</td>
<td>a=4.4940, b=7.6520, c=7.3740</td>
</tr>
<tr>
<td>3</td>
<td>F</td>
<td>a=4.1535, b=8.1906, c=7.3266</td>
</tr>
<tr>
<td>4</td>
<td>F</td>
<td>a=4.1447, b=8.1972, c=7.3253</td>
</tr>
<tr>
<td>5</td>
<td>F</td>
<td>a=4.1460, b=8.1950, c=7.3310</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>a=4.1568, b=8.1964, c=7.3257</td>
</tr>
<tr>
<td>7</td>
<td>F</td>
<td>a=4.1478, b=8.1967, c=7.3231</td>
</tr>
<tr>
<td>8</td>
<td>F</td>
<td>a=4.1490, b=8.1970, c=7.3250</td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>a=4.1500, b=8.1940, c=7.3250</td>
</tr>
<tr>
<td>10</td>
<td>F</td>
<td>a=4.5217, b=7.5877, c=7.3392</td>
</tr>
<tr>
<td>11</td>
<td>A</td>
<td>a=4.5603, b=7.6051, c=7.2344</td>
</tr>
<tr>
<td>12</td>
<td>A</td>
<td>a=4.5571, b=7.4029, c=7.3801</td>
</tr>
<tr>
<td>13</td>
<td>F</td>
<td>a=4.5871, b=7.4872, c=7.3162</td>
</tr>
<tr>
<td>14</td>
<td>F</td>
<td>a=4.1438, b=8.3494, c=7.3294</td>
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<tr>
<td>15</td>
<td>A</td>
<td>a=4.3750, b=7.8035, c=7.3948</td>
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<tr>
<td>16</td>
<td>F</td>
<td>a=4.3875, b=7.8135, c=7.3648</td>
</tr>
<tr>
<td>17</td>
<td>F</td>
<td>a=4.4002, b=7.8234, c=7.3207</td>
</tr>
<tr>
<td>18 (cmc21)</td>
<td>F</td>
<td>a=4.1347, b=8.2026, c=7.3298</td>
</tr>
<tr>
<td>19</td>
<td>F</td>
<td>a=4.6102, b=7.5630, c=7.1948</td>
</tr>
</tbody>
</table>

Table 7.4: PM3 calculations results.

<table>
<thead>
<tr>
<th>Ice Structure</th>
<th>ΔHf, kcal/mole</th>
<th>µ, Debye/Unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-9.0377</td>
<td>8.11</td>
</tr>
<tr>
<td>2 (Pna21)</td>
<td>-9.1430</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>-8.8833</td>
<td>5.08</td>
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<td>-8.6783</td>
<td>10.38</td>
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<tr>
<td>7</td>
<td>-8.6631</td>
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<tr>
<td>8</td>
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<td>13.04</td>
</tr>
<tr>
<td>9</td>
<td>-8.8042</td>
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<td>10</td>
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<td>-9.0288</td>
<td>5.21</td>
</tr>
<tr>
<td>17</td>
<td>-8.9265</td>
<td>9.16</td>
</tr>
<tr>
<td>18 (cmc21)</td>
<td>-9.0435</td>
<td>8.06</td>
</tr>
<tr>
<td>19</td>
<td>-8.7346</td>
<td>14.34</td>
</tr>
</tbody>
</table>

Table 7.5: PM3 calculations results cont'd.
equilibrium structure for the following reason. The heats of formation presented in this work are not corrected for thermal corrections. Zero - point energy is a direct manifestation of the basis principles of quantum mechanics. In preliminary cluster studies it was shown that adding zero - point corrections shifted the values of $\Delta H$. Because of this it is not certain that another structure will not predominate at bulk when zero point corrections are included.

