INVESTIGATIONS OF THE STATE OF WATER IN VARIOUS POROUS MEDIA WITH NUCLEAR MAGNETIC RESONANCE RELAXATION

A Dissertation in

Chemistry

by

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ABSTRACT

Deuterium NMR relaxation experiments, low temperature deuterium NMR lineshape analysis, and FTIR spectra are consistent with a new model for solid state jump dynamics of water in \(^2\)H\(_2\)O-synthesized kanemite, \(^2\)H\(_2\)O-hydrated Na\(^+\)-Zeolite A and \(^2\)H\(_2\)O hydrated tricalcium silicate. Exchange occurs between two populations of water: one in which water molecules are directly coordinated to sodium ions and experience C\(_2\) symmetry jumps of their OH bonds, and a population of interstitial water molecules outside the sodium ion coordination sphere that experience tetrahedral jumps of their OH bonds. For both samples the C\(_2\) jump rate is much faster than the tetrahedral jump rate. \(^2\)H NMR relaxation experiments match well with the fast exchange regime of the model over a wide range of temperatures, including room temperature and above. For hydrated Zeolite A, the kinetic activation parameters for the tetrahedral and C\(_2\) symmetry jumps are \(\Delta H_{tet}^i = +17\) kJ/mol, \(\Delta S_{tet}^i = -109\) J/(mol K), \(\Delta H_{C2}^i = +19\) kJ/mol, and \(\Delta S_{C2}^i = -20\) J/(mol K). For kanemite, \(\Delta H_{tet}^i = +23\) kJ/mol, \(\Delta S_{tet}^i = -69\) J/(mol K), \(\Delta H_{C2}^i = +23\) kJ/mol, and \(\Delta S_{C2}^i = -11\) J/(mol K).

Additional evidence is shown that supports the hypothesis that a phase change of the water used for the hydration of tricalcium silicate is at least partly responsible for the initial hardening and strength gain of this type of cement paste. This process is shown to be reversible and fits well with other mechanical strength tests.
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Chapter 1

Introduction

Water is one of the most physically and chemically unusual naturally occurring compounds. Its anomalous behavior has been the subject of both elegant and controversial studies [1-7]. A few particularly atypical properties of water are its unusually high melting point, boiling point, and critical point compared to other molecular oxides. Unlike most pure substances its density increases upon heating from 0 °C to 3.984 °C and then decreases. The surface of water is denser than the bulk [8, 9]. And of particular interest it has been found that it may be found in the solid state, even in an extended ice-like structure, at atmospheric pressure well above 0 °C.

The properties of water have long been a subject of debate in scientific disciplines ranging from materials engineering to theoretical physics. The behavior of water in restricted geometries [10] and on solid surfaces [11] is particularly controversial. In this thesis deuterium nuclear magnetic resonance (2H-NMR) is used to show that the water in several important materials is in the solid state at room temperature and above. In particular Na-Zeolite-A, a common desiccant and well known catalyst has been studied. An investigation of the mineral kanemite, a layered silicate known as a phyllosilicate as well as tricalcium silicate, the main ingredient/clinker phase found in Portland cement have been carried out. Tricalcium silicate is most responsible for the setting and overall strength of cement. This thesis proposes a model describing the nuclear relaxation of the deuterons in water in which the O-2H bonds of the water experience tetrahedral jumps
that are in fast exchange with a population that experience faster C2 symmetry jumps. This relaxation model for water in porous materials is named the C2TET model.

Although water is one of the most abundant naturally occurring compounds found on earth, it is the least well understood. In particular, Hynes and Laage have hypothesized that even in the liquid state water can form dynamic hydrogen bond networks [12]. They propose a molecular jump system for liquid state water and suggest that this motion is concerted in nature rather than successive. They go on to postulate that the mechanism involves large amplitude 60° jumps rather than the small step isotropic rotational diffusion [13]. These new ideas are exciting and controversial, and in fact align themselves with this dissertation quite well.

Many of the anomalies associated with water are derived from its ability to form dynamic hydrogen bond networks [13]. The network configuration is constantly changing because of the rotations of individual water molecules [13]. The reorientation of a water molecule is critical in many processes including proton transport in fuel cells, proton transfer, and in proteins and biochemistry. These transfer or transport steps are often rate limiting [13]. Hydration of polymers, macromolecules and proteins is also critical for proper protein and polymer function as well as for the strengthening of Portland cement and the formation of certain minerals and zeolites.

Instead of studying pure bulk water, this research investigates water within several hydrated porous or layered silicate and aluminosilicate materials. The naturally occurring mineral, kanemite (NaHSi2O5•3H2O); Linde type 4A or more commonly,
sodium zeolite A (Na$_{12}$[Al$_{12}$Si$_{12}$O$_{48}$]·27H$_2$O), and tricalcium silicate (Ca$_3$SiO$_5$), the main clinker phase of Portland cement.

1.2 Dynamics of Water in Crystalline Hydrates.

For some crystalline hydrates such as K$_2$C$_2$O$_4$·2H$_2$O, LiO$_2$H·2H$_2$O, and Sr(HCOO)$_2$·22H$_2$O, rigid powder $^2$H NMR spectra are observed at room temperature (Fig. 1.1).

In other crystalline hydrates such as Li$_2$SO$_4$·2H$_2$O, Ba(ClO$_3$)$_2$·22H$_2$O, and CaSO$_4$·22H$_2$O, characteristic powder line shapes in $^2$H NMR spectra at room temperature show that the two $^2$H nuclei in a given hydrate water molecule interchange positions rapidly ($v > 10^6$ s$^{-1}$)[14, 15]. This is achieved either by rapid 180° jump motions of the intact water molecule about the C$_2$ symmetry axis, or by jumps of the $^2$H nuclei between the two equivalent covalent bonds to oxygen (Fig. 1.2) [14, 15].

However, if the latter hydrates are cooled to sufficiently low temperatures, the jump rate slows sufficiently to yield a rigid powder line shape [14, 15]. The two types of behavior therefore actually represent a continuum in which the measured $C_2$ symmetry jump rate is a direct reflection of the lattice energy of the hydrate and consequently the mobility of the O-$^2$H bonds at a given temperature.

In contrast, dynamics of pure water in the solid state (i.e. ice) has distinctly different dynamics. In ice that forms at the freezing point at atmospheric pressure (ice $I_h$), both $^1$H and $^2$H NMR techniques show that the O-H covalent bonds experience tetrahedral jumps around their molecular oxygen atom [17, 18]. The jumps are thought to be caused by
diffusion of Bjerrum defects in the ice lattice [18]. The jump rate is sufficiently fast even at 10 °C below the freezing point that the solid state $^1$H or $^2$H NMR spectrum shows a single isotropic peak visually indistinguishable from that of liquid $^{1,2}$H$_2$O (Fig. 1.3) [18].

1.3 Kanemite

Kanemite (NaHSi$_2$O$_5$•3H$_2$O) [19, 20, 21] is a layered silicate sheet mineral that has the structure of Fig. 1.4. It was first discovered occurring naturally in Lake Chad, Africa [22]. Kanemite was used as a simple model to represent an alkali silicate hydrate (gel) commonly found in concrete under attack by sodium salts [38]. The gel is expansive and destructive and can cause hazardous conditions due to spalling and pothole formation [24]. It can be synthesized in a variety of ways but most commonly by dispersing Na$_2$Si$_2$O$_5$ in water [23]. Kanemite is a building block for many mesoporous (pores ranging from 2 nm to 50 nm) materials.

Kanemite consists of alternating single layer sheets of [Si$_2$O$_4$OH]$_n$$^{n-}$ and hydrated sodium ions [19]. The silicon in the silicate layers is known from solid-state $^{29}$Si NMR to be exclusively Q$^3$. The fourth bond for each silicon atom is to alternating –OH or –O$^-$ groups. Interlayer Na$^+$ ions in kanemite are each coordinated by up to six water
Fig. 1.1: A calculated rigid $^2$H powder pattern with a $\text{qcc} = 216$ kHz and $\eta = 0$. $\nu_{\text{motion}} \ll \text{qcc}$. 9 kHz of Gaussian line broadening was applied. The powder average was done with a list of 5253 $\alpha, \beta$ pairs, and a weighting of each pair according to the REPULSION [16] method.
Fig. 1.2: A calculated powder pattern for $\text{C}_2$ motion with a rigid $\text{qcc} = 213$ kHz, $\eta = 0$, at a $^2\text{H-O}^2\text{H}$ bond angle of $\frac{1}{2}$ the tetrahedral angle. 4kHz of Gaussian line broadening was applied. The powder average was done as in Fig. 1.1.
Fig. 1.3: Experimental “frozen” D$_2$O in zeolite-A quadrupole echo spectrum at 251K.
molecules, but may also coordinate to the silicate layers. The hydrated Na$^+$ ions are fixed in the crystal lattice as shown by both X-ray diffraction and solid-state $^{23}$Na NMR. Reasonable positions for the Na$^+$ coordinated water molecules in kanemite could be determined from residual electron densities in the X-ray derived structure (Fig. 1.4), but additional water is known to be located within the puckered region of the silicate sheets [19].

1.4 Zeolite-A

Zeolites are aluminosilicate minerals that are microporous due to their nanostructures [25]. A microporous structure is a structure with pores smaller than 2 nm [25]. As many as 175 different zeolitic frameworks have been identified as of January 2008, eighty of which are naturally occurring [25].

Due to the porous nature and negative charge that zeolites’ possess they can coordinate various cations in their cage, usually Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$ as well as others. These positive ions are not tightly bound and as a result are easily exchanged with other cations to facilitate functional changes of the zeolite such as water capacity, molecular sieve properties and others. Zeolites are known as molecular sieves because they have the physical property of being able to separate molecules based on size exclusion.

Zeolites are often used in ion exchange columns for water purification systems. They are also suitable for the removal or separation of gases such as H$_2$O, CO$_2$, and SO$_2$ from natural gas. Zeolites are also used as catalysts in the petroleum industry as the protonated form of zeolites act as excellent solid state acids.
Fig. 1.4: A cross section of the crystal structure of kanemite [19, 26]: O : red, H : white, Si : gray, and Na : purple. Water molecules are octahedrally coordinated to sodium ions, as shown by the broken blue lines. The structure does not show missing water molecules that are expected in the puckered regions of the silicate sheets.
Na-Zeolite-A was chosen for this study because it is widely available and reproducibly synthesized. It is an extremely hygroscopic material that easily incorporates water into its structure after drying at a suitable temperature. It is so hydrophilic that one only needs a bell jar with a Petri dish of water inside to hydrate the zeolite. Also, its pores hold only a few layers of water in the supercage and less than that in the sodalite cages and channels (Fig. 1.5). Zeolite-A is a well known desiccant and is often used in machinery and electronics to remove any water that may become a problem. It has been used to replace phosphates in common household detergents, acting as a water softener by exchanging the Ca\(^{2+}\) in the water for the Na\(^{+}\) in the cage, and therefore does not have negative effects on the environment as phosphates do having the molecular formula of \((\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\cdot 27\text{H}_2\text{O})\). It is a caged structure made up of a super cage and smaller sodalite cages with interconnecting tunnels. (Fig.1.5a) The sodalite cage has an inner diameter that varies from 9.07 Å to 9.89 Å (Fig.1.5b) depending on the direction of measurement. The supercage has an inner diameter (oxygen to oxygen distance) of 14.05 Å (Fig. 1.5c). The channels interconnecting the cages have a diameter of 3.8 Å and a length of 5.6 Å (Fig 1.5d) [27].

1.5  **Tricalcium Silicate**

The kinetics and microstructural evolution of tricalcium silicate (\(\text{Ca}_3\text{SiO}_5\)) hydration are often studied by cement chemists in order to gain insight into the synergistic physical and chemical processes taking place during the setting and hardening of cement pastes (Fig. 1.6). A second but less rigorous reason for studying a simplified
model system is based on the assumption that reactions observed in the simple system can be used to explain similar but more complex reactions taking place in the more complex system known as hydrating Portland cement. That is to say, the systems are chemically different, yet they do seem to have parallel sequences of reaction.

Early studies, such as those by Flint and Wells [28] and Roller and Ervin [29] generally focused on delineating the chemistry of the solution phase in equilibrium with various combinations of lime and silica mixed with water. Although the work was groundbreaking, it left many questions about the nature of the solid phases unanswered. Once Kondo and Ueda [30] demonstrated that isothermal calorimetry could be used to track heat evolution as a function of reaction time, the research community realized that the hydration process was far more complex than they had imagined. Researchers began to initiate studies that, to a greater extent, emphasized the crystal chemistry, kinetics and microstructure of the solid hydrates that were forming in the solution.

Conduction calorimetry evolved and it became clear that something odd was happening. The reaction of tricalcium silicate and Portland cement mixed with water had an induction period. The cause of this “inactivity” or dormancy makes it possible to mix and place Portland cement paste before it sets, but it also adds a modeling complexity that has not yet been resolved. If the processes occurring prior to and during the induction period are neglected for the time being, calorimetry tells us that the dormancy period is followed by a so called acceleratory period during which large amounts of heat are given off, the cement sets and then hardens. This process normally occurs 4-5 hours after mixing and continues through 18-24 hours. During this time period the solution
Fig. 1.5: The cage structure of hydrated Zeolite A, $\text{Na}^+$ form [27], with water and $\text{Na}^+$ omitted for clarity. Dehydrated Zeolite A ($\text{Na}^+$) has the same structure. The figures were prepared with program Mercury (freeware available from the Cambridge Crystallographic Data Centre) [26]. Atom key: $\text{O}$ : red, $\text{Si}$ : gray, $\text{Na}^+$: purple, and $\text{Al}$ : brown. a. skeletal view of the Zeolite A cage structure showing characteristic 6-membered ring sodalite connected by 4-membered connectors. b. expansion ball and stick view of a sodalite cage c. expansion ball and stick view of the large central cage d. expansion ball and stick view of a 4-ring connector between cages.
Fig. 1.6: Microstructures of C₃S pastes. A= anhydrous. #3= 240 min. #7= 385 min. #8= 485 min. Massive foils present 385 minutes and later.
composition changes dramatically [31, 32] as C-S-H and Ca(OH)$_2$ precipitate and form growing networks of interlocking foils interspersed with larger Ca(OH)$_2$ crystals [33].

1.6 Models of Ca$_3$SiO$_5$ hydration

A hydration model that has stood the test of time is one originally proposed by Taylor [34]. His model and modifications thereof generally deal with the structure and composition of the phases that form during and long after the acceleratory period. The phases that form within a few minutes of mixing and their causative role in initiating the induction period are generally not discussed in detail. Although there is a burst of heat during the first 15 minutes after mixing [28], subsequent heat evolution typically decreases to very low values for the next 4-6 hours as active dissolution, precipitation and growth slow and reactions grind to a halt. ESCA data for the first few minutes of C$_3$S hydration [35-38] suggest that the surface of the C$_3$S undergoes an almost immediate transition from Ca-rich to Ca-poor and then back again to Ca-rich in a matter of 15 minutes or so. Whatever is happening causes the solid C$_3$S in the system to become inactive (i.e. become nearly insoluble). Various theories (most often evoking some type of barrier layer) have been put forth, but the related issues of what causes the barrier layer and what causes it to end are still not fully resolved. There is however almost universal agreement that once the induction period ends and the acceleratory period begins, there is a resurgence of chemical activity, a layer structured C-S-H having a tobermorite/jennite-like structure and Ca(OH)$_2$ crystals nucleate, grow and interlock [39]. Evidence offered in support of this model are 1) the large increase in the rate of heat liberation (an exothermic
process) during the early part of the acceleratory period, and 2) the fact that the paste sets about \(\frac{1}{2}\) way through the acceleratory period.

This thesis will cover all materials discussed within the introduction. A number of techniques, specifically \(^2\text{H NMR},\) will be used to probe the state of water within all of these materials. Complimentary techniques such as FTIR, AFM, isothermal calorimetry, and ASTM testing methods will also be used to support the model presented in this thesis.
References


4. J. Donohue, 1969, **166**, 1000-1002.


Chapter 2

Introduction to Nuclear Magnetic Resonance Theory

2.1 Introduction to NMR

Nuclear magnetic resonance (NMR) is one of the most powerful tools available to a chemist today. Not only can one use NMR to elucidate molecular structures of small organic molecules or a protein approaching 50 kDa, NMR is also a useful tool when investigating molecular dynamics of both solids and liquids. NMR can also be used to study bulk molecular transport of molecules with translational diffusion experiments. Imaging parts of the body, animals, plants, and even cells is possible through NMR using gradients of known direction and strength. This is known as magnetic resonance imaging (MRI).

Through the analysis of hyperfine structure of spectral lines in 1924, Pauli first proposed that nuclei must possess an intrinsic spin parallel to its magnetic moment [1]. The energy level spacings observed were indeed quite small [1]. In 1931 Rabi and Breit used the deflection of an atomic beam in an external magnetic field to calculate the magnetic moments of both hydrogen and deuterium through measurement of their ground state hyperfine structure [2]. The splitting of the spectral line of both UV and visible light was the first indirect evidence of nuclear magnetic moments and quantized nuclear spin angular momentum [2]. In 1940 Felix Bloch used beam techniques to prove the existence of a magnetic moment for the neutron [3]. Due to the difficulties and
inaccuracies associated with the molecular beam studies, Bloch proposed using radio-
frequency methods to detect an ensemble of nuclear magnetic moments [3]. It was not
until 1946 that Felix Bloch and Edward Purcell began to independently refine the
technique that Bloch named nuclear induction [4, 5].

Because the Zeeman levels of nuclear spins are only slightly perturbed by other
interactions there are “exact” mathematical solutions for some types of NMR
experiments. Simulations carried out in a number of ways can match experimental
results. Simple NMR experiments on an ensemble of uncoupled spin $\frac{1}{2}$ nuclei can be
described classically through the Bloch equations and vector diagrams. One may extend
this classical analysis to include magnetic field gradients and may even use it to describe
diffusion NMR.

### 2.2 Introduction to theory: a classical perspective

Classically, one can consider the nucleus to be a spinning positive electric charge
with a specific mass, $m$, and spin angular momentum, $L$. The spinning charge will create
a magnetic dipole moment for the nucleus in the same manner that a current traveling
through a loop of conductive wire will create a magnetic dipole moment, $\mu$. The classical
derivation yields [6],

$$\frac{\mu}{4\pi} = \gamma L$$

(Eq. 2.1)
where classically $\gamma = \frac{Ze}{2mc}$ and $e$ is the charge of the nucleus, $Z$ is the atomic number, $m$ is the mass of the nucleus, $c$ is the speed of light, and $\mu$ is the magnetic dipole moment of the nucleus.

The classical derivation shows that the nucleus will have a magnetic moment that is proportional to the nuclear spin angular momentum, and that the gyromagnetic ratio is proportional to $Z/m$. However, this prediction is inconsistent with experimental observations. The gyromagnetic ratio does not generally increase with increasing $Z$. Nuclei such as $^{16}$O and $^{12}$C have no magnetic moment at all. This is a shortcoming of the classical description of NMR. Nevertheless, the classical approach does yield some very useful results.

Eqn. 2.1 is one derivative away from Newton’s second law: [7]

$$\frac{dL}{dt} = N \tag{Eq. 2.2}$$

which states that the rate of change for angular momentum, $L$, equals the torque, $N$. In a magnetic field, $B_0$, the torque is given by:
Using [Eqn. 2.4] and assuming $\mathbf{B}_o$ to be aligned with the laboratory $z$ axis, it follows that the spin angular momentum precesses about the external magnetic field (Z-axis) with angular frequency, $\omega_o$:

$$\omega_o = -\gamma \mathbf{B}_o$$  \hspace{1cm} (Eq. 2.5)
with Eqn. 2.4 this yields:

$$\frac{dM}{dt} = M \times \gamma B_o$$

(Eq. 2.7)

The classical energy of $\mu$ or $M$ in $B_o$ is given by:

$$E = \mu \cdot B_o = -\gamma L \cdot B_o$$

(Eq. 2.8)

The energy of the scalar (dot) product of [Eqn. 2.8] is in $\hbar$ units.

2.3 Signal Detection in NMR

Nuclear magnetic resonance is one of the only spectroscopic techniques in which the source of excitation and the receiver for the signal are the same. Hahn realized in 1953 that high power short pulses of oscillating radiofrequency fields could uniformly excite a wide range of frequencies simultaneously [23]. This eliminated the need for continuous wave NMR where the frequency is held constant and the magnetic field is swept continuously [8]. When the flip angle of this applied pulse is equal to $\pi/2$ the system yields pure transverse (detectable) magnetization. The
Fig. 2.1: Larmor precession of a nuclear magnetic moment.
precession of the transverse magnetization induces an oscillating voltage within the coil that is transmitted back to and processed in the spectrometer. Without other internal and external perturbations that promote relaxation (which will be discussed in the next chapter) the transverse magnetization would remain indefinitely.

Magnetic field inhomogeneities and local fluctuations drive the transverse magnetization back to equilibrium (i.e. zero) with time constant $T_{2}^*$. This is why a free induction decay (FID) is a decaying cosine or sine wave. The NMR FID signal itself is given by:

$$S(t) = \cos(\Delta \omega t) \exp\left(\frac{-t}{T_{2}^*}\right)$$  \hspace{1cm} (Eq. 2.9)

$\Delta \omega$ is the frequency offset of the system and contains chemical shift information for each unique chemical environment. The NMR signal contains contributions from all of the excited nuclei. Very important to our research is the fact that local magnetic field oscillations near the Larmor frequency drive the longitudinal (Z) magnetization back to equilibrium with time constant $T_1$.

The data are collected in the time domain, but Fourier analysis [9] is used to transform from the time domain into the frequency domain. Computers have some limitations when trying to handle these integrals. With newer instrumentation the signal is first digitized and then the computer uses a fast Fourier transform (FFT), which is a numerical matrix implementation of the Fourier transform [22],

$$F(\omega) = \int_{-\infty}^{\infty} dt \, S(t) \exp(i \omega t)$$  \hspace{1cm} (Eq. 2.10)
The reproducibility of the NMR signal compared to the randomness of noise allows one to improve the signal to noise ratio (S/N) by accumulation of multiple transients [21].

2.4 The Bloch Equations and the Vector Model

The Bloch equations are a classical treatment of the behavior of the bulk nuclear magnetization vector $\mathbf{M}$. They describe the motion of the magnetization under a static magnetic field, $\mathbf{B}_0$, and effects of radiofrequency pulses. One may express the Bloch equations as a single matrix equation,

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} - \begin{pmatrix} \frac{1}{T_2} & 0 & 0 \\ 0 & \frac{1}{T_2} & 0 \\ 0 & 0 & \frac{1}{T_1} \end{pmatrix} (\mathbf{M} - \mathbf{M}_o)$$

(Eq. 2.11)

where with RF on: $\mathbf{B} = \{ B_x \cdot \cos(\omega_{RF}t + \phi), B_y \cdot \sin(\omega_{RF}t + \phi), B_z \}$

and with RF off: $\mathbf{B} = \{0,0,B_z\}$

where $\mathbf{M}_o$ is the equilibrium magnetic moment, $\{0,0,\mathbf{M}_{eq}\}$. The 3 x 3 matrix is the empirical operator that describes the effects of $T_1$ and $T_2$ relaxation. The Bloch equations, although classical in design, are still an excellent way of visualizing the motion of macroscopic magnetization under simple conditions.
The Bloch equations can be solved in either the laboratory or interaction frame of reference. For the laboratory frame of reference in the absence of a radiofrequency pulse (i.e. $B_1 = 0$, $B = \{0,0,B_0\}$):

\[
\frac{dM_x(t)}{dt} = B_0 \gamma M_y - \frac{M_x}{T_2}
\]

\[
\frac{dM_y(t)}{dt} = -B_0 \gamma M_x - \frac{M_y}{T_2}
\]  
(Eqn. 2.12)

\[
\frac{dM_z(t)}{dt} = \frac{M_z - M_0}{T_1}
\]

Eqn. 2.12 shows that $M_z$ relaxes as $exp[-t/T_1]$ while both $M_x$ and $M_y$ relax as $exp[-t/T_2]$.

In the rotating (or interaction) frame of reference the equations are simplified by choosing a reference frame that rotates around the z axis at $\omega = \omega_{RF}$. This changes the effective magnetic field to $B_{ROT} = \left\{ \cos(\phi) B_1, \sin(\phi) B_1, -\frac{\delta}{\gamma} \right\}$ where $\delta = \omega_0 - \omega_{RF}$. The $B_1$ field is static in this frame and, and $B_0$ disappears as $\delta$ goes to 0. Any transverse magnetization will precess near the same frequency as $\omega_{RF}$, so relative to this frame, the frequency $\delta$ will be in the kHz range instead of the MHz range. There are no changes in the components of $M$ along the z direction since the new reference frame rotates around the z axis.
The mathematics of the rotating frame are the same as for the laboratory frame. The principle of relativity requires this to be true [24]. A single pulse experiment on resonance ($\delta = 0$) (Bloch experiment) in the rotating frame may be graphically expressed as shown in Fig. 2.2 and 2.3. The visualization of the macroscopic magnetization vector derived from the Bloch equations is often called the vector model of NMR.

\[
M_x = \exp\left(\frac{-t}{T_2}\right)\left[ M_x(0)\cos(\delta t) + M_y(0)\sin(\delta t) \right]
\]

\[
M_y = \exp\left(\frac{-t}{T_2}\right)\left[ -M_x(0)\sin(\delta t) + M_y(0)\cos(\delta t) \right]
\]

(Eq. 2.13)

where $\delta = \omega_0 - \omega_{rf}$
Fig. 2.2: A typical on-resonance Bloch decay experiment showing $T_2^*$ relaxation.

Fig. 2.3: Vector diagram describing the motion of the macroscopic magnetization of a spin $\frac{1}{2}$ system at various stages during the application of a $\pi/2$ RF pulse along the X axis of the rotating frame. By the right hand rule convention [21] all of the magnetization lies along the $-y$ axis immediately after the pulse.
2.5 Density matrix representation in NMR

The quantum mechanics of ensembles of nuclear spins is elegantly represented in the density operator. The density operator describes the quantum state of the spin ensemble without individual knowledge of spin states [21]. The Liouville von Neumann equation describes the time evolution of the density operator and is derived directly from the time dependent Schrödinger wave equation [21].

For NMR, the most convenient basis set in which to express the density operator are the eigenstates of the Zeeman Hamiltonian. These are expressed in terms of the spin angular momentum eigenstates, \( |I,m\rangle \)

\[
I^2 |I,m\rangle = \left( I(I+1)\right) |I,m\rangle \\
I_z |I,m\rangle = m |I,m\rangle \\
I^+ |I,m\rangle = \{I(I+1) - m(m+1)\}^{1/2} |I,m+1\rangle \\
I^- |I,m\rangle = \{I(I+1) - m(m-1)\}^{1/2} |I,m-1\rangle
\] (Eq. 2.14) (Eq. 2.15)

The \( I_z \) and \( I^2 \) operators yield eigenvalues \( m \) and \( I(I+1) \) respectively. The ladder operators \( I^+ \) and \( I^- \) raise or lower the state by unity.

These operators act on the ket \( |I,m\rangle \) to return a different ket state and thus the solutions are not eigenvalues as they were previously in [Eqn. 2.14]. One may convert to Cartesian operators leaving:
The spin angular momentum operators are conveniently expressed in matrix form:

\[ I^+ = I_x + iI_y \]
\[ I^- = I_x - iI_y \]
\[ I_x = \frac{I^+ + I^-}{2} \]
\[ I_y = \frac{I^+ - I^-}{2i} \]  \hspace{1cm} \text{(Eq. 2.16)}

The spin angular momentum operators are conveniently expressed in matrix form:

\[
I_z = \begin{pmatrix}
\langle \frac{1}{2}, \frac{1}{2} | I_z | \frac{1}{2}, \frac{1}{2} \rangle & \langle \frac{1}{2}, \frac{1}{2} | I_z | \frac{1}{2}, -\frac{1}{2} \rangle \\
\langle \frac{1}{2}, -\frac{1}{2} | I_z | \frac{1}{2}, \frac{1}{2} \rangle & \langle \frac{1}{2}, -\frac{1}{2} | I_z | \frac{1}{2}, -\frac{1}{2} \rangle
\end{pmatrix}
\]  \hspace{1cm} \text{(Eq. 2.17)}

Orthonormality and Eqn. 2.14 yield:

\[
I_z = \begin{pmatrix}
\frac{1}{2} & 0 \\
0 & -\frac{1}{2}
\end{pmatrix}
\]  \hspace{1cm} \text{(Eq. 2.18)}
Similarly and using Eqs. 2.15:

\[
I^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}
\]

(Eq. 2.19)

\[
I^- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}
\]

From these one can express \(I_x\) and \(I_y\) in matrix form using Eq. 2.16:

\[
I_x = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}
\]

(Eq. 2.20)

\[
I_y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix}
\]

The reduced density matrix for a nuclear spin system under equilibrium conditions is easily calculated because it is determined by classical thermal energy partitions:
where the Zeeman Hamiltonian $H_z$, is given by $H_z = -\gamma B_o I_z$. At sufficiently high temperatures, one may approximate the exponentials with the first two terms of the Taylor series expansion to yield:

$$\rho_{eq} = \frac{\exp \left[-\frac{\hbar H_z}{kT}\right]}{\sum_k \langle k | \exp \left[-\frac{\hbar H_z}{kT}\right] | k \rangle}$$  \hspace{1cm} \text{(Eq. 2.21)}$$

where $\rho_{eq}$ is the equilibrium density matrix.

More generally for an ensemble of $N$ spins with arbitrary $I$:

$$\langle m_{z_{eq}} \rangle = \frac{\hbar^2 \gamma^2}{4kT}$$ \hspace{1cm} \text{(Eq. 2.23)}$$

The nuclear spin system is only weakly coupled to the rest of the universe through a few interactions (Hamiltonians). Because the Zeeman Hamiltonian ($H_z$) is dominant in
all cases except for very strong quadrupolar interactions, the other interactions
(quadrupolar, chemical shift, coupling, etc…) may be treated as perturbations to \( H_z \).

The Zeeman interaction, \( H_z \), is not large compared to those encountered in other
spectroscopic techniques, and is why NMR is inherently an insensitive technique. The
equilibrium spin density matrix reflects the small population difference for a spin \( \frac{1}{2} \)
system.

\[
\rho_{eq} = \begin{bmatrix}
\frac{1}{2} + b & 0 \\
0 & \frac{1}{2} - b
\end{bmatrix}
\]  
(Eq. 2.25)

Where \( b = \frac{\gamma h B_z}{2kT} \) and represents the small population difference between the two
substates. This is the only part of the density matrix that yields an NMR signal, so one
may ignore the diagonal \( \frac{1}{2} \) terms and simplify to yield the reduced density matrix
pertinent for NMR:

\[
\rho_{NMR} = \begin{bmatrix}
b & 0 \\
0 & -b
\end{bmatrix}
\]  
(Eq. 2.26)

The part of the spin equilibrium density operator giving rise to an NMR signal is thus:

\[
\rho_{NMR} = 2bI_z
\]  
(Eq. 2.27)
\( \rho_{\text{NMR}} \) will be perturbed by any Hamiltonians with transverse components such as the radiofrequency Hamiltonian, \( H_{\text{rf}} \).

### 2.6 The Liouville von Neumann equation of motion

The Liouville von Neumann (LVN) equation is the master equation that determines the time dependence of the density operator in response to applied RF and internal Hamiltonians.

Ignoring relaxation, which will be described in the next chapter; the LVN equation is:

\[
\frac{d}{dt} \rho_{\text{NMR}}(t) = -i \left( \frac{\hbar}{\hbar} \left[ H(t), \rho_{\text{NMR}}(t) \right] \right)
\]

(Eq. 2.28)

Or in units of frequency,

\[
\frac{d}{dt} \rho_{\text{NMR}}(t) = -i \left( \left[ H(t), \rho_{\text{NMR}}(t) \right] \right)
\]

or

(Eq. 2.29)

\[
\frac{d}{dt} \rho_{\text{NMR}}(t) = -i \left( H \cdot \rho - \rho \cdot H \right)
\]

Where the dot indicates the matrix product.

Incorporating relaxation, the equation becomes:
\[
\frac{d}{dt} \rho_{NMR}(t) = -i \left[ H(t), \rho_{NMR}(t) \right] - \hat{\Gamma} \left( \rho_{NMR}(t) - \rho_{eq, NMR}(0) \right) 
\]  
(Eq. 2.30)

where \( \hat{\Gamma} \) is the relaxation superoperator.

In NMR there are two main methods to solve the Liouville von Neumann equation. The first method solves the equation through commutation relations. This is convenient for liquid state NMR spectroscopy of spin \( \frac{1}{2} \) nuclei in liquids. The commutator approach is the basis of the product operator formalism [13] that is widely used to describe multi-pulse experiments on \( j \)-coupled spin \( \frac{1}{2} \) nuclei in the liquid state. Solid state NMR spectroscopists usually solve the LVN equation using the density matrix method.

### 2.7 Rotations of Spin Operators

Because of the anisotropic nature of many of the interactions in solid state NMR irreducible or Cartesian tensors must be used to calculate the Hamiltonians. Rotations of the principal axis system of the interaction Hamiltonian are used to bring the PAS into coincidence with a new reference frame, often a crystal fixed frame, or the main magnetic field. The transformation to the new frame may be carried out by three rotations about successive Cartesian axes \( z, y', \) and \( z'' \). Euler angles \((\alpha, \beta, \gamma)\) are used to describe these rotations. The three rotations are most easily visualized as follows: an initial rotation around the \( z \) axis of the PAS by \( \alpha \) followed by a second rotation by \( \beta \) around the new \( y' \) axis followed by a third rotation, \( \gamma \), around the new \( z'' \) axis. It can be shown that this is
equivalent to rotations about the original PAS axis system in reverse order [14]. The mathematical representation is:

$$\hat{R}(\alpha, \beta, \gamma) = \exp(-i\alpha \hat{I}_z) \exp(-i\beta \hat{I}_y) \exp(-i\gamma \hat{I}_z)$$  \hspace{1cm} \text{(Eq. 2.31)}$$

The coordinate transformation is given by [13, 14]:

$$A'_{kq} = R(\alpha, \beta, \gamma)A_{kq} R^{-1}(\alpha, \beta, \gamma)$$ \hspace{1cm} \text{(Eq. 2.32)}$$

where $A'_{kq}$ is the tensor in the new frame and $A_{kq}$ is the tensor in the original frame. The same transformation can be more efficiently carried out using Wigner rotations:[14]

$$A'_{kq} = \sum_{p=-k}^{+k} A_{kp} D^k_{pq}(\alpha, \beta, \gamma)$$ \hspace{1cm} \text{(Eq. 2.33)}$$

$D^k_{pq}$ is defined as:
and are described explicitly by Mehring in Table 2-1 [17, 14, 20]. These are known as Wigner rotations and are used often in solid state NMR. Figure 2.4 illustrates the three Euler rotations necessary to bring an arbitrary PAS into coincidence with a new coordinate system.

**2.8 Interactions in NMR**

NMR signals are determined by the quantum mechanics of several Hamiltonians which can be described by,

\[ H_{total} = H_{internal} + H_{external} \]  

(Eq. 2.35)

\( H_{external} \) includes the Zeeman Hamiltonian, \( H_z \), and the radiofrequency pulse Hamiltonian, \( H_{rf} \). \( H_{internal} \) includes \( H_Q \), \( H_{Dipolar} \), \( H_{CS} \), and \( H_J \) or \( H_j \).
In most liquids both the quadrupolar and dipolar Hamiltonian components are averaged to their isotropic values because of the rapid molecular reorientation and do not affect the NMR spectrum, at least to a first approximation ($T_{0,0} = 0$ for both Hamiltonians). For an isotropic liquid, only the $A_{00} T_{00}$ term contributes to the observed spectrum. However, there are other tensor elements that contribute to the solid state NMR spectrum and to relaxation of the system.

In general for liquids there are simplified isotropic Hamiltonians:

$$H_j = 2\pi J_{12} I_{1z} \cdot I_{2z}$$  \hspace{1cm} (Eq. 2.36)

where $H_j$ is the isotropic scalar coupling constant for the weak coupling Hamiltonian.

The strong coupling Hamiltonian is:

$$H_j = 2\pi J_{12} I_1 \cdot I_2$$  \hspace{1cm} (Eq. 2.37)

The isotropic chemical shift Hamiltonian for a spin is:

$$H_{CS} = \delta_1 I_{1z}$$  \hspace{1cm} (Eq. 2.38)

where $\delta_1$ is the chemical shift relative to the rotating frame.

One external Hamiltonian, radiofrequency (RF), is expressed as a phase modulated field giving rise to a nutation frequency $\omega_1 = \gamma B_1$:

$$H_{RF} = \omega_1 (\cos \phi) I_z + \omega_1 (\sin \phi) I_y$$  \hspace{1cm} (Eq. 2.39)
where $\phi$ is the phase of the radio-frequency pulse in the rotating frame and $\omega_i$ is the RF nutation frequency in radians per second.