7.6 Conclusions

The possible ordered structures of ice-Ih have been investigated. Pauling’s assumed that there was no spread in energy for the different H-bond arrangement structure. However, we find a spread on 0.5 kcal/mol. We find that the energy spread between our nineteen structures to be larger than kT at ice temperatures. Further work is necessary to obtain the energy ordering at low temperature, but these are much smaller corrections then adding ZPE to ab initio electronic energies. Although Cmc21 has been identified experimentally as the lowest energy structure, the possibility that some other structure might have lower energy can not be ruled out.
Figure 7.1: Eight water unit cell illustration of all 19 structures.
Figure 7.2: Energy diagram illustrating zero point energy.
Figure 7.3: 2x2x2 Cmc21 and Pna21 structures generated by MAKPOL program.
forcefield opls
sys 0
view 40 0.16869 55 15 -0.09970782 0.2476746 0.9636989 -0.0008082784 0.9685048 -0.2489934
seed -1111
mol 1
atom 1 O ** h 0 0 2.614 4.126 2 2 s 3
atom 2 H ** h 0 0 2.625 5.102 1 1 s
atom 3 H ** h 0 0 3.616 3.798 1 1 s
endmol 1
mol 2
atom 1 O ** h 0 0 5.26 3.202 2 2 s 3
atom 2 H ** h 0 0.795 5.655 3.53 1 1 s
atom 3 H ** h 0 -0.794 5.655 3.53 1 1 s
endmol 2
mol 3
atom 1 H ** h 0 0 5.175 1.438 1 2 s
atom 2 O ** h 0 0 5.184 0.4624 2 1 s 3
atom 3 H ** h 0 0.182 0.134 1 2 s
endmol 3
mol 4
atom 1 H ** h 0 2.251 1.276 1.438 1 2 s
atom 2 O ** h 0 2.251 1.285 0.4624 2 1 s 3
atom 3 H ** h 0 0.293 0.136 1 2 s
endmol 4
mol 5
atom 1 H ** h 0 2.251 7.515 3.798 1 3 s
atom 2 H ** h 0 2.251 6.513 4.126 2 2 s 3
endmol 5
mol 6
atom 1 H ** h 0 3.046 6.042 7.194 1 3 s
atom 2 H ** h 0 1.456 6.042 7.194 1 3 s
atom 3 O ** h 0 2.251 6.437 6.866 2 2 s 1
endmol 6
mol 7
atom 1 H ** h 0 3.046 1.756 3.53 1 3 s
atom 2 H ** h 0 1.456 1.756 3.53 1 3 s
atom 3 O ** h 0 2.251 1.316 3.203 2 2 s 1
endmol 7
mol 8
atom 1 H ** h 0 -0.794 2.143 7.194 1 2 s
atom 2 O ** h 0 2.538 6.866 2 2 s 3
atom 3 H ** h 0 0.795 2.143 7.194 1 2 s
endmol 8
mol 9
atom 1 - F ** - 0 4.5019 2.614 4.126 0
endmol 9
mol 10
atom 1 - F ** - 0 0 10.4118 4.126 0
endmol 10
mol 11
atom 1 - F ** - 0 0 2.614 11.4540 0
endmol 11

Figure 7.4: Hyperchem (.hin) sample file of structure number seven.
Figure 7.5: Hyperchem first converted (.zmt) zmt sample file.
Name: 1st.hin
MOPAC file created on 3/2 12:54:23 2001 by HYPERCHEM
O     00000.0000 0  00000.0000 0  00000.0000 0 0 0 0
H     00000.9760 1  00000.0000 0  00000.0000 0 1 0 0
H     00001.0543 1  00107.5972 1  00000.0000 0 1 2 0
O     00001.7487 1  00178.1984 1  00179.9999 1 3 1 2
H     00000.9463 1  00105.9182 1  00060.8727 1 4 3 2
H     00000.9455 1  00105.9327 1  00299.1579 1 4 3 2
O     00000.9756 1  00176.7127 1  00064.4978 1 7 4 6
H     00001.0544 1  00107.6177 1  00237.8377 1 8 7 6
H     00003.7526 1  00136.0169 1  00120.2578 1 1 2 3
O     00000.9756 1  00135.4770 1  00181.3019 1 10 1 2
H     00001.0544 1  00107.6177 1  00238.8095 1 11 10 1
H     00002.3772 1  00151.6589 1  00299.5161 1 5 4 6
H     00001.6390 1  00067.3979 1  00145.4890 1 13 5 4
O     00000.9760 1  00037.8177 1  00041.5614 1 14 13 5
H     00002.2888 1  00148.8725 1  00179.6452 1 14 13 5
H     00001.5899 1  00069.6756 1  00214.5511 1 16 14 15
O     00000.9463 1  00045.8866 1  00187.2504 1 16 14 15
H     00002.2888 1  00058.5933 1  00335.8730 1 10 1 2
H     00001.5899 1  00069.6756 1  00145.4484 1 19 10 11
O     00000.9656 1  00046.2916 1  00176.0850 1 19 10 11
H     00002.2885 1  00155.8051 1  00122.1618 1 12 13 3
O     00000.9455 1  00045.8874 1  00172.7457 1 22 2 1
H     00000.9463 1  00114.2565 1  00232.4573 1 23 22 2
xx    00001.7919 1  00133.3621 1  00358.1048 1 19 10 11
xx    00003.6832 1  00104.5417 1  00035.2499 1 13 5 4
xx    00004.3588 1  00143.8552 1  00178.7251 1 22 2 1