In the solid state, the spectra, interpretations, and experiments are more complex because molecular reorientation is usually too slow to average out certain interactions. Solid state NMR investigates samples that are usually in their powdered form. Each microcrystal in the powder is oriented randomly, leading to all possible angles for the PAS of any interaction relative to the lab frame. The NMR signals from the different microcrystals combine to yield a broad and characteristic powder lineshape. Following the conventions of Mehring [15], the anisotropy of real space spin interactions may be represented as a second rank Cartesian tensor or as a spherical tensor. The Cartesian representation of an arbitrary Hamiltonian is given by [16]:
Table 2-1: Expressions of the $d_{pq}^k(\beta)$ for $k = 1/2, 1, 3/2, 2$ [17, 14, 20]

\[
\begin{align*}
d_{1/2}^{1/2} &= d_{-1/2}^{1/2} = \cos \frac{1}{2} \beta; d_{-1/2}^{1/2} = -d_{1/2}^{1/2} = \sin \frac{1}{2} \beta \\
d_{1}^{1} &= d_{-1}^{1} = \cos^2 \frac{1}{2} \beta; d_{1}^{1} = d_{-1}^{1} = \sin^2 \frac{1}{2} \beta \\
d_{0}^{1} &= d_{-1}^{1} = -d_{0}^{1} = -d_{1}^{1} = \frac{1}{2} \sin \beta; d_{00}^{1} = \cos \beta
\end{align*}
\]

\[
\begin{align*}
da_{3/2}^{3/2} &= d_{-3/2}^{3/2} = \cos^3 \frac{1}{2} \beta \\
da_{3/2}^{1/2} &= d_{1/2}^{3/2} = -d_{-1/2}^{3/2} = -d_{3/2}^{1/2} = -\sqrt{3} \cos \frac{1}{2} \beta \sin \frac{1}{2} \beta \\
da_{3/2}^{3/2} &= d_{3/2}^{3/2} = d_{-3/2}^{3/2} = d_{3/2}^{1/2} = \sqrt{3} \cos \frac{1}{2} \beta \sin^2 \frac{1}{2} \beta \\
da_{3/2}^{3/2} &= -d_{3/2}^{3/2} = -d_{-3/2}^{3/2} = -d_{3/2}^{1/2} = -\sin \frac{1}{2} \beta \\
da_{1/2}^{3/2} &= d_{-1/2}^{3/2} = \cos \frac{1}{2} \beta \left(3 \cos^2 \frac{1}{2} \beta - 2\right) \\
da_{1/2}^{3/2} &= -d_{1/2}^{3/2} = \sin \frac{1}{2} \beta \left(3 \sin^2 \frac{1}{2} \beta - 2\right)
\end{align*}
\]

\[
\begin{align*}
da_{2}^{2} &= d_{-2}^{2} = \cos^2 \frac{1}{2} \beta \\
da_{-2}^{2} &= d_{2}^{2} = \sin^2 \frac{1}{2} \beta \\
da_{2}^{2} &= -d_{1}^{2} = -d_{-1}^{2} = d_{2}^{2} = -\frac{1}{2} \sin \beta \left(1 + \cos \beta\right) \\
da_{2}^{2} &= -d_{2}^{2} = -d_{-2}^{2} = -d_{1}^{2} = -d_{-1}^{2} = \frac{1}{2} \sin \beta \left(\cos \beta - 1\right) \\
da_{0}^{2} &= d_{0}^{2} = d_{2}^{2} = -d_{-2}^{2} = \frac{3}{8} \sin^2 \beta \\
da_{1}^{2} &= d_{1}^{2} = d_{-1}^{2} = \frac{1}{2} \left(2 \cos \beta - 1\right) \left(1 + \cos \beta\right) \\
da_{-1}^{2} &= d_{-1}^{2} = \frac{1}{2} \left(2 \cos \beta + 1\right) \left(1 - \cos \beta\right) \\
da_{10}^{2} &= d_{0}^{2} = -d_{1}^{2} = -d_{-1}^{2} = \frac{3}{2} \sin \beta \cos \beta \\
da_{00}^{2} &= \frac{1}{2} \left(3 \cos^2 \beta - 1\right)
\end{align*}
\]
Fig. 2.4: A generic spherical tensor undergoes Euler rotations to bring the original coordinate system into coincidence with another. There are three individual rotations through $\alpha$, then $\beta$, then $\gamma$. 
Any arbitrary Hamiltonian in NMR can also be expressed in terms of spherical tensor 
components by:

\[
\mathcal{H} = \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} = \begin{pmatrix} I_x, I_y, I_z \end{pmatrix} \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}
\]  \hspace{1cm} (Eq. 2.40)

Real spatial elements \(A_{l,m}\) relate the Hamiltonian’s principal axis system to the lab frame. 
The spin space elements, \(T_{l,-m}\), relate the nuclear spin angular momenta and magnetic 
moments to the lab frame. Tables 2-3 and 2-4 show the correlations of the Hamiltonian 
spherical tensors in relation to their Cartesian coordinates (Table 2-3) and their spin 
operators (Table 2-4). Figure 2.5 shows the simulation of a powder lineshape carried out 
in Mathematica for a second order quadrupolar Hamiltonian assuming \(q_{cc} = 8.0 \, \text{MHz}\) 
and \(\eta = 0\).

The Zeeman Hamiltonian, \(\mathcal{H}_Z\), is easily calculated using the Cartesian method 
although the spherical tensor method yields the same result.

\[
\mathcal{H}_Z = \mathbf{I} \cdot \mathbf{Z} \cdot \mathbf{B}_o
\]  \hspace{1cm} (Eq. 2.42)
where \( \mathbf{Z} \) is the Zeeman interaction tensor, \(-\gamma\mathbf{1}\):

\[
\mathcal{H}_Z = \begin{pmatrix}
I_x & I_y & I_z \\
-\gamma & 0 & 0 \\
0 & -\gamma & 0 \\
0 & 0 & -\gamma
\end{pmatrix}
\begin{pmatrix}
B_{o,x} \\
B_{o,y} \\
B_{o,z}
\end{pmatrix}
\]  
(Eq. 2.43)

By convention, the external magnetic field, \( \mathbf{B}_o \), is oriented in the Z direction, at least in NMR, so the magnetic field column vector is \( \{0,0,B_o\} \), yielding:

\[
\mathcal{H}_Z = -\gamma B_o I_z = \omega_o \mathbf{I}_z
\]  
(Eq. 2.44)

All of the Hamiltonians in Table 2-2 can be constructed in the same manner using either the spherical tensor method or the Cartesian method.
Table 2-2

Table 2-2: Cartesian Forms of NMR Hamiltonians [17]

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Form of the Hamiltonian</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Shift</td>
<td>$\mathcal{H}_g = \gamma \mathbf{1} \cdot \mathbf{\hat{\sigma}} \cdot \mathbf{B}_o$</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>$\mathcal{H}<em>d = \sum</em>{i&lt;j} h\gamma_i \gamma_j r_{ij}^{-3} \left( \mathbf{I}_i \cdot \mathbf{\hat{D}} \cdot \mathbf{I}_j \right)$</td>
</tr>
<tr>
<td></td>
<td>$\mathcal{H}<em>D = \sum</em>{i&lt;j} \mathbf{I}_i \cdot \mathbf{\hat{D}} \cdot \mathbf{I}_j$</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>$D_{\alpha\beta} = h\gamma_i \gamma_j r_{ij}^{-3} \left( \delta_{\alpha\beta} - 3e_\alpha e_\beta \right)$</td>
</tr>
<tr>
<td>J-coupling</td>
<td>$\mathcal{H}<em>J = \sum</em>{i\neq j} \mathbf{I}_i \cdot \mathbf{\hat{J}} \cdot \mathbf{I}_j$</td>
</tr>
<tr>
<td>Spin-rotation</td>
<td>$\mathcal{H}_{CR} = \sum_i \mathbf{I}_i \cdot \tilde{\mathbf{C}}_i \cdot \mathbf{J}$</td>
</tr>
<tr>
<td>Quadrupolar</td>
<td>$\mathcal{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \mathbf{I} \cdot \mathbf{\tilde{V}} \cdot \mathbf{I}$</td>
</tr>
<tr>
<td></td>
<td>$\mathbf{\tilde{V}} = \left{ \nu_{\alpha\beta} \right}; \alpha, \beta = a, y, z$</td>
</tr>
</tbody>
</table>
Table 2-3: Correlation of spherical tensors with Cartesian tensors for real space spin interactions [17,20]

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$A_{\alpha\beta}(\alpha,\beta=x,y,z)$</th>
<th>$A_{k,q}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Shift</td>
<td>$\gamma\sigma_{\alpha\beta}$</td>
<td>$A_{00} = -\frac{1}{\sqrt{3}} \left( A_{xx} + A_{yy} + A_{zz} \right) = -\frac{1}{\sqrt{3}} \text{Tr} { A_{\alpha\beta} }$</td>
</tr>
<tr>
<td>Dipole-dipole (k = 2)</td>
<td>$D_{\alpha\beta}$</td>
<td>$A_{10} = -\frac{i}{\sqrt{2}} \left( A_{yy} - A_{yx} \right)$</td>
</tr>
<tr>
<td>J-coupling</td>
<td>$J_{\alpha\beta}$</td>
<td>$A_{1\pm 1} = \frac{1}{2} \left[ A_{zz} - A_{xx} \pm i \left( A_{yy} - A_{yx} \right) \right]$</td>
</tr>
<tr>
<td>Spin-rotation</td>
<td>$C_{\alpha\beta}$</td>
<td>$A_{20} = \frac{1}{\sqrt{6}} \left[ 3 A_{zz} - \left( A_{xx} + A_{yy} + A_{zz} \right) \right]$</td>
</tr>
<tr>
<td>Quadrupole (k = 2)</td>
<td>$\frac{eQ}{2I(2I-1)\hbar} V_{\alpha\beta}$</td>
<td>$A_{2\pm 1} = \pm \frac{1}{2} \left[ A_{zz} + A_{xx} \pm i \left( A_{yz} + A_{yz} \right) \right]$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_{2\pm 2} = \pm \frac{1}{2} \left[ A_{xx} - A_{yy} \pm i \left( A_{xx} + A_{xy} \right) \right]$</td>
</tr>
</tbody>
</table>
Table 2-4

Table 2-4: Spherical tensor values of spin space operators (with $I_\pm = I_x \pm iI_y$) [17, 20]

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$T_{00}$</th>
<th>$T_{10}$</th>
<th>$T_{1\pm1}$</th>
<th>$T_{20}$</th>
<th>$T_{2\pm1}$</th>
<th>$T_{2\pm2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Shift</td>
<td>$-\frac{1}{\sqrt{3}} I_z B_o$</td>
<td>$0$</td>
<td>$-\frac{1}{2} I_z B_o$</td>
<td>$\frac{2}{\sqrt{3}} I_z B_o$</td>
<td>$\pm \frac{1}{2} I_z B_o$</td>
<td>$0$</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$\frac{1}{\sqrt{6}} (3I_z S_z - \mathbf{I} \cdot \mathbf{S})$</td>
<td>$\pm \frac{1}{2} (I_z S_z + I_s S_s)$</td>
<td>$\frac{1}{2} I_s S_s$</td>
</tr>
<tr>
<td>J-coupling</td>
<td>$-\frac{1}{\sqrt{3}} I \cdot S$</td>
<td>$-\frac{1}{2\sqrt{2}} (I_x S_x - I_y S_y)$</td>
<td>$+\frac{1}{2} [I_x S_x - I_y S_y]$</td>
<td>$\frac{1}{\sqrt{6}} (3I_z S_z - \mathbf{I} \cdot \mathbf{S})$</td>
<td>$\pm \frac{1}{2} (I_z S_z + I_s S_s)$</td>
<td>$\frac{1}{2} I_s S_s$</td>
</tr>
<tr>
<td>Spin-rotation</td>
<td>$-\frac{1}{\sqrt{3}} I \cdot J$</td>
<td>$-\frac{1}{2\sqrt{2}} (I_x J_x - I_y J_y)$</td>
<td>$+\frac{1}{2} [I_x J_x - I_y J_y]$</td>
<td>$\frac{1}{\sqrt{6}} (3I_z J_z - \mathbf{I} \cdot \mathbf{J})$</td>
<td>$\pm \frac{1}{2} (I_z J_z + I_s J_s)$</td>
<td>$\frac{1}{2} I_s J_s$</td>
</tr>
<tr>
<td>Quadrupolar</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$\frac{1}{\sqrt{6}} (3I_z^2 - I(I+1))$</td>
<td>$\pm \frac{1}{2} (I_z I_z + I_s I_s)$</td>
<td>$\frac{1}{2} I_s I_s$</td>
</tr>
</tbody>
</table>
Fig. 2.5: The simulation of a second order quadrupolar lineshape of a spin 5/2 nucleus. Calculations for all of the $A_{2\text{ab}}$ terms were carried out in Mathematica using the conventions of Mehring and Wigner rotations (example output available in the appendices). In this case $\eta = 0$ and the $q_{cc} = 8 \times 10^6$ Hz. The x axis is in Hz and y axis is arbitrary.
For simplicity both the equilibrium density matrix (2b $I_z$) and the Hamiltonians are described in the interaction representation (the rotating frame) so that off diagonal terms are truncated (i.e. only diagonal terms survive). Using the above Hamiltonians and the Liouville von Neumann equation one may act on the density matrix of a given spin system to calculate its time evolution. This is known as the propagation of the density operator, $\rho$. The time evolution of the density matrix, $\rho$, starting at any state, can be broken into segments of constant Hamiltonian interaction. For example, after two time intervals with Hamiltonians $H_1$ for $\tau_1$ and $H_2$ for $\tau_2$, the initial density matrix, $\rho(t)$, yields:

$$\rho(t + \tau_1 + \tau_2) = \exp[-iH_2\tau_2] \exp[-iH_1\tau_1] \rho(t) \exp[iH_1\tau_1] \exp[iH_2\tau_2]$$  \hspace{1cm} (Eq. 2.45)

Two examples are shown below:

1. For an ensemble of spins at equilibrium acted on by a $\pi/2$ pulse of phase $\phi = 0$ external radio frequency Hamiltonian, $\omega_\tau = \frac{\pi}{2}$, where $\rho_{eq} = 2bI_z$ this yields:

$$\rho(t, \tau) = \exp\left[-i\frac{\pi}{2} I_x\right] 2bI_z \exp\left[i\frac{\pi}{2} I_x\right]$$  \hspace{1cm} (Eq. 2.46)

Using commutation relationships for spin angular momenta and converting from the complex exponential to the trigonometric form:
Thus,

\[
\rho(t, \tau) = 2b \left( I_z \cos\left(\frac{\pi}{2}\right) - i[I_x, I_z] \sin\left(\frac{\pi}{2}\right) \right) = 2b \left(-i(-iI_y)\right)
\]

(Eq. 2.47)

Thus,

\[
\rho(\tau) = -2bI_y
\]

(Eq. 2.48)

The resulting density matrix is exactly what the classical vector description predicted when applying a \(\pi/2\) pulse of phase X to bulk magnetization (refer to figure 2.3).

Because the magnitude of the RF Hamiltonian is often much greater than the internal interactions that perturb the system one may often ignore the internal interactions during the RF Hamiltonian. Also because typical liquid internal Hamiltonians such as the \(H_j, H_{cs}\) commute, i.e. \([H_{cs}, H_j] = 0\), their propagators can be used in either order.

2. For a single pulse experiment with a delay, \(\tau_{\text{delay}}\), in which \(j\) coupling and the chemical shift evolve:

\[
\rho(\tau_{\text{delay}} + \tau_{\text{pulse}}) = \left\{ \exp\left[ -i\left( H_{cs} + H_j \right) \tau_{\text{delay}} \right] \exp\left[ -iH_{RF} \tau_{\text{pulse}} \right] \rho_{eq} \right. \\
\left. \exp\left[ iH_{RF} \tau_{\text{pulse}} \right] \exp\left[ i\left( H_{cs} + H_j \right) \tau_{\text{delay}} \right] \right\}
\]

(Eq. 2.49)

The result for any liquid state pulse sequence can be calculated in the same way.

2.9 Spin \(I = 1\) Systems in NMR
Most NMR active isotopes have half-integer quadrupolar spins where \( I = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \text{etc...} \). There are only seven NMR active isotopes with integer spins that are not radioactive, three of the seven being spin \( I = 1 \) nuclei.

The main nucleus of interest in this thesis is deuterium, \(^2\)H. Deuterium has a nuclear spin of 1 and has an electric quadrupole moment. Its NMR spectrum and relaxation are dominated by the quadrupolar Hamiltonian in the solid state.

\[
\|H_Q\| >> \|H_{CS}\|, \|H_{HD}\|, \|H_{DD}\|
\]

where \( \|H_Q\| = \sqrt{H_Q \cdot H_Q} \)

The eigenvalues of \( I_z \) for a spin 1 system are +1, 0, and -1. The Zeeman basis eigenstates are: \( |1, +1\rangle, |1, 0\rangle, |1, -1\rangle \).

\[
|1, +1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; |1, 0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; |1, -1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}
\]

(Eq. 2.50)

A spin 1 nucleus can take one of three possible orientations in a magnetic field: parallel, antiparallel, or transverse. The matrix representation of an operator, \( O \), in matrix form is therefore:
The matrix representations of the angular momenta are:

\[
\mathbf{O} = \begin{pmatrix}
O_{11} & O_{12} & O_{13} \\
O_{21} & O_{22} & O_{23} \\
O_{31} & O_{32} & O_{33}
\end{pmatrix}
\]

(Eq. 2.51)

The matrix representations of the angular momenta are:

\[
I_x \doteq \frac{1}{\sqrt{2}} \begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\]

\[
I_y \doteq \frac{i}{\sqrt{2}} \begin{pmatrix}
0 & -1 & 0 \\
1 & 0 & -1 \\
0 & 1 & 0
\end{pmatrix}
\]

(Eq. 2.52)

\[
I_z \doteq \begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

\[
\mathbf{I}^2 \doteq 2 \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]
Fig. 2.6: A spin 1 system without and with the influence of the quadrupolar coupling constant. Only allowed single quantum transitions are shown. The forbidden energy levels are not shown [18].
For $^2$H, the Zeeman interaction is dominant. All other interactions are perturbations to the Zeeman basis set in the interaction frame of reference (rotating frame). In deuterium NMR the dominant internal interaction is the quadrupolar Hamiltonian. To a good approximation one may neglect other interactions such as the chemical shift and dipolar coupling and calculate lineshapes and relaxation times using only the on-resonance quadrupolar Hamiltonian.

$$
\mathcal{H}_e = \frac{1}{3} \omega_Q \left( 3I_z^2 - I^2 \right) \quad \text{(Eq. 2.53)}
$$

where $\omega_Q$ is a function of the powder Euler angles relating the PAS to the laboratory frame.

For an x phase RF pulse, the propagator along the x axis of the rotating frame is

$$
U = \exp(-i\theta \mathbf{1}_x) \quad \text{where} \quad \theta = \omega_{\tau_{\text{pulse}}}
$$

Its effect is to create superpositions of all three eigenstates of the Zeeman basis set. The matrix representation for the pulse propagator, $H_{\text{rf}}$, is then:
Using the above relationships and the density operator, an example of a Hahn type echo experiment, \(((\pi/2)x_{\tau}-(\pi)y_{\tau})\), \([8]\) applied to a spin 1 system can be compared to a quadrupolar echo experiment is shown below. This effectively demonstrates why the quadrupole echo experiment is one of the most useful experiments in $^2$H NMR.