Figure 7.6: First converted (.zmt) zmt sample file modified for generic ghost atoms.
Figure 7.7: Converted (.zmt) zmt sample file modified for generic ghost atoms and translation parameters added.
Figure 7.8: MAKPOL input file for generating a 2x2x2 unit cell.
Figure 7.9: MOPAC input file for a 2x2x2 unit cell periodic PM3 calculation generated by MAKPOL.
Table 7.10: Truncated MOPAC input file for a 2x2x2 unit cell periodic PM3 calculation.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>X'</th>
<th>Y'</th>
<th>Z'</th>
<th>Charge</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
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<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
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<td>0.000000</td>
<td>0.000000</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>0.976000</td>
<td>1.054300</td>
<td>1.748700</td>
<td>1.054400</td>
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<td>H</td>
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<td>0.946300</td>
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<td>0.976000</td>
<td>1.766000</td>
<td>0.975600</td>
<td>0.946300</td>
<td>0.946300</td>
<td>0.946300</td>
<td>0.976000</td>
<td>0.946300</td>
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<tr>
<td>H</td>
<td>0.976000</td>
<td>1.766000</td>
<td>0.975600</td>
<td>0.946300</td>
<td>0.946300</td>
<td>0.946300</td>
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<tr>
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<td>0.946300</td>
<td>0.976000</td>
<td>0.946300</td>
</tr>
</tbody>
</table>

Figure 7.10: Truncated MOPAC input file for a 2x2x2 unit cell periodic PM3 calculation.
PM3 SINGLET CHARGE=0 MERS=(2,2,2) DDMIN=0.0 T=24H BFGS

File made with 1.hin see pg 008 in book

Generated from hyperchem and axum

HERBERTS TEST WAS SATISFIED IN BFGS
SCF FIELD WAS ACHIEVED

PM3       CALCULATION
MOPAC2000 Version 1.00
20-JUL-01 10:33:47

FINAL HEAT OF FORMATION = -3999.78814 KCAL = -16735.11356 KJ

TOTAL ENERGY = -20819.22558 EV
ELECTRONIC ENERGY = -48405173.32994 EV
CORE-CORE REPULSION = 48384354.10436 EV
GRADIENT NORM = 13.09774
IONIZATION POTENTIAL = 12.08132
NO. OF FILLED LEVELS = 256
MOLECULAR WEIGHT = 1152.973

MOLECULAR DIMENSIONS (Angstroms)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
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<td>O 1</td>
</tr>
<tr>
<td>H</td>
<td>116</td>
<td>H 83</td>
</tr>
<tr>
<td>H</td>
<td>63</td>
<td>H 125</td>
</tr>
</tbody>
</table>

VOLUME OF UNIT CELL = 1987.889 CUBIC ANGSTROMS
DENSITY = 0.963 GRAMS/CC

SCF CALCULATIONS = 11
COMPUTATION TIME = 8 MINUTES AND 6 SECONDS
WALL CLOCK TIME = 8 MINUTES AND 6 SECONDS

Figure 7.11: Truncated MOPAC output file for a 2x2x2 unit cell periodic PM3 calculation.
APPENDIX A

Density Matrix Formalism

*Power is given only to him who dares to stop and take it...one must have the courage to dare.* Crime and Punishment. Fedor Dostoevsky

A.1 Density Matrix Formalism

Consider an ensemble of spins subject to an external field $\mathcal{H} = \vec{k} \mathcal{H}$. The total $< I >_x$ is represented in the following manner \[1, 2\]

$$< I^{\text{tot}} >_x = \sum_{i=1}^{N} < I^i >_x .$$  \hfill (A.1)

Inserting the individual state function for each spin our expression is re-written in the following manner. We should keep in mind that, although the state function differ among spins $I_x$, is the same.

$$< I^{\text{tot}} >_x = \sum_{i=1}^{N} < \Psi_i | I^i_x | \Psi_i >$$  \hfill (A.2)

Substituting the state functions with the projector operator, our expectation value becomes,
\[ < I_{\text{tot}} >_x = \sum_{i=1}^{N} Tr(P_i I_x) \]  
(A.3)

\[ < I_{\text{tot}} >_x = \sum_{i=1}^{N} Tr(P_{\text{Total}} I_x). \]  
(A.4)

Since, the density operator is defined as[2]

\[ \rho = \frac{1}{N} \sum_{i=1}^{N} P_i \]  
(A.5)

we can write our observable expectation value for \( \mathcal{I}_x \) as

\[ < I_{\text{tot}} >_x = N Tr(\rho I_x). \]  
(A.6)

The time evolution of the density matrix is written as the following

\[ \rho(t) = \frac{1}{N} \sum_{i}^{N} U(t,0)P_{i(0)}U^\dagger(t,0). \]  
(A.7)

\( U(t,0) \) is the unitary operator and \( U^\dagger(t,0) \) its adjunct[7]. Since \( U(t,0) \) and \( U^\dagger(t,0) \) are the same for all values they are factored out to obtain,

\[ \rho(t) = U(t,0) \left( \frac{1}{N} \sum_{i}^{N} P_{i(0)} \right) U^\dagger(t,0) \]  
(A.8)

\[ \rho(t) = U(t,0) \rho(0) U^\dagger(t,0) \]  
(A.9)

The importance of this result is, we know that at thermal equilibrium the equilibrium density operator is expressed as,
\[ \rho_{eq} = \frac{1}{Z} \exp \left( \frac{\hbar \omega_0 \vec{I}_z}{kT} \right) \quad (A.10) \]

Here \( Z \) is the partition function equal to the \( \text{Tr}(\rho(0)) \). When \( kT \gg \omega_0 \) a Taylor series expansion of \( \rho_{eq} \) leaves only the following term,

\[ \rho_{eq} \approx \frac{1}{Z} \left( 1 - \frac{\hbar \omega_0 \vec{I}_z}{kT} \right). \quad (A.11) \]

Dropping the identity operator from our expression we are left with,

\[ \rho_{eq} \approx \beta \vec{I}_z \quad (A.12) \]

Finally with equation A.12 and Louisville-Von Neumann equation[5],

\[ \Im \hbar \frac{d\rho}{dt} = [H, \rho] \quad (A.13) \]

which describes the time evolution of the density matrix we are able to calculate the resulting NMR signal after a pulse and under internal interactions.

\section*{A.2 Evolution of Density Matrix}

We will give a simple example of how the previously developed tools are applied[4, 7]. In a simple one pulse experiment the initial density matrix has the following form

\[ \rho(0) \approx I_z. \quad (A.14) \]

\footnote{The following expression assumes that the Zeeman Hamiltonian is greater than all other interactions.}
Under the Zeeman interaction, the time dependent density operator evolves as follows,

\[ \rho(t) = \exp\left(\frac{\mathbf{S} t}{\hbar}\right) I_z \exp\left(-\frac{\mathbf{S} t}{\hbar}\right) = I_z. \]  

(A.15)

During this time the density matrix is unchanged, however, what happens during an r.f. pulse?