Treating a spin 1 system classically using a vector analysis and invoking the right hand rule convention of the motion of macroscopic magnetization under radiofrequency one would expect a full refocusing of magnetization along the $-y$ axis for the Hahn echo at a time $2\tau$. The equilibrium density operator for a spin 1 system,

$$
\rho_{eq} = c I_z = \begin{pmatrix} c & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -c \end{pmatrix}
$$

after propagation is given by:

$$
\begin{align*}
&\exp[-i\mathcal{H}_z\tau] \exp[-i(\pi)I_y] \exp[-i\mathcal{H}_y\tau] \exp[-i(\pi/2)I_x] \rho_{eq} \\
&\exp[i(\pi/2)I_x] \exp[i\mathcal{H}_y\tau] \exp[i(\pi)I_y] \exp[i\mathcal{H}_y\tau]
\end{align*}
$$

(Eq. 2.55)
where $\mathcal{H}_Q$ takes the form: 
\[ \frac{1}{\sqrt{6}} \omega_Q (3I_z^2 - I_z) \]
The observable NMR signal is obtained by evaluating $\text{Tr}[\Gamma \cdot \rho]$ at the final state, yielding:

\[ \text{Tr} \left[ I^+ \rho (2\tau) \right] = -ic \exp \left[ -i\sqrt{6} \tau \omega_Q \right] - ic \exp \left[ i\sqrt{6} \tau \omega_Q \right] \tag{Eq. 2.56} \]

$\omega_Q$ has angular dependence and so the echo does not fully refocus for all frequencies $\omega_Q$ with a $\pi$ refocusing pulse. The signal from the Hahn echo is dependent on $\omega_Q$ and therefore on the orientation of the crystallites with respect to the magnetic field.

The quadrupole echo ($((\pi/2)_x-\tau- (\pi/2)_y-\tau)$) operator propagated with the quadrupole echo sequence (Fig. 2.7.B) is given by:

\[ \exp \left[ -i\mathcal{H}_Q \tau \right] \exp \left[ -i\frac{\pi}{2} I_y \right] \exp \left[ -i\mathcal{H}_Q \tau \right] \exp \left[ -i\frac{\pi}{2} I_x \right] \rho_{eq} \]

\[ \exp \left[ i\frac{\pi}{2} I_x \right] \exp \left[ i\mathcal{H}_Q \tau \right] \exp \left[ i\frac{\pi}{2} I_y \right] \exp \left[ i\mathcal{H}_Q \tau \right] \tag{Eq. 2.57} \]

This yields the observable NMR signal:

\[ \text{Tr} \left[ I^+ , \rho \right] = -2ic \]

or more clearly
\[ \text{Tr} \left[ I_y , \rho \right] = -2c \tag{Eq. 2.58} \]

A full refocusing of the magnetization on the $-y$ axis is evident. The same result is obtained immediately after a $(\pi/2)_x$ pulse.
A Hahn echo experiment and quadrupolar echo experiment are generally formed as:

Fig. 2.7

Fig. 2.7: Typical pulse diagrams for (A.) a spin ½ Hahn echo sequence [8], and (B.) a quadrupolar, or solid echo sequence.
One may calculate lineshapes of spin 1 nuclei in the motionally slow exchange limit quite readily (\( v_{\text{motion}} \ll q_{cc} \)). In Fig 2.8 contributions from specific microcrystalline angles arise as doublets in the \(^2\)H NMR signal. Since there are many angles due to the various crystallite orientations the sum of all the crystallite angles result in a \(^2\)H NMR powder pattern.
Fig. 2.8: A rigid deuterium quadrupole echo powder pattern on the bottom, calculated with $\eta=0$ and $q_{cc} = 206$ kHz. The powder spectrum, using 5253 angles, is due to the sum of the doublets. The horns correspond to the $90^\circ$ doublet and the lateral edges to the $0^\circ$ doublet [18, 19].
References


7. E.O. Stejskal and J.D. Memory, In “*High Resolution NMR in the Solid State:*


9. J. Fourier, Bulletin *des sciences par la Société philomatique de Paris*, **1**, 1807,
   215-221.

    Springer-Verlag.

    Press.

12. J.J. Sakurai, *Modern Quantum Mechanics, Revised Ed.* 1994, Reading,
    Massachusetts: Addison-Wesley Publishing.


3.1 The Quadrupolar Hamiltonian in Irreducible Tensor Form

This section is an in depth discussion about relaxation in NMR. More specifically, the focus is spin 1 NMR. The conventions of Mehring, also described in Chapter 2 [1-3], are used here. In the interaction representation (rotating frame), the observed NMR spectrum is determined by the \( l=2, m=0 \) term of the quadrupolar Hamiltonian:

\[
H_{Q}^{lab} = A_{20}^{lab} T_{20}^{rot}
\]

where \( A_{20}^{lab} \) describes the \( l=2, m=0 \) angular dependence of quadrupolar frequency relative to the laboratory reference frame (magnetic field). \( T_{20}^{rot} = T_{20}^{lab} = \sqrt{3} (3I_z^2 - I^2) \) describes the \( l=2, m=0 \) term of the spin angular momentum (magnetization) in the rotating frame.

The calculation of deuterium NMR relaxation times is more complicated and requires other \( A_{2m}^{lab} \) and \( T_{2m}^{rot} \) components of the quadrupolar Hamiltonian.
For the description of molecular motion in a static probe, $A_{2m}^{lab}$ values are calculated by means of the following coordinate transformations, Scheme 1:

$$
\Omega_{PC} \quad \Omega_{CL}
$$

PAS frame $\rightarrow$ Crystal Fixed Frame $\rightarrow$ LAB \hspace{1cm} (Scheme I)

where $\Omega_{PC}$ are the Euler angles that take the $^2$H PAS (e.g. O-$^2$H bond) to a crystal fixed reference frame, and $\Omega_{CL}$ are the static Euler angles (powder average angles) that take the crystal fixed frame to the laboratory frame (magnetic field). If there is molecular motion, the Euler angles $\Omega_{PC}(t)$ change with time in accordance with the details of the motion. If $\Omega_{PC}(t)$ is known, spectra and relaxation times can be calculated. If there is no molecular motion, the transformation to a crystal fixed reference frame is unnecessary and the transformation from PAS to laboratory frame can be carried out in a single step with static powder average Euler angles $\Omega_{PL}$. If $\Omega_{CL}$ has a time dependence, $\Omega_{CL}(t)$ must be known in order to calculate $<A_{2m}^{lab}(t)>$.

The advantage of the spherical tensor representation of the Hamiltonian, Eq. [3.1], is that transformations between reference frames can be efficiently accomplished with Wigner rotations. The transformation from the PAS to the crystal reference frame is given by:

$$A_{2p}^{C} = \sum_{q=-2}^{2} A_{2q}^{PAS} D_{qp}^{2} (\Omega_{PC})$$ \hspace{1cm} (3.2)
Where \( A_{2p}^C \) is the value in the crystal fixed frame (CFF).

All nonzero elements of \( A_{2q}^{PAS} \) contribute to \( A_{2p}^C \). The transformation to the laboratory reference frame is achieved with a second Wigner rotation over the Euler angles \( \Omega_{CL} \) relating the crystal axis system to the laboratory axis system. For powder samples composed of a multitude of small crystals, the angles \( \Omega_{CL} \) can take all possible values. The corresponding frequency distribution yields the characteristic powder pattern in the NMR spectrum.

\[
A_{2m}^{lab} = \sum_{m=-2}^{2} A_{2p}^C D_{pm}^2(\Omega_{CL})
\]

For the quadrupolar Hamiltonian of an \( I=1 \) nucleus such as \(^2\)H, the \( A_{2q}^{PAS} \) elements are [1]:

\[
A_{20}^{PAS} = \sqrt{\frac{3}{8}} \frac{e^2 qQ}{\hbar} = \sqrt{\frac{2}{3}} \omega_Q
\]
3.2 Calculation of the $T_1$ and $T_2$ Relaxation Times

The following derivation is based on the formalism developed by Torchia and Szabo [4]. The observed deuterium $T_1$ and $T_2$ values are given by [5, 6]:

\[
\frac{1}{T_1} = \frac{\omega_q^2}{3} \left( J_1(\omega) + 4J_2(2\omega) \right) \tag{3.7}
\]

\[
\frac{1}{T_2} = \frac{\omega_q^2}{3} \left( \frac{3}{2} J_0(0) + \frac{5}{2} J_1(\omega) + J_2(2\omega) \right) \tag{3.8}
\]
where \( \omega \) is the Larmor frequency in radians/sec, and \( J_0(0), \ J_1(\omega) \) and \( J_2(2\omega) \) are the spectral densities at integer multiples of the Larmor frequency that depend on the details of the molecular motion. The superscripts in the \( J_n(\omega) \) indicating \( l = 2 \) have been omitted to simplify the notation. The calculation of the spectral densities is discussed below.

### 3.3 Calculation of Correlation Functions

The spectral densities \( J_0(0), \ J_1(\omega) \) and \( J_2(2\omega) \) are twice the half-sided Fourier cosine transforms of the corresponding laboratory frame normalized correlation functions \( C_0(t), \ C_1(t), \) and \( C_2(t) \) (the superscript denoting \( l = 2 \) has been omitted) describing the motion of the deuterium PAS (with primary \( z \) axis parallel to the O\(^-\)H covalent bond axis) [7]:

\[
J_m (m\omega) = 2\int_0^{\infty} C_{m}^{\text{lab}} (t) \cos(m\omega t) dt \tag{3.9}
\]

where the normalized correlation functions are given by:
The angle brackets indicate the ensemble (powder) average. The $A_{2p}^{lab}$ elements are calculated using Eq. [3.2, 3.3]. Details of the motion are manifested in the time dependence of the Euler angles $\Omega_{PC}(t)$ relating the deuterium nucleus principal axis system $z$ axis (the O-$^2$H bond axis) and the crystal fixed axis system. This gives rise to time dependence $A_{2p}^{C}(t)$ in the crystal fixed reference frame. This time dependence is carried into the laboratory reference frame by means of Eq. [3.3] and the time independent (powder) Euler angles $\Omega_{CL}$.

The laboratory frame correlation functions in Eq. [3.10] are given by [4]:

$$C_{m}^{lab}(t) = \sum_{a=-2}^{2} \sum_{a'=-2}^{2} C_{aa'}^{C}(t) \tilde{D}_{am}^{2*}(\Omega_{CL}) \tilde{D}_{a'm}^{2}(\Omega_{CL})$$  \hspace{1cm} 3.11

where the $C_{aa'}^{C}(t)$ are the correlation functions in the crystal fixed reference frame:
The angle brackets indicate the ensemble average, and the $A_{2p}^{\text{PAS}}$ values are given by Eq. [3.2, 3.3].

### 3.4 Correlation Times and Spectral Densities for Isotropic Rotational Diffusion

The dynamic model that has been most widely used for liquid state water is small step isotropic rotational diffusion (IRD). The laboratory frame correlation functions $C_{m}^{\text{lab,IRD}}(t)$ for IRD are well known. They are independent of orientation and m value. For $m = -2$ to $+2$, and with the rotational rate $= 6 D_{\text{rot}}$ [8]:

$$C_{m}^{\text{lab,IRD}}(t) = \frac{1}{5} \left( 1 + \frac{\eta^2}{3} \right) e^{-6D_{\text{rot}}t}$$  \hspace{1cm} 3.13

The corresponding isotropic rotational diffusion spectral densities are obtained from Eq. [3.9]:

$$J_{0}^{\text{IRD}}(0) = \frac{1}{5} \left( 1 + \frac{\eta^2}{3} \right) \frac{2}{6D_{\text{rot}}}$$  \hspace{1cm} 3.14
\[ J_{1}^{IRD}(\omega) = \frac{1}{3} \left( 1 + \frac{\eta^2}{3} \right) \frac{12D_{rot}}{(6D_{rot})^2 + \omega^2} \]

and

\[ J_{2}^{IRD}(2\omega) = \frac{1}{5} \left( 1 + \frac{\eta^2}{3} \right) \frac{12D_{rot}}{(6D_{rot})^2 + 4\omega^2} \]

where \( J_{m}^{IRD}(m\omega) = J_{-m}^{IRD}(-m\omega) \). With \( 6D_{rot} = 1/\tau_c \), these expressions yield the same results derived by Sudmeier et al [9].

3.5 Spectral Densities for Tetrahedral Jumps

The O-\(^2\)H bond vector (and deuterium PAS z axis) can jump with equal probability and rate constant \( k_{tet} \) from one tetrahedral orientation to any of the three others in the crystal fixed frame. The N-site jump model formalism of Torchia and Szabo [4] is used, but the general result for \( \eta \neq 0 \) is implemented. Starting with the 4-site jump rate matrix and the four sets of allowed polar angles of the O-\(^2\)H bond vector in a convenient crystal fixed axis system, the four sets of allowed polar angles in this reference frame are: \( \{ \theta = 0, \phi = 0 \}, \{ \theta = \text{ArcCos}[\frac{-1}{3}], \phi = 0 \}, \{ \theta = \text{ArcCos}[\frac{-1}{3}], \phi = \frac{2\pi}{3} \}, \{ \theta = \text{ArcCos}[\frac{-1}{3}], \phi = \frac{4\pi}{3} \} \}. \) The four sets of polar angles are related to the four sets of allowed Euler angles \( \Omega_{pc} \) by \( \alpha_{PC} = 0, \beta_{PC} = \theta, \gamma_{PC} = \pi - \phi [4] \).
The rate matrix is:

\[
R = \begin{pmatrix}
-3k_{\text{tet}} & k_{\text{tet}} & k_{\text{tet}} & k_{\text{tet}} \\
k_{\text{tet}} & -3k_{\text{tet}} & k_{\text{tet}} & k_{\text{tet}} \\
k_{\text{tet}} & k_{\text{tet}} & -3k_{\text{tet}} & k_{\text{tet}} \\
k_{\text{tet}} & k_{\text{tet}} & k_{\text{tet}} & -3k_{\text{tet}}
\end{pmatrix}
\]

Using Eq. [3.17], the tetrahedral jump spectral densities in the laboratory reference frame are calculated (See Appendix C):

\[
J^\text{tet}_0(0) = \frac{1}{5184 \left( \omega^2 + 16 k_{\text{tet}}^2 \right)} \left( -4(288 + \eta(-672 + 149 \eta)) \cos[2 \beta] - (2016 + \eta(480 + 341 \eta)) \right) \\
\cos[4 \beta] - 256 \sqrt{2} (3 + \eta)(-12 + 5 \eta) \cos[3 \alpha] \cos[\beta] \sin[\beta]^3 + 9(864 + \eta(96 + 161 \eta) + 24 \eta(-3 \eta \cos[4 \alpha] \sin[\beta]^4 + 4(3 + \eta) \cos[2 \alpha] \sin[2 \beta]^2)) k_{\text{tet}}^2
\]

3.18
$$J_2^{tet}(2\omega) = \frac{1}{82944} \frac{(k_{tet} (9(3744 + \eta(-864 + 871 \ \eta)) + (2016 + \eta(480 + 341 \ \eta)) \cos[4\beta] + 648 \ \eta^2 \cos[4\alpha] \sin[\beta]^4 + 4 \cos[2\beta] (288 + \eta(-5856 + 851 \ \eta) - 432 \ \eta (3 + \eta) \cos[2\alpha] \sin[\beta]^2) + 64(3 + \eta) \sin[\beta]^2 (-81 \ \eta \cos[2\alpha] + 2\sqrt{2}(-12 + 5\eta) \cos[3\alpha] \sin[2\beta]))}{(4k_{tet}^2 + \omega^2)}$$ \hspace{1cm} (3.20)

where $k_{tet}$ is the tetrahedral jump rate constant in sec$^{-1}$, $\eta$ is the asymmetry parameter, and $\alpha = \alpha_{CL}$ and $\beta = \beta_{CL}$ are the (powder average) Euler angles ($\gamma_{CL} = 0$ is chosen with no loss of generality) relating the crystal reference frame to the laboratory reference frame, i.e. magnetic field.

The spectral densities and corresponding $T_1$ and $T_2$ values, Eq. [3.19, 3.20], have an angular dependence. The relaxation times are shortest at one half of the tetrahedral angle, i.e. the magic angle ($\beta_{CL} = \text{ArcCos}[-1/3]/2$) and $\alpha_{CL} = 0$, and longest at the parallel edges ($\beta_{CL} = 0$, independent of $\alpha_{CL}$). The magnitude of the variation of the $T_1$ value with the angles $\alpha_{CL}$ and $\beta_{CL}$ depends on the $\eta$ value and the tetrahedral jump rate $k_{tet}$. For jump rates $k_{tet} > 1 \times 10^8$ sec$^{-1}$ and $\eta$ values $\leq 0.1$, the variation of the $T_1$ with respect to the powder average value is $\pm 11\%$ or less. At slower jump rates, the deviation from the powder average $T_1$ value can be $\pm 25\%$. The angular dependence of the $T_2$ value is somewhat larger throughout the range of jump rates, but is still no more than $\pm 25\%$ if $\eta = 0.1$ or less. The perfect symmetry of fast tetrahedral jumps ($k_{tet} > qcc$) yields a dynamically reduced powder lineshape that is a sharp, apparently isotropic, peak. Any
effects of the angular dependence show up as a deviation from exponentiality of the relaxation of this peak.

### 3.6 Spectral Densities for C₂ Symmetry Jumps

The water molecules directly coordinated to Na⁺ experience C₂ symmetry jumps about the angle bisector of their H-O-H bonds. The O-²H bond vector (and deuterium PAS z axis) can jump with equal probability and rate $k_{C₂}$ from one C₂ orientation to the other. Again, the N-site jump model formalism of Torchia and Szabo [4] is used, but the general result for $\eta \neq 0$ is found. The 2-site jump rate matrix and the two sets of polar angles describing the O-²H bond vector are exposed in a convenient crystal fixed axis system. The two sets of allowed polar angles in this reference frame are: $\{\{\theta = \theta_{\text{bisector}}, \phi = 0\}$ and $\{\theta = \theta_{\text{bisector}}, \phi = \pi\}$. The two sets of polar angles are related to the two sets of allowed Euler angles $\Omega_{PC}$ by $\alpha_{PC} = 0$, $\beta_{PC} = \theta$, $\gamma_{PC} = \pi - \phi$ [4].

The rate matrix is:

$$
R = \begin{pmatrix}
-k_{C₂} & k_{C₂} \\
k_{C₂} & -k_{C₂}
\end{pmatrix}
$$

Using Eq. [3.21], the C₂ jump spectral densities in the laboratory reference frame is calculated:
$J^c_0 = \frac{1}{48k_C^2} ( (3 + \eta)^2 (1 + \cos[\alpha]^2 \cos[4 \beta] + \cos[2 \beta] \sin[\alpha]^2) \sin[2 \theta]^2 )$

$J^c_1 = \frac{(3 + \eta)^2 (1 + \cos[\alpha]^2 \cos[4 \beta] + \cos[2 \beta] \sin[\alpha]^2) \sin[2 \theta]^2 k_{C^2}}{12 (\omega^2 + 4k_{C^2}^2)}$

$J^c_2 = \frac{- (3 + \eta)^2 (-3 + \cos[2 \alpha] - 2 \cos[\alpha]^2 \cos[2 \beta]) \sin[\beta]^2 \sin[2 \theta]^2 k_{C^2}}{96 (\omega^2 + k_{C^2}^2)}$

where $k_{C^2}$ is the C_2 jump rate constant in sec$^{-1}$, $\theta$ is one half the $^2$H-O-$^2$H bond angle, $\eta$ is the asymmetry parameter, and $\alpha = \alpha_{CL}$ and $\beta = \beta_{CL}$ are the (powder average) Euler angles ($\gamma_{CL} = 0$ is chosen with no loss of generality) relating the crystal reference frame to the laboratory reference frame, i.e. magnetic field.