The r.f. Hamiltonian is expressed as

\[ H_{\text{rf}} = -\omega_1 I_z. \]  

(A.16)

The total Hamiltonian including Zeeman is

\[ H_{\text{total}} = -\omega_0 I_z - \omega_1 I_z. \]  

(A.17)

In the rotating frame \( H_{\text{total}} \) is

\[ H_{\text{total}} = -\delta \omega I_z - \omega_1 I_z. \]  

(A.18)

In the rotating frame \( \delta \omega \) is the difference between the rf field frequency and the Larmor frequency. The equilibrium density matrix in the rotating frame is unchanged. Hence, under r.f. irradiation we have \(^{16}\)

\[ \rho(t) = \exp(\mathbf{\Im} \omega_1 I_z t_p) I_z \exp(-\mathbf{\Im} \omega_1 I_z t_p). \]  

(A.19)

\(^{16}\omega_1 \gg \delta \omega.\)
Here $\omega t_p$ is the pulse angle i.e. $\pi/2$. When $\omega t_p$ is $\pi/2$ the resulting density operator is $I_y$. After the pulse is turned off the system now evolves under the Zeeman interaction, $-\delta \omega I_z$. Under this evolution the time dependent density operator is,

$$\rho(t) = \exp(\Im \delta \omega I_z t) I_y \exp(-\Im \delta \omega I_z t) = I_y \cos(\delta \omega t) + I_z \sin(\delta \omega t).$$  \hfill (A.20)

Finally, knowing that the signal is calculated as

$$S(t) = Tr(\rho I_x) + \Im Tr(\rho I_y),$$  \hfill (A.21)

along with the phenomenological addition of relaxation we come to the final expression for our signal of

$$S(t) = \exp(-t/T_2) \sin(\omega t).$$  \hfill (A.22)

The above equation shows that the signal after one pulse is sinusoidal with a frequency $\omega$. The signal also decays with the characteristic time constant $T_2$. This same treatment is expanded to multi-pulse sequences and used to calculate the resulting signal under internal interaction$^{17}$.

$^{17}$Barring that the interaction Hamiltonians are well described.
APPENDIX B

Coherence Transfer Pathways and Phase Cycling

Growing old is like being increasingly penalized for a crime you haven’t committed.

Anthony Powell

Temporary Kings

B.1 Coherence Transfer Pathways (CTP)

Coherence transfer pathways allow for a rigorous and elaborate way of picturing the evolution of the nuclear spin system under r.f. pulse irradiation. The initial step in understanding coherence transfer pathways is to group the density operators into their coherence order [4]. For $O^{17}$ this is done in the following manner.

The following treatment will entail a single nuclei. Several coupled spins can, however be treated in the same manner except the coherence are grouped according to rank and order. For a single spin the coherence are described by the following relation [4, 7],

$$-2I \leq p \leq 2I. \quad (B.1)$$

For $O^{17}$ the coherence levels are $\pm 5$, $\pm 3$, $\pm 2$, $\pm 1$ and 0, see figure A1.
When using CTP with a system that evolves under a Hamiltonian linear in $\mathcal{I}_z$ the coherence order and rank are unchanged. This is described by the following

$$\exp(\Im \Omega I_x t) I_{i,p} \exp(-\Im \Omega I_x t).$$  \hspace{1cm} (B.2)

In the above equation $\Omega$ is the angle of rotation of the magnetization and $\mathcal{I}_x$ is the Hamiltonian under which the initial density operator ($\mathcal{I}_{i,p}$) evolves. In the case where the Hamiltonian is non-linear in $\mathcal{I}_z$, the coherence order stays constant; the rank, however changes. During r.f. irradiation both rank and order are changed. This is illustrated in the following manner. If the initial density operator is,

$$\rho(0) = I_0$$  \hspace{1cm} (B.3)

and a pulse is applied, $\rho_0$ then evolves under the r.f. Hamiltonian for the duration of the pulse. The pulse has the ability to of transfer $\mathcal{I}_0$ to one of three possible coherence: $\mathcal{I}_0$, $\mathcal{I}_1$ or $\mathcal{I}_{+1}$. It is appropriate to write the following expression during the evolution time $\tau_1$ as

$$\rho(t) = a_{0,1} I_1 + a_{0,0} I_0 + a_{0,-1} I_{-1}.$$  \hspace{1cm} (B.4)

Here the coefficient contains past and current coherence order information[7]. The first number of the subscript denotes the previous coherence order and the second the current order. A graphical representation of this is shown in figure B.1.

During the time after the pulse, the spin system evolves under internal fields, chemical shift, dipolar and/or quadrupolar interactions.

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Figure B.1: (a) Central transition. (b) Inversion recovery and Echo coherence transfer pathway-IR keep all three pulses for echo remove the first pulse. Phases are identical for both sequences.

### B.2 Phase Cycling

Phase cycling allows the selection of desired coherences while leaving unwanted ones behind. This is achieved in the following manner. As mentioned in the above section after a single pulse there are several possible coherences to detect signal along. In the case of $O^{17}$ there are 11 different pathways possible. However, since there are signals that exist that are not unique (i.e. mirrored about $p=0$ coherence), we have only six unique coherences. If the receiver is a perfect detector of the observable $I_+$ then only the signal at the $p=-1$ coherence level need to considered.

The signal from each pathway is phase modulated during each pulse by the phase of that particular pulse multiplied by the $\Delta$ of coherence order during the pulse. This change of coherence is termed $\Delta p$ figure B.1. The modulated signal from this pathway is modulated in the following way
\[ S(\phi_1, \phi_2, \tau) = S(0, 0, \tau) = \exp(-3(\phi_1 - \phi_2)). \]  

(B.5)

Once \( S(\phi_1, \phi_2, \tau) \) is multiplied by the receiver phase, \( \phi_r \) in the form of \( \exp(-3\phi_r) \), before adding the signals with different pulse phases, the signal \( S(0,0,\tau) \) will always add up and never cancel. However, signals from other pathways with different phases will cancel. For complete cancellation of signal from unwanted pathways, the phase of each pulse through \( N \) steps\cite{4,7} must be cycled independently. This is achieved with the following relation

\[ \phi_i = \frac{k_i 2\pi}{N_i}. \]  

(B.6)

Here \( \phi_i \) is the phase of the \( i^{\text{th}} \) pulse, \( N_i \) the number of steps \( \phi_i \) is cycled through, and \( k_i \) spans the range \( 1, \ldots, N_i - 1 \).

For an experiment with \( n \) pulses \( N=\{1, \ldots, N_n\} \) experiments need to be conducted. Finally, to determine the number of steps for each individual pulse, the coherence order change sought must be determined. A two pulse experiment with coherences \( I_1, I_0 \) and \( I_{-1} \) will be used to illustrate how this is done. Shown in figure B.1 is the coherence transfer pathway for this example. The first pulse creates possible coherence changes \( I_0 \rightarrow I_1, I_0 \rightarrow I_0 \) or \( I_0 \rightarrow I_{-1} \). This results in the following,

\[ \Delta p_1 = +1, 0, -1 \]  

(B.7)

The other coherence must be cycled out because the \( \Delta p_1 = +1 \) coherence is the coherence of interest. This is done by selecting the next available coherence \( \Delta p_1 = -2 \). For a
\( I = 1/2 \) spin system the limit of coherence order is \( \pm 1 \), so allowed coherences beyond this limit allow no signal. Hence, recalling the relation

\[
\phi_i = \frac{k_i \, 2\pi}{N_i} \tag{B.8}
\]

\( \Delta p = 1 \) then requires a phase step of \( 2\pi/3 \)

\[
\phi_1 = 0^\circ, 120^\circ, 270^\circ. \tag{B.9}
\]

For the second pulse \( \Delta p_2 \) is

\[
\Delta p_2 = 0, -1, -2. \tag{B.10}
\]

Here \( \Delta p_2 = -2 \) is selected resulting in a step of \( 2\pi/3 \). The complete phase cycle for both pulse are as follows

\[
\begin{align*}
\phi_1 &= 0^\circ \\
&\quad 120^\circ \\
&\quad 270^\circ \\
\phi_2 &= 0^\circ \\
&\quad 120^\circ \\
&\quad 270^\circ \\
&\quad 270^\circ \\
\end{align*} \tag{B.11}
\]

The receiver phase is now calculated with the following equation.

\[
\phi_r = -\phi_1 - 2\phi_2 \tag{B.12}
\]
This phase cycle will eliminate all pathways except the one desired. Now this dissertation will give experimental phase cycle and CTPs used during the echo and inversion recovery experiments presented throughout this work.