Fast C_2 symmetry jumps yield a dynamically reduced deuterium powder lineshape, not an isotropic sharp line (see Fig. 3.1). The deuterium spectral densities and relaxation are also anisotropic. The spectral densities vanish at specific $\alpha_{CL}$ and $\beta_{CL}$ values, but there are always $\alpha_{CL}$ values at any $\beta_{CL}$ value for which the spectral density is nonzero. Both $T_1$ and $T_2$ relaxation times are shortest at the perpendicular edges, $\beta_{CL} = \pi/2$ and $\alpha_{CL} = \pi/2$, and longest at the parallel edges ($\beta_{CL} = 0$, $\alpha_{CL} = \pi/4$). With $\alpha_{CL}$
averaged, both relaxation times vary by a factor of 4 for the perpendicular and parallel edges throughout the range of the C\textsubscript{2} jump rates k\textsubscript{C2}. The deuterium relaxation times are also very sensitive to the $^2$H-O-$^2$H bond angle, with the shortest relaxation times obtained when the $^2$H-O-$^2$H angle is the tetrahedral angle (i.e. $\theta_{\text{bisector}}$ is the magic angle).

### 3.7 Exchange Between Tetrahedral Jump and C\textsubscript{2} Symmetry Jump Populations

Kanemite (NaHSi\textsubscript{2}O\textsubscript{5}•3$^2$H\textsubscript{2}O) and hydrated Na\textsuperscript{+}-Zeolite A (Na\textsubscript{12}Al\textsubscript{12}Si\textsubscript{12}O\textsubscript{48}•27$^2$H\textsubscript{2}O) contain water molecules that are directly coordinated to Na\textsuperscript{+} and water molecules that are outside the direct coordination sphere of Na\textsuperscript{+} [10, 11]. Silicate and aluminosilicate surfaces in both hydrated solids provide oxygen lone pairs and O-H groups in kanemite that serve as hydrogen bonding sites for water molecules. The coordination of water molecules to the Na\textsuperscript{+} cation via the oxygen lone pairs and the hydrogen bonding of water hydrogen atoms to the aluminosilicate oxygen lone pairs promote a fixed lattice structure for water molecules in both environments. The hypothesis proposed here is that the O-\(^2\)H bonds of water molecules directly coordinated to Na\textsuperscript{+} experience C\textsubscript{2} symmetry jumps, that those of water molecules outside the direct coordination sphere of Na\textsuperscript{+} experience tetrahedral jumps, and that there is exchange between the two populations with rate constant $k_{\text{exch}}$ (Scheme 2):

\[
k_{\text{exch}}
\]

\[
\text{Scheme 2) Tetrahedral} \leftrightarrow C_2
\]
Fig. 3.1: Deuterium lineshapes calculated for fast ($k_{C2} \gg q_{cc}$) $C_2$ symmetry jumps and various D-O-D bond angle bisector ($\theta$) values ($q_{cc} = 213$ kHz, $\eta = 0$). The black lineshape, for example, is calculated for perfectly tetrahedral D-O-D bond angles ($\theta = 54.74^\circ$, the magic angle). The two D-O-D bond angles known from the X-ray structure of water molecules coordinated to Na$^+$ in kanemite are $83.0^\circ$ ($\theta = 41.5^\circ$) and $114.4^\circ$ ($\theta = 57.2^\circ$) [10]. The broad gray spectrum is the "rigid" powder lineshape for $q_{cc} = 213$ kHz, $\eta = 0$. 
where tetrahedral and $C_2$ identify the populations of water molecules experiencing tetrahedral and $C_2$ symmetry jumps of their O-H bond axes, respectively; and $k_{\text{exch}}$ is the rate constant for exchange between the populations. For convenience, Scheme 2 is called the C2TET model.

At sufficiently low temperatures the jump rates and exchange are "frozen out" on the deuterium timescale, with $k_{C_2}$, $k_{\text{tet}}$, $k_{\text{exch}} << \chi_{\text{cc}}$. A "rigid" deuterium powder lineshape is expected. As the temperature is increased, the jump and population exchange rates continuously increase, first reaching intermediate exchange ($k \sim \chi_{\text{cc}}$), then ultimately fast exchange ($k \gg \chi_{\text{cc}}$). The deuterium spectrum is expected to change accordingly. At lower temperatures, where $k_{\text{exch}} \leq \chi_{\text{cc}}$, separate contributions to the spectral lineshape and relaxation times from the $C_2$ and tetrahedral populations (Scheme 2) are expected.

At high enough temperatures fast exchange between the two populations of water molecules allows for the $C_2$ symmetry jump powder lineshape to be further dynamically averaged by octahedral jumps. The exchange with the tetrahedral jump population provides O-^2H bonds with access to all of the octahedral $C_2$ binding sites of the Na^+ ions, resulting in approximately octahedral jumps of the O-^2H bond. This produces an isotropic single resonance rather than a $C_2$ jump lineshape. Furthermore, the fast exchange relaxation rate model predicts [12]:

$$\frac{1}{T_n}_{\text{observed}} = \chi_{C_2} \frac{1}{T_n}_{C_2} + \chi_{\text{tet}} \frac{1}{T_n}_{\text{tet}}$$

3.25
where \( n = 1 \) or \( 2 \) for \( T_1 \) or \( T_2 \) relaxation, \( \chi_{C2} = \) mole fraction of water molecules that are experiencing rapid \( C_2 \) symmetry jumps of their \( O-H \) bonds, \( (1/T_n)_{C2} = \) inverse of the \( C_2 \) jump relaxation time, \( T_{n,C2} \), \( \chi_{tet} = (1-\chi_{C2}) = \) mole fraction of water molecules experiencing tetrahedral jumps of their \( O-H \) bonds, and \( (1/T_n)_{tet} = \) inverse of the tetrahedral jump relaxation time \( T_{n,tet} \) [13].

The effects of jump rates (or rotational diffusion coefficient) and magnetic field on the powder average deuterium \( T_1 \) and \( T_2 \) values calculated for isotropic rotational diffusion, tetrahedral jumps, \( C_2 \) symmetry jumps, and for fast exchange between water molecules experiencing \( C_2 \) symmetry jumps of their \( O-H \) bonds (assuming \( \chi_{C2} = 0.5 \)) with those experiencing tetrahedral jumps of their \( O-H \) bonds (assuming \( \chi_{tet} = 0.5 \)) are shown in Fig. 2 and Fig. 3. In both Figures it is assumed for convenience that \( k_{C2}/k_{tet} (=1000) \) is constant as \( k_{tet} \) varies [14]. The assumption of fast exchange used in the calculations will not hold at temperatures for which \( k_{exch} \leq qcc \).

The most notable feature in the theoretical results is the double minimum in the dynamic frequency vs. theoretical \( T_1 \) dependence of the \( C2TET \) model (Fig. 3.2.). This is caused by the difference in the dynamic frequencies \( k_{C2} \) and \( k_{tet} \), each of which contributes to the observed relaxation. The dependence of the deuterium NMR relaxation times on temperature follows the dependence on jump rates, so two minima in the \( T_1 \) values as a function of temperature are also expected. Therefore an extended temperature range with short \( T_1 \) values is predicted in contrast to "pure" relaxation processes such as isotropic rotational diffusion, \( C_2 \) symmetry jumps, or tetrahedral jumps that have a single
Fig. 3.2: Theoretical powder average deuterium T₁ values as a function of the frequency of motion, ν, calculated at four magnetic fields and corresponding Larmor frequencies: For C₂ symmetry jumps (dark blue) ν = k_C₂, for tetrahedral jumps (green) ν = k_tet, for isotropic rotational diffusion (light blue) ν = 6 D_rot, and for fast exchange with equal contributions of C₂ jumps and tetrahedral jumps (red) ν = k_tet and k_C₂ = 1000 k_tet [15]. ²H quadrupolar values are qcc = 200 kHz and η = 0. Deuterium Larmor frequencies at the four magnetic fields are 45.84 MHz, 61.42 MHz, 76.78 MHz, and 92.13 MHz. In all cases the T₁ values increase with Larmor frequency, so the lowest curve in any set corresponds to 45.84 MHz and the highest to 92.13 MHz.
Fig. 3.3: Theoretical powder average deuterium $T_2$ values as a function of the frequency of motion, $\nu$, calculated at four magnetic fields and corresponding Larmor frequencies: For $C_2$ symmetry jumps (dark blue) $\nu = k_{C2}$, for tetrahedral jumps (green) $\nu = k_{tet}$, for isotropic rotational diffusion (light blue) $\nu = 6 \, D_{rot}$, and for fast exchange with equal contributions of $C_2$ jumps and tetrahedral jumps (red) $\nu = k_{tet}$ and $k_{C2} = 1000 \, k_{tet}$ [15]. $^2$H quadrupolar values are $q_{cc} = 200$ kHz and $\eta = 0$. Deuterium Larmor frequencies at the four magnetic fields are 45.84 MHz, 61.42 MHz, 76.78 MHz, and 92.13 MHz. In all cases the $T_2$ values increase with Larmor frequency, so the lowest curve in any set corresponds to 45.84 MHz and the highest to 92.13 MHz.
minimum in $T_1$ values. Furthermore, the contribution from a "slow" dynamic process, i.e. the tetrahedral jumps in this case, also allows magnetic field-dependent $T_1$ values to be observed at higher temperatures than for the "pure" relaxation processes.

As for liquid state isotropic rotational diffusion, the $T_1$ curves shown in light blue in Fig. 3.2 are unlikely to occur at ambient conditions, since such low rotational diffusion coefficients ($6 \, D_{\text{rot}} \leq 10^9 \, \text{sec}^{-1}$) have only been observed in supercooled liquid water at very cold temperatures and very high pressures [16].

Lastly noted, the $T_2$ values for all models are essentially field independent.
References


7. In our earlier work, we omitted the factor of 2 so the spectral densities and $T_1$ values were also off by a factor of two.


11. V. Gramlich, W.M. Meier, The crystal structure of hydrated NaA: A detailed refinement of a pseudosymmetric zeolite structure. Z. Kristallographie 133 (1971) 134-149.


13. No liquid state water was detected in the experiments, but it is possible that small mole fractions of liquid water in fast exchange with the solid water may have been masked by the much slower relaxation rate. For example, at room temperature $T_{1\text{liq}} \approx 0.40$ sec$^{-1}$, so $(1/T_{1})_{\text{obsd}} = \chi_{\text{liq}} (2.5$ sec$^{-1}) + \chi_{\text{sol}} (1/T_{1})_{\text{sol}}$ with $(1/T_{1})_{\text{sol}} > 100$ sec$^{-1}$.


15. This assumption anticipates the results obtained from experiment that show $k_{C2} >> k_{tet}$. It also allows us to avoid assumptions about the activation energies for $k_{C2}$ and $k_{tet}$ at this point in the discussion.
Chapter 4

Probing the State of Water in Zeolite A and Kanemite

4.1 Introduction

Evidence from deuterium NMR and infrared spectroscopy shows that solid state water exists at ambient temperatures in a variety of $^2$H$_2$O-hydrated porous silicates [1, 2, 3]. The NMR evidence is based on the sharp $^2$H$_2$O resonance observed in the deuterium spectrum and its extremely short and field dependent deuterium NMR $T_1$ values. Both characteristics were previously shown to be consistent with tetrahedral jumps of the O-$^2$H bonds on a fixed lattice rather than liquid state isotropic rotational diffusion[1,2]. Here a more detailed model is proposed for $^2$H$_2$O-Synthesized Kanemite ($\text{Na}_2\text{HSi}_2\text{O}_5$$\cdot$$3^2$H$_2$O) and $^2$H$_2$O-Hydrated Na$^+$-Zeolite A. The experimental data support this model over a wide range of temperatures from below room temperature to above the boiling point of pure water at atmospheric pressure.

$^2$H NMR is particularly advantageous for characterization of angular dynamics because it is dominated by the single nucleus $^2$H quadrupolar interaction. The strong quadrupolar interaction, arising from the coupling of the electric field gradient tensor with the nuclear electric quadrupole moment $Q$, dominates the much weaker $^2$H chemical shift and dipolar interactions [4, 5]. For $^2$H in various “rigid” solids, the deuterium qcc
(qcc \equiv e^2qQ/h) varies from 160 to 340 kHz with $0 \leq \eta \leq 0.15$. The small $\eta$ values indicate nearly axial symmetry of the electric field gradient tensor, with the $V_{zz}$ axis parallel to the $X-^2H$ covalent bond. This holds true for water, where the electric field gradient tensor in $^2H_2O$ has nearly axial symmetry about the O-$^2H$ covalent bond axis. Therefore, the spectrum and relaxation times for $^2H_2O$ can be used to monitor the time dependence of the angle made by the O-$^2H$ covalent bond with the magnetic field [1, 6].

A repertoire of deuterium NMR techniques are sensitive to O-$^2H$ motions with frequencies ($\nu_{\text{motion}}$) of $1 \times 10^{-2} < \nu_{\text{motion}} < 1 \times 10^{15}$ sec$^{-1}$ [7, 8]. These encompass most of the range of frequencies of reorientational and translational motions of water and other molecules in condensed phases.

For bulk liquid and supercooled liquid water, the $^2H$ $T_1$ and $T_2$ relaxation times show that the O-$^2H$ bonds experience isotropic rotational diffusion. However there is the recent proposal by Hynes and Laage that bulk liquid water undergoes a concerted 60° jump mechanism with characteristic jump rates close to $6D_{\text{rot}}$ values obtained for the isotropic rotational motion model [37]. Assuming isotropic rotational diffusion at 292 K and atmospheric pressure, the rotational rate constant for liquid $^2H_2O$ is $2.8 \times 10^{11}$ sec$^{-1}$ ($= 6D_{\text{rot}}$, where $D_{\text{rot}}$ is the rotational diffusion coefficient) [1], while for supercooled liquid water at high pressures and cold temperatures the rotational rate constants are several orders of magnitude lower [8, 9]. Although it occurs in some solids with spherically symmetric molecules [10], isotropic rotational diffusion is typical of liquids. In contrast, for pure solid Ice $I_h$ at atmospheric pressure, $^2H$ NMR lineshape analysis and stimulated echo experiments show that the O-$^2H$ bonds experience tetrahedral jumps (jump rate $\sim 10^4$ sec$^{-1}$ several degrees °C below freezing) due to the diffusion of Bjerrum defects.
through the ice lattice [6, 11]. On a slower time scale, there is also a seven site reorientation mediated by proton transfer and interstitial translational diffusion. For most crystalline hydrates, variable temperature $^2$H NMR lineshape analysis shows that the O-$^2$H bonds experience rapid $C_2$ symmetry jumps around the bisector of the HOH bond angle with jump rates $\geq 10^6$ sec$^{-1}$ at ambient temperatures [12, 13]. In a few cases, spectral analysis for crystalline hydrates shows that the water molecules are rigid on the “NMR timescale” ($v_{\text{jumps}} < q_{\text{cc}}$) except for librations that reduce the effective $^2$H qcc. $^2$H NMR stimulated echo experiments on tetrahydrofuran clathrate hydrate show that the O-$^2$H bonds of the water molecules experience tetrahedral jumps (ascribed to Bjerrum defects) on a distorted tetrahedral lattice as well as a slower randomization process ascribed to a combination of Bjerrum and ionic defects [14]. Dynamics characterized by jumps on a fixed lattice provides atomic level evidence of the solid state.

4.2 Experimental

4.2.1 Materials

Kanemite (NaHSi$_2$O$_5$$\cdot$$^3$H$_2$O), a simple phyllosilicate, was synthesized by adding $^2$H$_2$O (NMR) or $^1$H$_2$O (IR) to a mixture of $\delta$-Na$_2$Si$_2$O$_5$ and silica gel (SiO$_2$) as described previously [1]. Powder X-ray analysis verified the structure of kanemite, although the presence of some amorphous material was also indicated. All samples were
sealed. The weights of all samples were monitored and remained constant. Samples were stored at 21 ± 1 °C in the tightly controlled environment of the NMR Facility.

Phase pure hydrated Zeolite A (Na\textsubscript{12}Al\textsubscript{12}Si\textsubscript{12}O\textsubscript{48}\textbullet 27H\textsubscript{2}O), was purchased from Aldrich Chemical Co. The phase pure Zeolite A was heated at 550°C for at least 2 hours to completely remove its waters of hydration. Samples were then rehydrated by equilibrating them with H\textsubscript{2}O vapor (FT-IR) or \textsuperscript{2}H\textsubscript{2}O vapor (NMR) in an environmental chamber. The ratio of \textsuperscript{2}H\textsubscript{2}O to dehydrated Zeolite A in the rehydrated samples was determined gravimetrically to be within 1% of the stoichiometric loading of 27 moles of \textsuperscript{2}H\textsubscript{2}O per mole of Zeolite A. All samples were sealed, and their weights remained constant throughout the experiments.

4.2.2. X-Ray Crystallography and Previous NMR Results

The single crystal X-ray crystallography of kanemite shows fixed electron density for half of the water hydrogen atoms, specifically those that are octahedrally coordinated to Na\textsuperscript{+} [22]. The positions of the other water hydrogen atoms in kanemite and of all of the water hydrogen atoms in hydrated Na\textsuperscript{+}-Zeolite A are unresolvable with x-ray crystallography [22, 23]. The interlayer spacing between adjacent silicate layers in kanemite is 1.03 nm [22]. The nearly spherical pore diameters in Zeolite A are 1.43 and 0.99 nm, and the approximately cylindrical channels connecting the pores have diameters of about 0.33 nm [23]. For comparison, the effective diameter of a water molecule is 0.28 nm and the diameter of a Na\textsuperscript{+} ion is 0.19 nm [26]. X-ray crystallography and \textsuperscript{23}Na
solid state NMR of kanemite both show one Na\(^+\) binding site [22, 27], but NMR studies of Zeolite A have shown variation in the location and coordination of Na\(^+\) ions [28].

4.3 NMR measurements

\(^2\)H NMR experiments were carried out over a range of temperatures at various magnetic fields, specifically 6.98, 7.01, 7.05, 7.11, 9.41, 11.73, 11.75, and 14.099 Tesla on eight different NMR spectrometers: a solid state Chemagnetics CMX-300, two different liquid state Bruker DPX-300s, a home-built solid state spectrometer, a liquid state Bruker DRX-400, a solid state Chemagnetics/Varian Infinity 500, a liquid state Bruker AMX-2-500, and a liquid state Bruker DRX-600 spectrometer respectively, at a range of carefully calibrated temperatures (± 1 °C).

The quadrupole echo pulse sequence, (\(\pi/2\))\(_x\)-\(\tau_1\)-(\(\pi/2\))\(_{xy}\)-\(\tau_2\)-Acquire\(_x\) with Cyclops phase cycling added to all pulse phases and the receiver phase, was used to obtain \(^2\)H spectra on the solid state CMX-300 and Infinity 500 spectrometers at 45.65 and 76.77 MHz respectively (\(\pi/2 = 1.9\) to 2.5 μsec, \(\tau_1 = 35\) μsec, \(\tau_2 = 27\) μsec, spectral width = 2 MHz). The T\(_1\) value of the sharp central aqueous peak was determined at various magnetic fields as a function of temperature with the inversion recovery pulse sequence, \(\pi_x\) - \(\tau_{\text{variable}}\) - (\(\pi/2\))\(_{\phi 1}\) - Acquire\(_{\phi \text{ref}}\), with \(\phi 1 = x, y, -x, -y\) and \(\phi \text{ref} = x, y, -x, -y\), the inversion recovery quadrupole echo experiment, \(\pi_x\) - \(\tau_{\text{variable}}\) - (\(\pi/2\))\(_x\)-\(\tau_1\)-(\(\pi/2\))\(_{xy}\)-\(\tau_2\)-Acquire\(_x\) (with Cyclops), or the saturation recovery quadrupole echo experiment [((\(\pi/2\))\(_x\) -
\[ \tau_{n} - \tau_{\text{variable}} - (\pi/2)_{x} - \tau_{1} - (\pi/2)_{xy} - \tau_{2} - \text{Acquire}_{x} \text{ (with Cyclops)} \].  The T\(_2\) value of the sharp central peak was determined either from the peak width at half height for fully relaxed T\(_1\) spectra or with one of the following pulse sequences: 1. the CPMG single echo experiment: \((\pi/2)_{x} - \tau_{\text{variable}} - \pi_{xy} - \tau_{\text{variable}} - \text{Acquire}_{x} \text{ (with Cyclops)}\); or 2. the CPMG double echo experiment: \((\pi/2)_{x} - \tau_{\text{variable}} - \pi_{xy} - 2 \tau_{\text{variable}} - \pi_{-y} - \tau_{\text{variable}} - \text{Acquire}_{x} \text{ (with Cyclops)}\).  At temperatures where the central peak is sufficiently sharp, \(\Delta v_{1/2} < 3 \text{ kHz}\), the data from liquid state spectrometers was obtained using "soft" pulses on the lock channel of a liquid state probe with \(\pi/2 \approx 90 \mu\text{sec}\) and \(\pi \approx 180 \mu\text{sec}\).  As verified by separate experiments with hard pulses (\(\pi/2 \leq 3.0 \mu\text{sec}\)) on the solid state CMX-300 and Infinity-500 spectrometers, this was adequate for uniform excitation of the sharp central peak at temperatures where it could be resolved.  At lower temperatures where the sharp central peak could no longer be excited with soft pulses, the T\(_1\) values were determined with \(\pi/2\) pulse widths of 3 \(\mu\text{sec}\) or less either with the inversion recovery pulse sequence, the inversion recovery quadrupole echo pulse sequence, or the saturation recovery quadrupole echo pulse sequence.  For kanemite, very low temperature T\(_1\) data were acquired at 46.46 MHz by using the saturation recovery quadrupole echo pulse sequence and monitoring the relaxation of the echo maximum [29].  Low temperature quadrupole echo spectra were obtained on solid state CMX-300 and Infinity 500 spectrometers using a Chemagnetics variable temperature apparatus.  The temperature was calibrated with a copper constantan thermocouple taped in place inside the empty sample coil of the intact probe/variable temperature apparatus operating inside the magnet.  The temperatures reported on these instruments are accurate to ca. \(\pm 3 \text{ K}\) down to 123 K.
Single pulse excitation $^{29}$Si, $^{27}$Al, and $^{23}$Na MAS spectra for $^2$H$_2$O-synthesized kanemite and $^2$H$_2$O-hydrated Zeolite A were obtained at room temperature on the solid state CMX-300 and Infinity 500 spectrometers.

Theoretical $^2$H NMR calculations were carried out with Mathematica® programs developed partially by the author. The theoretical basis of these calculations was described in the previous chapter.

The infrared absorption spectrum of kanemite synthesized with $^1$H$_2$O is presented in Fig. 4.1. The O-$^2$H stretching region of the $^2$H$_2$O-synthesized kanemite spectrum is also included and the corresponding frequencies have been multiplied by 1.36 to account for the deuterium isotope effect. Overlap observed in the O-$^1$H and O-$^2$H regions of these spectra clearly show broad absorption peaks between $2200 \text{ cm}^{-1} \sim 3700 \text{ cm}^{-1}$ due to O-H(D) vibration in kanemite. The lattice vibration peaks in the $700 \text{ cm}^{-1} \sim 1200 \text{ cm}^{-1}$ range do not show any H/D exchange effect or isotope effect. Five distinct broad peaks appear in the O-H(D) stretching region. These broad peaks occur around $\sim 3620 \text{ cm}^{-1}$, $\sim 3360 \text{ cm}^{-1}$, $\sim 2995 \text{ cm}^{-1}$, $\sim 2620 \text{ cm}^{-1}$, and $\sim 2225 \text{ cm}^{-1}$. The $3620 \text{ cm}^{-1}$ peak might be attributed to free silanol groups. Other peaks are due to the strong perturbation of the O-H(D) stretching vibration inside of the kanemite crystal structure, likely due to strong hydrogen bonding and coordination to the Na$^+$ ion. These broad vibrational peaks for hydroxyl groups are commonly observed for kanemite [30], but their origin is not well understood. In any case, these IR spectra clearly indicate that water in kanemite is much different than bulk water or ice, with low O-H bond stretching frequencies that are consistent with the
solid state. The multiple peaks are consistent with the multiple forms of -O-H expected from the crystal structure, where the electron densities for silanol (Si-O-H) hydrogens and the O-H hydrogens of the water molecules directly coordinated to Na$^+$ are resolved, and at least two other types of water have been proposed [22, 27]. Further detailed information must be obtained from the NMR analysis.

The infrared absorption spectrum of Zeolite A as a function of time of hydration with $^1$H$_2$O is shown in Fig. 4.2. An approximately 200 µm thick pellet of dry Zeolite A was placed inside a fully enclosed home-built environmental infrared (IR) cell with AMTIR windows. Transmission spectra were collected using a Thermo-Nicolet Nexus 670 spectrometer and a MCT detector. The system was kept at room temperature and water vapour from a liquid water reservoir was allowed to enter the environmental IR-cell. Spectra were collected approximately every 100 min following the addition of water vapour to the system. The hydrated sample spectra were divided by the background spectrum from the dry Zeolite A. The growth of the OH stretching vibration peak of water molecules absorbed in the zeolite A was monitored as a function of time in the wavenumber region from 3000 to 3600 cm$^{-1}$. Upon exposure to the near saturation vapor pressure of water, the IR peak corresponding to the absorbed water increased fast in the first 300 minutes and grew slowly thereafter. After approximately 600 minutes, the peak intensity did not grow significantly, indicating that the Zeolite-A was almost fully saturated with water.
4.4 Results and Discussion

4.4.1 Infrared Spectroscopy

Fig. 4.1: Infrared Fourier Transform Spectrum of the water stretching region for H₂O-synthesized and D₂O-synthesized kanemite.
The primary IR peak of the absorbed water in the Zeolite-A is approximately 3230 cm\(^{-1}\) which is equivalent to that observed for fully hydrogen-bonded “ice-like” water [3]. It is well known that the IR adsorption band of pure liquid water is primarily made up of a broad peak around 3400 cm\(^{-1}\). As the number of hydrogen bonds in water increases, this peak shifts to lower wavenumbers. In ice I\(_h\), which is completely hydrogen bonded, the peak appears near 3200 cm\(^{-1}\). The shoulder peak near 3360 cm\(^{-1}\) can be attributed to either defects in the ice-like water network inside the zeolite pores or water coordinated around the sodium ion in the zeolite structure. The peak for the water O-H stretching band for the first hydration layer of Na\(^+\) in liquid solutions appears at \(~3423\) cm\(^{-1}\), suggesting that the peak at 3360 cm\(^{-1}\) is from Na\(^+\)-coordinated water [31]. The apparent simplicity of the hydrated Zeolite-A IR spectrum in comparison to that of hydrated kanemite is not fully understood and will be investigated in future work.

Overall, the FT-IR data show that the water in both materials is not bulk liquid water but is more indicative of a substantially hydrogen bonded network of water coordinated to ions.

4.4.2. NMR Results

The \(^{29}\)Si MAS spectrum of \(^2\)H\(_2\)O-synthesized kanemite is shown in Fig. 4.3. It shows, in addition to the main Q\(^3\) kanemite peak at -97 ppm, about 12% Q\(^4\) and Q\(^2\) impurities (by deconvolution).
Fig. 4.2: Infrared absorption spectra of the water OH stretching region for water adsorption in Zeolite A are illustrated as a function of time (0, 210, and 520 min – from bottom to top). Two broad primary peaks exist around (A) 3230 cm\(^{-1}\) (by deconvolution) and (B) 3360 cm\(^{-1}\) (by deconvolution) corresponding to completely hydrogen-bonded ice-like water and water coordinated to Na\(^+\), respectively [31].
The $^{27}\text{Al}$ MAS ($\nu_{\text{rot}} = 10$ kHz) NMR spectrum of $^2\text{H}_2\text{O}$-hydrated Zeolite A is shown in Fig. 4.4. It shows the main tetrahedral peak, no octahedral or 5-coordinate aluminium sites, and almost no impurities.

The $^{23}\text{Na}$ MAS ($\nu_{\text{rot}} = 10$ kHz) spectrum of $^2\text{H}_2\text{O}$-synthesized kanemite (Fig. 4.5) shows a slightly broadened second order quadrupolar lineshape.

Nutation spectra (not shown) verify that only the central transition was excited, which is consistent with the solid state. The $^{23}\text{Na}$ MAS spectrum of $^2\text{H}_2\text{O}$-hydrated Zeolite A (Fig. 4.5.) shows a partially averaged second order quadrupolar lineshape, suggesting that sodium exchanges between several binding sites. The exchange is fast compared to the second order quadrupolar powder linewidth ($\sim 2.5$ kHz), but slow compared to the $^{23}\text{Na}$ qcc ($\sim 2.5$ MHz). The nutation spectra (not shown) verify that the central transition was selectively excited, again consistent with the solid state.
Fig. 4.3: Single pulse excitation $^{29}\text{Si}$ MAS ($v_{\text{rot}} = 3.5$ kHz) NMR spectrum of $^2\text{H}_2\text{O}$-synthesized kanemite at 59.08 MHz ($pw = 6$ µsec, $sw = 40$ kHz, $pd = 180s$, 476 transients, $al = 1k$). Tetrakis(trimethylsilyl)silane was used as a secondary reference. A glitch at -76 ppm is also present in the spectrum of an empty rotor.
Fig. 4.4: $^{27}\text{Al}$ MAS ($v_{rot} = 10$ kHz) NMR spectrum of $^{2}$H$_2$O-hydrated Zeolite A at 130.26 MHz. (pw = 1 $\mu$s, sw = 40 kHz, relaxation delay = 2s, ns = 960, td = 1k). 1M AlCl$_3$ (aq) (0 ppm) was as used as a secondary reference.
Fig. 4.5: a. $^{23}\text{Na}$ MAS single pulse spectrum of $^2\text{H}_2\text{O}$-synthesized kanemite at 132.16 MHz (spinrate = 10 kHz, pw = 1 $\mu$sec, sw = 50 kHz, pd = 1s, 3072 transients, al = 1k).
b. $^{23}\text{Na}$ MAS single pulse spectrum of $^2\text{H}_2\text{O}$-hydrated Zeolite A at 132.16 MHz (spinrate = 10 kHz, pw = 1 $\mu$sec, sw = 50 kHz, pd = 1s, 3424 transients, al = 1k).
4.4.3. Theoretical Intermediate Exchange $^2$H NMR Spectra

Theoretical intermediate exchange $^2$H powder lineshapes as a function of the tetrahedral jump rate $k_{tet}$ are shown in Fig. 4.6. The method described by Vega and Luz was used to calculate intermediate exchange quadrupole echo time domain signals [32]. Effects of motion during the $\tau$ delays of the quadrupole echo experiment were included in the calculations of the time domain signals. The spectra were obtained by Fourier transformation of the calculated time domain signals. The echo intensities for tetrahedral jumps in the intermediate exchange regime are severely attenuated in the range $10^4$ sec$^{-1} \leq k_{tet} \leq 10^6$ sec$^{-1}$. If the C2TET model holds, this would be expected to be manifested in the experimental quadrupole echo data.

Theoretical intermediate exchange powder lineshapes as a function of the C$_2$ jump rate $k_{C2}$ are shown in Fig. 4.7. Unlike the tetrahedral jump quadrupole echo intensity, the C$_2$ jump quadrupole echo intensity does not fall below 12% of its maximum value.

Quadrupole echo intensities for octahedral jumps have been calculated as a function of the octahedral jump rate $\nu$ in Fig. 4.8. Consideration of the octahedral jump rate is necessary with the C2TET model because exchange between the O-$^2$H populations experiencing C$_2$ symmetry jumps and tetrahedral jumps generates approximately octahedral jumps of O-$^2$H bond vectors as they sample the different water binding sites of the Na$^+$ ions. Assuming that the exchange process is rate limiting, the C2TET kinetic
Fig. 4.6: Deuterium powder lineshapes calculated for tetrahedral jumps of the O-2H bond as a function of the tetrahedral jump rate \( k_{\text{tet}} \). The \( k_{\text{tet}} \) values are shown on top of the corresponding lineshapes, and the echo intensities are shown underneath the corresponding lineshapes. The isotropic peaks at the highest jump rates have been truncated to fit on scale. The following parameters were used: \( q_{cc} = 200 \) kHz, \( \eta = 0 \), \( \tau = 35 \) µsec (echo delay in quadrupole echo experiment).
Fig. 4.7: Deuterium powder lineshapes calculated for C$_2$ symmetry jumps of the O-$_2$H bond as a function of the jump rate $k_{C2}$. The $k_{C2}$ values are shown on top of the corresponding lineshapes, and the echo intensities are shown underneath the corresponding lineshapes. The following parameters were used: $q_{cc} = 200$ kHz, $\eta = 0$, $\tau = 35 \mu$sec (echo delay in quadrupole echo experiment), and an equally weighted mixture (0.5 weight each) of $\theta = 52.5^\circ$ and $\theta = \text{magic angle}$.
Fig. 4.8: Deuterium powder echo intensities calculated for octahedral symmetry jumps of the O-2H bond as a function of the jump rate $\nu = k_{\text{exch}}$. The following parameters were used: $q_{cc} = 200$ kHz, $\eta = 0$, $\tau = 35$ $\mu$sec (echo delay in quadrupole echo experiment).
parameter $k_{\text{exch}}$ can be identified with the octahedral jump rate. For $10^4 \text{ sec}^{-1} \leq k_{\text{exch}} \leq 10^6 \text{ sec}^{-1}$, the quadrupole echo intensity for octahedral jumps nearly vanishes. If the C2TET model holds, the corresponding loss of echo intensity would be expected in the experimental data.

4.4.4. Experimental Low Temperature $^2\text{H}$ NMR Spectra

Zeolite A contains no silanol groups, so the low temperature $^2\text{H}$ powder spectra of $^2\text{H}_2\text{O}$-hydrated Zeolite A are simpler than those of kanemite. The experimental quadrupole echo spectra of $^2\text{H}_2\text{O}$-hydrated Zeolite-A are shown in Fig. 4.9 with theoretical simulations. At the lowest temperature maintained, 141 K, the quadrupole echo spectrum is consistent with the rigid deuterium powder spectrum of $^2\text{H}_2\text{O}$ with $\nu_{\text{motion}} \ll q_{cc}$, $q_{cc} \approx 200 \text{ kHz}$, and $0 \leq \eta \leq 0.1$, Table 1. At 203 and 210 K, the spectra are consistent with a combination of nearly rigid $^2\text{H}_2\text{O}$ and a lineshape close to that calculated for $\text{C}_2$ symmetry jumps with $k_{c2} > q_{cc}$. Therefore the “rigid” parts of these spectra are assigned to the population of O-$^2\text{H}$ bonds experiencing tetrahedral jumps with $k_{\text{tet}} \ll q_{cc}$. The resolvability of both deuteron populations, C2 and tetrahedral, also shows that $k_{\text{exch}} \ll q_{cc}$. At 222 and 232 K, the rigid deuterium powder pattern is not resolvable, but the $\text{C}_2$ symmetry jump powder lineshape is still observable. This is consistent with the loss of intensity for tetrahedral jumps as they approach the intermediate exchange regime, $k_{\text{tet}} \approx q_{cc}$, (Fig. 4.9.). The extremely low experimental quadrupole echo intensities and limited resolvability of the remaining $\text{C}_2$ symmetry jump lineshapes, suggests further that $k_{\text{exch}}$ approaches $q_{cc}$ at these temperatures, consistent with octahedral jumps in intermediate exchange and the C2TET model. The theoretical
echo intensities in Fig. 4.9 do not include the effects of octahedral jumps. The simultaneity of the decrease in $k_{tet}$ and $k_{exch}$ suggests that the exchange process may require tetrahedral jumps. Above 251 K the quadrupolar echo spectra show a single apparently isotropic peak. This is consistent with the C2TET model if $k_{exch} > q_{cc}$ and $k_{c2} \gg q_{cc}$.

Eyring plots [33] of the temperature dependent rate constants are shown in Fig. 4.10, where the estimated values of $k_{c2}$ and $k_{tet}$ values from Fig. 4.6, 4.7 have been used. For the hydrated Zeolite A, the kinetic activation parameters for the tetrahedral and C$_2$ symmetry jumps are $\Delta H_{tet}^\ddagger = +17$ kJ/mol, $\Delta S_{tet}^\ddagger = -111$ J/(mol K), $\Delta H_{c2}^\ddagger = +20$ kJ/mol, and $\Delta S_{c2}^\ddagger = -15$ J/(mol K).

The variable temperature quadrupole echo $^2$H spectra of $^2$H$_2$O-synthesized kanemite are complicated by the presence of a dynamic silanol (Si-O-2H) powder pattern with a notable downfield silanol chemical shift [2] that persists throughout the temperature range, Fig. 4.11. At the lowest temperature maintained, 132 K, the broad powder pattern of rigid $^2$H$_2$O ($k_{c2} < q_{cc}$, $k_{tet} << q_{cc}$, Table 1) is dominant, but the narrower silanol powder pattern is still apparent. At 218 K, there is still a rigid powder pattern assigned to O-$^2$H bonds experiencing tetrahedral jumps ($k_{tet} << q_{cc}$), a silanol powder pattern, and also a central bump assigned to O-$^2$H bonds experiencing C$_2$ symmetry jumps ($k_{c2} \sim q_{cc}$). At 256 K, the rigid powder pattern has disappeared and the
Fig. 4.9: Experimental (left) and simulated (right) variable temperature quadrupole echo spectra of $^2$H$_2$O-hydrated Zeolite A. The quadrupole echo pulse sequence ($((\pi/2)_x$-t$_1$-$(\pi/2)_{xy}$-t$_2$-Acquire, with Cyclops phase cycling added to all pulse phases and the receiver phase) was used to obtain $^2$H spectra on the solid state Infinity 500 spectrometer at 76.77 MHz ($\pi/2 = 2.0$ μsec, $\tau_1 = 35$ μsec, $\tau_2 = 27$ μsec, spectral width 2 MHz). Approximate theoretical spectra and echo intensities were calculated assuming equal contributions from deuterium populations experiencing C$_2$ symmetry jumps of their O-$^2$H bonds and tetrahedral jumps of their O-$^2$H bonds, each with $\gamma_{cc} = 200$ kHz, $\eta = 0$. The C$_2$ population was further subdivided into two equal populations with $\theta = \text{magic angle}$.
and \( \theta = 52.5^\circ \). The theoretical spectrum for 251 K was simulated by assuming that the \( \text{C}_2 \) symmetry jumps had been isotropically averaged by octahedral exchange between different \( \text{C}_2 \) binding sites.