### B.3 Coheneence Trafer Pathways and Phase Cycling for Echo Sequence

Shown in figure B.1 is the CTP and pulse sequence used for the echo experiment. The notation used is as follows: for pulses the Tecmag notation is

\[
\phi_1 = \begin{bmatrix}
0 & 0 \\
8 & 0 \\
0 & 12 \\
8 & 12 \\
12 & 12 \\
4 & 12 \\
12 & 8 \\
4 & 8 \\
\end{bmatrix}, \quad \phi_2 = \begin{bmatrix}
0 & 0 \\
8 & 0 \\
0 & 12 \\
8 & 12 \\
12 & 12 \\
4 & 12 \\
12 & 8 \\
4 & 8 \\
\end{bmatrix}
\]

(B.13)

and for the receiver

\[
\phi_r = \begin{bmatrix}
0 \\
2 \\
2 \\
0 \\
1 \\
3 \\
3 \\
1 \\
\end{bmatrix}.
\]

(B.14)

In Cartesian coordinate the pulses are represented as 0=X, 8=\overline{X}, 4=Y and 12=\overline{Y} and the receiver as 0=X, 1=Y, 2=\overline{X} and 3=\overline{Y}. For the desired pathway, \(p_0 \rightarrow p_{+1} \rightarrow p_{-1}\), the following receiver phase is,

\[
\phi_r = -\phi_1 + 2\phi_2.
\]

(B.15)

\(^{18}\)The overline denoted minus X and Y
Now changing the pulse notation to the acquisition notation for book keeping

\[
\begin{array}{ccc}
0 & 0 & 0 \\
2 & 0 & 3 \\
0 & 2 & 0 \\
1 & 3 & 3 \\
3 & 2 & 3 \\
1 & 2 & 2
\end{array}
\]

\[\phi_1 = \begin{array}{c} 2 \\ 3 \\ 1 \\ 3 \\ 2 \\ 2 \end{array}, \quad \phi_2 = \begin{array}{c} 2 \\ 3 \\ 1 \\ 3 \\ 2 \\ 2 \end{array}, \quad \phi_3 = \begin{array}{c} 2 \\ 3 \\ 1 \\ 3 \\ 2 \\ 2 \end{array} \]  \quad (B.16)

Using the equations A-12 and A-13 shows that the appropriate coherence was selected.

The same will be illustrated for the inversion recovery sequence.

### B.4 Coherence Transfer Pathways and Phase Cycling for Inversion Recovery Sequence

Shown in figure B.1 is the coherence and three pulse sequence for the inversion recovery experiment. Working in the receiver notation gives the following

\[
\begin{array}{ccc}
0 & 0 & 0 \\
2 & 2 & 0 \\
0 & 0 & 3 \\
2 & 1 & 3 \\
0 & 3 & 2 \\
2 & 1 & 2
\end{array}
\]

\[\phi_r = \begin{array}{c} 0 \\ 2 \\ 2 \\ 0 \\ 1 \\ 3 \\ 3 \\ 1 \end{array} \]  \quad (B.17)

The receiver phase is again

\[
\begin{array}{c}
0 \\
2 \\
2 \\
0 \\
1 \\
3 \\
3 \\
1
\end{array}
\]  \quad (B.18)
The equation for the receive is

\[ \phi_r = 0 \times \phi_1 + -\phi_2 + 2\phi_3. \]  \hspace{1cm} (B.19)

Using the equations A-12 and A-13 shows that again that the appropriate coherence was selected.
BIBLIOGRAPHY