Fig. 4.9

Fig. 4.10

Fig. 4.10: Eyring plots [33] of the \( k_{\text{C}_2} \) and \( k_{\text{tet}} \) values in \( ^2\text{H}_2\text{O}\)-hydrated Zeolite A obtained from the simulations in Fig. 12. The activation parameters are \( \Delta H_{\text{tet}}^{\ddagger} = +17 \) kJ/mol, \( \Delta S_{\text{tet}}^{\ddagger} = -111 \) J/(mol K), \( \Delta H_{\text{C}_2}^{\ddagger} = +20 \) kJ/mol, and \( \Delta S_{\text{C}_2}^{\ddagger} = -15 \) J/(mol K).
The spectrum is a combination of the silanol powder pattern and a powder pattern assigned to fast $C_2$ symmetry jumps ($k_{C2} \gg qcc$). A powder lineshape from O-$^2$H bonds experiencing tetrahedral jumps is no longer observable, suggesting that $k_{tet}$ approaches $qcc$ with correspondingly low intensity, Fig. 9. At 275 K, the spectrum is a sum of the silanol powder pattern and an intense central peak. The central peak retains some features characteristic of the fast exchange $C_2$ jump lineshape, suggesting that $k_{exch} \sim qcc$. At 296 K, the central peak has narrowed, suggesting that $k_{exch} \gg qcc$. Unlike the case for $^2$H$_2$O-hydrated Zeolite A, there is not a huge loss of experimental echo intensity at temperatures where $k_{tet}$ and $k_{exch}$ are in intermediate exchange. This is consistent with a non-vanishing contribution from the silanol -$O^2$H. The presence of the silanol powder lineshape shows that the silanol deuterium nuclei are not exchanging rapidly with water deuterium nuclei.

4.4.5. Field Dependent Variable Temperature $^2$H Relaxation Data for the Sharp Central Resonance of the Kanemite and Zeolite A Samples

The $T_1$ data obtained for the sharp water peak at temperatures where it could be resolved and inverted with soft pulses, above $\sim 252$ K for $^2$H$_2$O-hydrated Zeolite A, and above 279 K for $^2$H$_2$O-synthesized kanemite, were monoexponential. When fit with the Kohlrausch
stretched exponential function, the $T_1$ relaxation data obtained for the sharp central peaks of both samples yield $\beta > .94$ in all cases with the lowest $\beta$ values obtained

Fig. 4.11

Fig. 4.11: Experimental variable temperature quadrupole echo spectra of $^2$H$_2$O-synthesized kanemite. The quadrupole echo pulse sequence was used on the solid state
Infinity 500 spectrometer at 76.77 MHz ($\pi/2 = 2.0\mu\text{sec}$, $\tau_1 = 35\mu\text{sec}$, $\tau_2 = 27\mu\text{sec}$, spectral width 2 MHz). Experimental echo intensities relative to the intensity at 132 K are shown on the right side of each spectrum. A vertical expansion of the spectrum at 296 K is included to show the silanol powder pattern that persists through the temperature range.

Table 4-1

Table 4-1: Summary of the estimates of C2TET rate constants relative to the O-$^2$H quadrupole coupling constant (qcc).

<table>
<thead>
<tr>
<th>Substance</th>
<th>T (K)</th>
<th>$k_{C2}$</th>
<th>$k_{tet}$</th>
<th>$k_{exch}$</th>
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<tr>
<td>With D$_2$O</td>
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<tr>
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<td>$&gt;251$</td>
<td>$&gt;&gt; qcc$</td>
<td>$\sim qcc$</td>
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<td>275</td>
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<td>$\sim qcc$</td>
<td>$\geq qcc$</td>
<td>DSP</td>
</tr>
</tbody>
</table>

$^1$ There is greater uncertainty in $k_{exch}$ estimates.

$^2$ A dynamic silanol pattern (DSP) persists throughout the temperature range.
at the lowest temperatures, consistent with monoexponential relaxation or a narrow range of relaxation times [34]. At lower temperatures the intermediate exchange powder lineshapes emerge and prevent direct determination of $T_1$ values for the sharp central peak.

Low temperature $T_1$ data for $^2$H$_2$O-synthesized kanemite (these experiments have not yet been run for $^2$H$_2$O-hydrated Zeolite A) were obtained at 46.46 MHz from the full echo intensity in a saturation recovery quadrupole echo experiment with hard pulses. Two types of deuterium spin lattice relaxation were observed: a slowly relaxing component ($\beta \approx 0.6$) that is tentatively assigned to the silanol deuterium and a faster relaxing monoexponential component ($\beta > 0.9$) that is assigned to the O-$^2$H bonds experiencing tetrahedral and $C_2$ symmetry jumps. At temperatures where both methods were used, 288 and 295 K, the fast relaxing component and the sharp central peak had the same $T_1$ values within experimental error (ca. ± 10%) at 46.46 and 46.07 MHz. The experimental $T_1$ and $T_2$ values for the sharp central peak of $^2$H$_2$O-synthesized kanemite and $^2$H$_2$O-hydrated Zeolite A are shown in Figs. 15 and 16, respectively.

The O-$^2$H bond motions in $^2$H$_2$O-synthesized kanemite and in $^2$H$_2$O-hydrated Zeolite A are very different than they are in bulk liquid water. In bulk liquid $^2$H$_2$O and in supercooled $^2$H$_2$O at atmospheric pressure, the extreme narrowing condition is met, with $D_{rot} >> \nu_{Larmor}$, and $T_1 = T_2$. From theory, the $T_1$ and $T_2$ values are magnetic field

| 296 | $>> q_{cc}$ | $> q_{cc}$ | $>> q_{cc}$ | DSP |
independent. This is not the case for $^2\text{H}_2\text{O}$ in $^2\text{H}_2\text{O}$-synthesized kanemite or in $^2\text{H}_2\text{O}$-hydrated Zeolite A, where the $T_1$ and $T_2$ values differ by 2.5 to 3 orders of magnitude,

Fig. 4.12

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Fig. 4.12: The experimental deuterium $T_1$ data for the sharp central resonance of $^2\text{H}_2\text{O}$-synthesized kanemite at 46.03 (purple squares) and 76.77 MHz (dark blue diamonds); $T_1$ data obtained at low temperature for the fast-relaxing component at 46.46 MHz (purple crosses), and $T_2$ data obtained with the double echo CPMG experiment at 76.77 MHz (orange squares) The temperature dependent $T_1 = T_2$ values (black triangles) for bulk $^2\text{H}_2\text{O}$ at atmospheric pressure are shown for comparison [35].
Fig. 4.13: The experimental deuterium T$_1$ data for the sharp central resonance of $^2$H$_2$O-hydrated Zeolite A at 46.03 (light blue x'es), 61.42 MHz (purple squares), 76.77 MHz (dark blue diamonds), and 92.13 MHz (filled blue circles). The T$_2$ values at 76.77 MHz obtained with the double echo CPMG experiment (orange squares) and from the sharp peak linewidth (orange crosses) are also shown. The temperature dependent T$_1$ = T$_2$ values (black triangles) for bulk $^2$H$_2$O at atmospheric pressure are shown for comparison [35].
and the $T_1$ values are dependent on the magnetic field. Therefore motions comparable to or slower than the Larmor frequency must occur throughout the experimental temperature range of both samples.

This is confirmed by the $^2$H NMR $T_1$ values for both $^2$H$_2$O-synthesized kanemite and $^2$H$_2$O-hydrated Zeolite A, which are nearly two orders of magnitude shorter than those of bulk liquid $^2$H$_2$O at the same temperatures. In addition, for both samples the $T_1$ values show significant magnetic field dependence that increases with temperature above 277 K. The field dependence exceeds the experimental uncertainty (ca. $\pm 10\%$) in the $T_1$ values at these temperatures. The minima in the experimental $T_1$ values occur near 284 K and 267 K, respectively, for $^2$H$_2$O-synthesized kanemite and $^2$H$_2$O-hydrated Zeolite A. The temperatures for these $T_1$ minima may be compared to the temperatures for the $T_1$ minima for isotropic rotational diffusion of supercooled liquid $^2$H$_2$O at comparable magnetic fields. For supercooled liquid water, the minima occur at temperatures below 200 K and pressures above 2000 atm [8].

The scatter in the $T_1$ data obtained for $^2$H$_2$O-synthesized kanemite with the saturation recovery method (black triangles) between 250 and 280 K (Fig. 4.12) may indicate that the tetrahedral jump rate $k_{tet}$ and the exchange rate $k_{exch}$ are both in the intermediate exchange region at these temperatures (see Fig. 4.13.). Other possible explanations for the differences are under investigation.

There were significant differences in the experimental $T_2$ values (76.77 MHz) determined by peak width, single echo CPMG experiments, and double echo CPMG
experiments. However, the values obtained with any given experiment at any temperature were reproducible. Residual powder lineshapes due to asymmetry in the tetrahedral, C2, or octahedral jumps may contribute to the observed peak width and reduce the linewidth-derived T2 value. The variation of the T2 values with the experimental method is also consistent with the effects of intermediate exchange on T2 relaxation [36]. In Figs. 4.12 and 4.13, the double echo CPMG T2 values are plotted, since these are the longest T2 values observed. The linewidth-derived T2 values for 2H2O-hydrated Zeolite A are also shown in Fig. 16 to illustrate the magnitude of the discrepancy between the values obtained with the different methods. T2 values determined for a few temperatures at 46.03 MHz with each of the three methods verified magnetic field (Larmor frequency) independence for each method within experimental error (ca. ± 10%). The lack of field dependence for T2 combined with the lack of consistent values from different experimental methods makes the experimental T2 dependence on temperature less reliable for comparison with theory than the T1 dependence.

4.4.6. Comparison of Theory and Experiment for T1 Relaxation

The experimental deuterium T1 data for the sharp central peak of 2H2O-hydrated Zeolite A obtained with "soft" pulses over a range of fixed temperatures at 46.03, 61.42, 76.77, and 92.13 MHz are plotted on the background of the best fit theoretical T1 values for the C2TET model in Figs. 4.14 and 4.15. Experimental T1 values obtained at the same temperature but at different magnetic fields were plotted against the theoretical curves that gave the best match, assuming that kC2/ktet is constant
for the C2TET model. This assumption is justified for $^2$H$_2$O-hydrated Zeolite A by the similar activation enthalpies for $k_{C2}$ and $k_{tet}$ calculated from the low temperature quadrupole echo spectra of Figs. 4.9 and 4.10, but this has yet to have been verified if this is also true for $^2$H$_2$O-synthesized kanemite. Nevertheless, this is the simplest possible assumption for the C2TET model. Experimental T$_1$ values for bulk water are off the scale of the plot and show no magnetic field dependence. The pure tetrahedral and pure C$_2$ symmetry jump models cannot reproduce the extended temperature range of the magnetic field dependence. The isotropic rotational diffusion model, with $\nu = 6$ D$_{rot}$ values characteristic of supercooled liquid water at 200 K and 2000 atm, cannot match the magnetic field dependence either. Only the fast exchange C2TET model was able to reproduce the experimental data. A more complete study of the relationship between $k_{C2}$ and $k_{tet}$ is underway. It is recognized that the assumption of equal activation enthalpies for $k_{C2}$ and $k_{tet}$ may have to be revised.

In Fig. 4.15, the plot is extended to lower temperatures, where the fit obtained for the C2TET model with $k_{C2}/k_{tet} = 25833$ no longer matches as well. The experimental values instead approach the values expected for pure C$_2$ jumps. This is easily explained in the context of the C2TET model. At lower temperatures the tetrahedral jump rate falls into the intermediate exchange regime ($k_{tet} \sim qcc$) and the contribution to the deuterium NMR intensity from the tetrahedrally jumping O-$^2$H bond population drops in comparison to that of the C$_2$ symmetry jumping O-$^2$H bond population, which is still in fast exchange ($k_{C2} \gg qcc$). The process represented by the C2TET exchange rate constant $k_{exch}$ may also go into intermediate exchange at the same temperatures. Further details will be elucidated in future work.
Fig. 4.14: The high temperature experimental $T_1$ data for the sharp central resonance of $^2\text{H}_2\text{O}$-hydrated Zeolite A are plotted on the background of the best fit theoretical $T_1$ values for the C2TET model ($\chi_{\text{tet}} = \chi_{C2} = 0.5$, $v = k_{\text{tet}}$, $k_{C2}/k_{\text{tet}} = 25833$) for deuterium frequencies of 46.03 MHz, 61.42 MHz, 76.77 MHz, and 92.13 MHz. The ratio of $k_{C2}/k_{\text{tet}}$ was assumed to be constant throughout the temperature range, and was chosen to yield the best possible fit of the resulting theoretical curves to the experimental data. Curves for pure tetrahedral jumps and pure isotropic rotational diffusion are off the scale of this figure. There was no way to fit the experimental data with the isotropic rotational diffusion model or the perfect tetrahedral jump model. The best fit was obtained with $q_{cc} = 200$ kHz and $\eta = 0$. 
Fig. 4.15: The low temperature experimental $T_1$ data for the sharp central resonance of $^2$H$_2$O-hydrated Zeolite A are plotted on the background of the best fit theoretical $T_1$ values for the C2TET model (black theoretical curves, $\chi_{tet} = \chi_{C2} = 0.5$, $\nu = k_{tet}$, $k_{C2}/k_{tet} = 25833$) and the pure C$_2$ jump model (red theoretical curves, where we have used $k_{C2} = 25833 \nu$ so direct comparison is possible with the C2TET model) for deuterium frequencies of 46.03 MHz, 61.42 MHz, 76.77 MHz, and 92.13 MHz. For the C2TET model, the ratio of $k_{C2}/k_{tet}$ was assumed to be constant throughout the temperature range, and was chosen to yield the best possible fit of the resulting theoretical curves to the experimental data. Curves for pure tetrahedral jumps and pure isotropic rotational diffusion are off the scale of this figure. There was no way to fit the experimental data with the isotropic rotational diffusion model or the perfect tetrahedral jump model. The best fit was obtained with $qcc = 200$ kHz and $\eta = 0$. 
Fig. 4.16 shows Eyring plots [33] of the rate constants $k_{C2}$ and $k_{tet}$ estimated from the C2TET model for $^{2}$H$_2$O-hydrated Zeolite A in Fig. 17 along with the $k_{C2}$ and $k_{tet}$ values estimated from the low temperature quadrupole echo spectra (Fig. 4.9). The best fit activation parameters for C$_2$ and tetrahedral jumps are $\Delta H_{tet}^{\ddagger} = +17$ kJ/mol, $\Delta S_{tet}^{\ddagger} = -109$ J/(mol K), $\Delta H_{C2}^{\ddagger} = +19$ kJ/mol, and $\Delta S_{C2}^{\ddagger} = -20$ J/(mol K) respectively, very close to the values estimated from the variable temperature quadrupole echo spectra alone. The consistency of the data obtained from the two different deuterium NMR techniques supports the C2TET model.

The experimental $T_1$ data obtained with "soft" pulses over a range of fixed temperatures at 46.03 and 76.77 MHz for the sharp central resonance of $^{2}$H$_2$O-synthesized kanemite are plotted on the background of the best fit theoretical $T_1$ values for the C2TET model in Figs. 20 and 21. As with Zeolite A, experimental $T_1$ values for bulk water are off the scale, pure tetrahedral and pure C$_2$ symmetry jump models cannot reproduce the extended temperature range of the magnetic field dependence, and isotropic rotational diffusion with $\nu = 6$ D$_{rot}$ values, characteristic of supercooled liquid water at 200 K and 2000 atm, cannot match the magnetic field dependence either. Only the C2TET model was able to reproduce the experimental data obtained at higher temperatures ($\geq 298$ K, Fig. 20). The optimal $k_{C2}/k_{tet}$ ratio is 1000. The fit between the experimental and best fit C2TET model is good for temperatures above 298 K, but
Fig. 4.16: Eyring plots [33] of the $k_{C_2}$ and $k_{tet}$ values in $^2$H$_2$O-hydrated Zeolite A obtained from the simulations in Fig. 12 (low temperature data) and from the $T_1$ data from Fig. 17 (high temperature data). $\Delta H_{tet}^\ddagger = +17$ kJ/mol, $\Delta S_{tet}^\ddagger = -109$ J/(mol K), $\Delta H_{C_2}^\ddagger = +19$ kJ/mol, and $\Delta S_{C_2}^\ddagger = -20$ J/(mol K).
deviates from the C2TET model at lower temperatures where the tetrahedral jump rate \( k_{\text{tet}} \) and exchange rate \( k_{\text{exch}} \) go into intermediate exchange (Figs. 4.9, 4.15). Based on the C2TET model, the experimentally observed relaxation times in this temperature region should therefore be dominated by the population of water molecules experiencing C2 jumps. This prediction is verified in Fig. 4.15 and 4.18.

Eyring plots [33] of the calculated \( k_{\text{tet}} \) and \( k_{\text{C2}} \) values for \(^2\text{H}_2\text{O}\)-synthesized kanemite from Figs. 4.17 and 4.18 are shown in Fig. 4.19. The activation parameters for kanemite are \( \Delta H_{\text{tet}}^{\ddagger} = +23 \text{ kJ/mol} \), \( \Delta S_{\text{tet}}^{\ddagger} = -69 \text{ J/(mol K)} \), \( \Delta H_{\text{C2}}^{\ddagger} = +23 \text{ kJ/mol} \), and \( \Delta S_{\text{C2}}^{\ddagger} = -11 \text{ J/(mol K)} \).

It is apparent for both \(^2\text{H}_2\text{O}\)-synthesized kanemite and \(^2\text{H}_2\text{O}\)-hydrated Zeolite A that the \( k_{\text{C2}} \) and \( k_{\text{tet}} \) jump rate values calculated from the \( T_1 \) data are consistent with the experimental low temperature quadrupolar echo lineshapes. The consistency of the data is also confirmed by the lowest temperature at which the sharp central resonance can be inverted in the \( T_1 \) experiments for both samples. Numerical Bloch equation calculations for tetrahedral jumps of O-\(^2\text{H}\) bonds show that soft pulses, such as those used in most of the \( T_1 \) experiments, are not able to invert the sharp central resonance obtained from tetrahedral jumps as \( k_{\text{tet}} \) falls below about \( 1 \times 10^6 \text{ s}^{-1} \). The ability to invert the part of the sharp central resonance arising from the population of water molecules experiencing C2 and octahedral jumps of their O-\(^2\text{H}\) bonds persists to slightly lower temperatures, presumably since \( k_{\text{C2}} \gg q_{\text{cc}} \) and \( k_{\text{exch}} \gg q_{\text{cc}} \). Experimentally, the loss of the ability to
Fig. 4.17: The high temperature experimental $T_1$ data for the sharp central resonance of $^2$H$_2$O-synthesized kanemite at 46.03 (red curve) and 76.77 MHz (blue curve) plotted on the background of the theoretical $T_1$ values the C2TET model ($\chi_{tet} = \chi_{C2} = 0.5$, $\nu = k_{tet}$, $k_{C2}/k_{tet} = 1000$). The ratio of $k_{C2}/k_{tet}$ (assumed to be constant throughout the temperature range) was chosen to yield the best possible fit of the resulting theoretical curves to the experimental data. Plots of the pure C2 model, calculated for $k_{C2} = 1000\nu$ so that the $T_1$ values can be expressed in terms of $k_{tet}$ at 46.03 (green) and 76.77 MHz (purple) are shown for comparison. Curves for pure tetrahedral jumps and pure isotropic rotational diffusion are off the scale of this figure. There was no way to fit the experimental data with the isotropic rotational diffusion model or the pure tetrahedral jump model. The best fit for the C2TET model was obtained with $q_{cc} = 210$ kHz and $\eta = 0.1$. 
Fig. 4.18: Lower temperature experimental $T_1$ data for the sharp central resonance of $^2$H$_2$O-synthesized kanemite at 46.03 and 76.77 MHz (red curves) plotted on the background of the theoretical C2TET $T_1$ values ($\chi_{\text{tet}} = \chi_{\text{C2}} = 0.5$, $v = k_{\text{tet}}$, $k_{\text{C2}}/k_{\text{tet}} = 1000$). The ratio of $k_{\text{C2}}/k_{\text{tet}}$ (assumed to be constant throughout the temperature range) was chosen to yield the best possible fit of the resulting theoretical curves to the experimental data obtained at higher temperatures, Fig. 20. Plots of the pure C2 model (blue curves), calculated for $k_{\text{C2}} = 1000 \, v$ at 46.03 (lower) and 76.77 MHz (upper) are shown for comparison. Curves for pure tetrahedral jumps and pure isotropic rotational diffusion are off the scale of this figure. There was no way to fit the experimental data with the isotropic rotational diffusion model or the perfect tetrahedral jump model. The best fit was obtained with $\omega_{\text{CC}} = 210$ kHz and $\eta = 0.1$. 

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**Fig. 4.18**

![Image of the graph showing $T_1$ data for different temperatures and models.](image-url)
Fig. 4.19: Eyring plots [33] of the tetrahedral jump rate k values for $^2$H$_2$O-synthesized kanemite obtained from Figs. 4.17 and 4.18. The activation parameters are $\Delta H_{tet}^{\ddagger} = +23$ kJ/mol, $\Delta S_{tet}^{\ddagger} = -69$ J/(mol K), $\Delta H_{C2}^{\ddagger} = +23$ kJ/mol, and $\Delta S_{C2}^{\ddagger} = -11$ J/(mol K). The $\Delta H^{\ddagger}$ values are the same because it was assumed that $k_{C2}/k_{tet}$ is constant and equal to 1000 in Figs. 20 and 21.
invert the sharp central resonance was observed at temperatures where the C2TET model predicts both \( k_{\text{tet}} \) and \( k_{\text{exch}} \) are in the intermediate exchange regime, \( k_{\text{tet}} \sim q_{\text{cc}} \) and \( k_{\text{exch}} \sim q_{\text{cc}} \).

### 4.4.7. Comparison of Theory and Experiment for \( T_2 \) Relaxation

The experimental \( T_2 \) data obtained over a range of temperatures at 76.77 MHz [37] for the sharp central resonances of \( ^2\text{H}_2\text{O}-\text{hydrated Zeolite A} \) and \( ^2\text{H}_2\text{O}-\text{synthesized kanemite} \) are plotted on the background of the theoretical \( T_2 \) values calculated for isotropic rotational diffusion (\( \nu = 6 \, D_{\text{rot}} \)), ideal \( C_2 \) symmetry jumps (\( \nu = k_{\text{tet}}, \, k_{C2} = 25833^*k_{\text{tet}} \) for Zeolite A; \( \nu = k_{\text{tet}}, \, k_{C2} = 1000^*k_{\text{tet}} \) for kanemite); ideal tetrahedral jumps (\( \nu = k_{\text{tet}} \)), and the C2TET model, in Figs. 4.20 and 4.21. In these plots it was assumed for the C2TET model that \( \nu = k_{\text{tet}} \) and \( k_{C2}/k_{\text{tet}} = 25833 \) for the Zeolite A data and \( k_{C2}/k_{\text{tet}} = 1000 \) for the kanemite data, respectively, the same values used for the \( T_1 \) plots in Figs. 4.14, 4.15, 4.17, 4.18.

The experimental \( T_2 \) values for both samples depend on the NMR method used to obtain them, consistent with intermediate exchange effects on the \( T_2 \) relaxation times [36]. Using the same \( k_{\text{tet}} \) and \( k_{C2} \) values and ratios as for the \( T_1 \) analyses, the experimental data lie between the theoretical \( T_2 \) for \( C_2 \) symmetry jumps and the theoretical \( T_2 \) expected for the other models (C2TET, pure tetrahedral, or isotropic rotational diffusion). This observation is consistent with the C2TET model, because \( T_2 \) relaxation is more sensitive to exchange effects than \( T_1 \) relaxation [36], and \( k_{\text{tet}} \) is in the intermediate exchange regime (Fig. 4.9). As a consequence, the contribution to the observed deuterium relaxation from the population of water molecules experiencing
Fig. 4.2.20: The experimental T<sub>2</sub> data (CPMG 2 π pulses, double echo) for the sharp central resonance of H<sub>2</sub>O-hydrated Zeolite A at 76.77 MHz plotted on the background of the theoretical T<sub>2</sub> values calculated for isotropic rotational diffusion (ν = 6 D<sub>rot</sub>, blue curves), ideal tetrahedral jumps (ν = k, black curves), and C2TET model ((ν = k<sub>ket</sub> , k<sub>C2</sub>/k<sub>ket</sub> = 25833, green curves). The ratio of k<sub>C2</sub>/k<sub>ket</sub> was the same as used in Figs. 17 and 18. It is also used in the plot of the "pure" C<sub>2</sub> curve (red curve), which is expressed in terms of ν = k<sub>ket</sub> (for example, if ν = 1 x 10<sup>5</sup> sec<sup>-1</sup>, k<sub>C2</sub> = 2.5833 x 10<sup>9</sup> sec<sup>-1</sup>). The temperatures shown in the figure are placed at the same ν = k values as used in the plots of the T<sub>1</sub> data made to fit the C2TET model in Figs. 17 and 18. The T<sub>2</sub> values for isotropic rotational diffusion of bulk liquid water are off the scale of this plot, over two orders of magnitude longer than the experimental values. The isotropic rotational diffusion coefficient range shown in the plot corresponds to supercooled liquid water at 200 K and extremely high pressure [8].
Fig. 4.21 The experimental $T_2$ data (CPMG $2\pi$ pulses, double echo) for the sharp central resonance of $^2$H$_2$O-synthesized kanemite at 76.77 MHz plotted on the background of the theoretical $T_2$ values calculated for isotropic rotational diffusion ($\nu = 6\, D_{rot}$, blue curves), ideal tetrahedral jumps ($\nu = k$, black curves), and C2TET model ($\nu = k_{tet}$, $k_{C2}/k_{tet} = 1000$, green curves) at both frequencies. The ratio of $k_{C2}/k_{tet} = 1000$ (assumed to be constant throughout the temperature range) was the same as used in Figs. 20 and 21, and is also used in the plot of the "pure" $C_2$ curve (red curve), which is expressed in terms of $\nu = k_{tet}$ (for example, at $\nu = 1 \times 10^6$ sec$^{-1}$, $k_{C2} = 1 \times 10^9$ sec$^{-1}$). The temperatures shown in the figure are placed at the same $\nu$ values as used in the plots of the $T_1$ data constructed to the C2TET model in Figs. 20 and 21.
tetrahedral jumps of their O-\textsuperscript{2}H bonds is severely attenuated, yielding results that are dominated by the population of water molecules experiencing C\textsubscript{2} symmetry jumps of their O-\textsuperscript{2}H bonds.

4.5. Conclusions

It is widely recognized that a variety of models can be used to match NMR relaxation data. The C\textsubscript{2}TET model is based on the principle of Occam's razor, namely that the simplest model that matches the data is probably the best. The well known tetrahedral jumps of the O-H bonds on the ice Ih lattice and C\textsubscript{2} symmetry jumps of the O-H bonds observed for crystalline hydrates provide a logical basis for this model.

The comparison of theoretical and experimental deuterium T\textsubscript{1} data for \textsuperscript{2}H\textsubscript{2}O-synthesized kanemite and \textsuperscript{2}H\textsubscript{2}O-hydrated Zeolite A shows that the C\textsubscript{2}TET model works well, and is the only one that successfully accounts for the magnetic field dependence of T\textsubscript{1} values observed experimentally at ambient and higher temperatures. FTIR and variable temperature deuterium lineshape analyses of both materials are also consistent with the C\textsubscript{2}TET model. The experimental deuterium T\textsubscript{2} data are imprecise due to exchange effects. Based on the T\textsubscript{1} relaxation and lineshape analysis, the kinetic activation parameters for the \textsuperscript{2}H\textsubscript{2}O-hydrated Zeolite A are \(\Delta H_{\text{tet}} = +17\) kJ/mol, \(\Delta S_{\text{tet}} = -109\) J/(mol K), \(\Delta H_{c2} = +19\) kJ/mol, and \(\Delta S_{c2} = -20\) J/(mol K). For the \textsuperscript{2}H\textsubscript{2}O-synthesized kanemite, the kinetic activation parameters are \(\Delta H_{\text{tet}} = +23\) kJ/mol, \(\Delta S_{\text{tet}} = -69\) J/(mol K).
K), $\Delta H_{C_2}^\ddagger = +23 \text{ kJ/mol}$, and $\Delta S_{C_2}^\ddagger = -11 \text{ J/(mol K)}$. For both samples the $C_2$ jumps of the $O-^2H$ bonds are much faster than the tetrahedral jumps at all temperatures.

The goal of future work is to uncover more details of the dynamics in these and other systems, in particular the details of the exchange between the water populations experiencing $C_2$ and tetrahedral jumps of their $O-H$ bonds. Other questions include the role of the cation in such systems and whether the C2TET model can successfully describe deuterium $T_1$ relaxation in other hydrated materials.
References


[4] We assume the sample is diamagnetic.


[18] In our earlier work, we omitted the factor of 2 so the spectral densities and T1 values were also off by a factor of two.


[21] The spectral densities provided as supplemental information in our previous publications, 1 and 2 above, are half of the correct value shown in Eq. [3a-c].


[24] No liquid state water was detected in the experiments, but it is possible that small mole fractions of liquid water in fast exchange with the solid water may have been masked by the much slower relaxation rate. For example, at room temperature $T_1_{\text{liq}} \approx 0.40$ sec$^{-1}$, so $(1/T_1)_{\text{obsd}} = \chi_{\text{liq}} (2.5$ sec$^{-1}) + \chi_{\text{sol}} (1/T_1)_{\text{sol}}$ with $(1/T_1)_{\text{sol}} > 100$ sec$^{-1}$.

[25] This assumption anticipates the results obtained from experiment that show $k_{C2}>>k_{tet}$. It also allows us to avoid assumptions about the activation energies for $k_{C2}$ and $k_{tet}$ at this point in the discussion.


[29] We thank Burkhard Geil for the low temperature $T_1$ data.


[37] We also obtained a few T$_2$ data values at 46.03 MHz to check for magnetic field dependence. None was found within the experimental error.
Chapter 5

Investigations of the State of Water Involved in the Setting of Tricalcium Silicate

5.1 Introduction

In cement chemistry formulae are often expressed, for simplicity, as sums of oxides. For example tricalcium silicate (Ca$_3$SiO$_5$) is often written as 3CaO•SiO$_2$, or more commonly, C$_3$S. This does not mean that these oxides in their pure forms exist within the structure [1]. Table 5-1 summarizes some of the most commonly used notations.

Table 5-1: Abbreviations most widely used in cement chemistry

<table>
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<th>C</th>
<th>S</th>
<th>A</th>
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<td>K$_2$O</td>
<td>SO$_3$</td>
<td>Na$_2$O</td>
<td>TiO$_2$</td>
<td>P$_2$O$_5$</td>
<td>H$_2$O</td>
<td>CO$_2$</td>
</tr>
</tbody>
</table>

In this study, $^2$H NMR T$_1$ relaxation times of the $^2$H nucleus in heavy water were monitored as a function of time for the hydration process of C$_3$S at 23 °C. The T$_1$ data were correlated with corresponding Vicat [2] needle, ASTM C191, and isothermal calorimetry data. To date it has been universally accepted that the growth of a layer-like C-S-H (calcium silicate hydrate product), coating the C$_3$S, during the acceleratory period was the cause of both the relatively large evolution of heat that takes place as well as the cause of setting and hardening as foils grow together and become physically joined. A
new hypothesis for the setting of C\textsubscript{3}S paste is proposed here based in part on previous T\textsubscript{1} studies of kanemite and zeolite A [3,4] and in part on T\textsubscript{1} data reported here.

During the hydration of C\textsubscript{3}S pastes, the deuterium T\textsubscript{1} times decrease rapidly from \(~ 400\) ms to much shorter values. At the time of the accelerated T\textsubscript{1} relaxation change, the bulk amount of heat is given off as seen through isothermal calorimetry (See Fig. 5.4) and Vicat needle penetration begins to decrease. This suggests that the initial setting of C\textsubscript{3}S paste is initiated by the formation of bridges of solid state water (4-5 molecular layers thick) [5] that form between adjacent C-S-H foils. As the growth rate of C-S-H increases, water filled pores become increasingly populated with hydrates. Relative spacing between adjacent foils decreases, which causes the formation of increasingly larger numbers of solid state water bridges. The rate of heat evolution, surface area, and connectivity increase, the paste becomes more viscous and firmer and finally it sets (no Vicat needle penetration).

Solid water bridges are composed of both hydrogen and covalently bonded arrays of tetrahedrally coordinated oxygen atoms as well as water molecules most likely coordinated to ions within the C-S-H matrix. The open oxygen network of these arrays allows for free Ca\textsuperscript{2+} and SiO\textsubscript{4}\textsuperscript{4-} diffusion causing the solid water bridges to change into stronger chemically bonded C-S-H with time [1]. It is proposed here that there is a fractional phase change of water from the liquid to the solid state during the initial setting period. From the observed data it seems plausible that the initial setting of C\textsubscript{3}S paste is in fact due to this phase change. However it is important to note that this does not mean that the overall hardening and strength of the cement / C-S-H product comes from that phase change.
5.2 Chemistry and Rheology

Tricalcium silicate (C₃S) is the major component in Portland cement (see Fig. 5.1) as well as the primary source of calcium and silica needed to form calcium silicate hydrate (C-S-H), the major strength producing phase in hydrated Portland cement and concrete. The use of C₃S as a model system is a well accepted experimental practice. Its study has continued through the last 100 years and continues as new techniques are developed and scientists try to grasp the underpinnings of the hydration process.

It has been the goal of researchers to explain the relation of microstructure and chemistry during the evolutionary process known as setting and hardening for many years. It has been the hope of each generation to fully understand the process and then use this knowledge to design a more durable Portland cement and concrete [7]. Researchers have come a long way [6-8] but still the underlying process is not well understood.

A model requiring physical intergrowth of foils and fibrils is troublesome for a number of reasons, the most evident being the ability of a paste to go through repeated cycles of rheological measurements and each time exhibit a nearly consistent yield stress followed by near Newtonian behavior [9-12]. From this point of view the solid water bridges of the hypothesis presented here fit well in that there is no strong intergrowth of fibrils and foils that will hold the paste together rigidly. The solid water bridges provide some rigidity and an increase in viscosity, and may explain repeated (non-Newtonian) Bingham behavior as viscous behavior is tracked as a function of sheer rate using a rotating cylinder/cup versus time.
Fig. 5.1

Fig. 5.1: Synthesized, pure $\text{C}_3\text{S}$ crystals. Purity was determined through XRD and solid state MAS NMR.
The intent of this work was to once again study the hydration of C\textsubscript{3}S pastes, but put greater emphasis on the nature and role of the solution phase during the setting and hardening process. The objective was to measure relaxation times as a means of tracking the development of solid state water in the system C\textsubscript{3}S - D\textsubscript{2}O and correlate them with corresponding Vicat needle, calorimetric and morphological data.

Recent evidence that silicate surfaces such as a mica are hydrophilic to the point that the strength of the hydrogen bonds that form between the protons in a water molecule and the lone pair electrons of the coordinated oxygen atoms present on the surface of a mica crystal (i.e. the Q\textsubscript{3} silicate ions) is large enough to immobilize the water molecule, i.e. large enough to cause the water to change state from liquid to solid [13]. NMR T\textsubscript{1} relaxation times have been measured for kanemite and a variety of other silicates and zeolites. The fact that the T\textsubscript{1} times are extremely short (~3-10 ms) and magnetic field dependent again suggests that solid water is present.

5.3 Hydration Theory

It is known that water will form hydrogen bonds with oxygen networks found on the surfaces of layer silicates [13]. The silicate tetrahedra that form the surface link together to form sheet-like arrays of 2D hexagonally arranged silicate ions, i.e., in the language of NMR, they have Q\textsubscript{3} connectivity. Due to the lone pair electrons that the oxygen ions have, the protons in liquid water molecules adjacent to these surfaces will form hydrogen bonds with the oxygens on the surface. Independent studies of the nature of layers of water on the surface of mica [13], kanemite [2] and sodium montmorillonite
[14] indicate that at a minimum of 2-3 monolayers of water on these surfaces is in the solid state - i.e. the strength of the hydrogen bonds is great enough to overcome the molecular motion of the water molecules associated with the liquid state. By definition, water molecules with dynamics that are confined to a lattice (at the atomic level) are in the solid state. Such adsorbed water is akin to the so called “zeolitic” water that one observes when one runs a TGA on clay or a mica or for that matter a C-S-H sample [15]. The water comes off gradually without distinct sharp vertical weight losses as seen in Ca(OH)$_2$ or CaSO$_4$·2H$_2$O. The gradual loss indicates that the water has some structural components to it and is confined to a lattice position that may be in the solid state.

C-S-H is purportedly “clay-like”. This is conjectural at this point, but based on the fact that C-S-H has a so called layer structure, and that the fact that the individual foil like layers are covered by rows of drierketten $[(Si_3O_9)^2]_n$ with occasional cross linking (i.e. predominantly Q$_2$ with a trace of Q$_3$ silicate ions) [16], and the fact that said layer structure has similar water adsorption/desorption behavior as exhibited by mica and clay, it is hypothesized that solid water exists on the surfaces of C-S-H as well.

The adsorbed water in C-S-H is often referred to as interlayer or interstitial water. The surface of the C-S-H layer consists of a pseudo-hexagonal arrangement of oxygen atoms whose two lone pairs point outward into interlayer space. Surface morphology and charge are ideal for the formation of solid water arrays having an “ice-like” structure, i.e. water molecules form hexagonal networks of hydrogen bonded water molecules that mimic the surface (i.e. the silicate surface acts as a template). One may think that the formation of hydrogen bonds imparts enough thermodynamic stability to overcome the
molecular motion of water molecules in the liquid state at temperatures well above ambient. The strength of the hydrogen bond is not unlimited and at some point enough thermal energy can be supplied to the system to disrupt the bond causing the water to liquefy and evaporate. Note that the water would liquefy gradually; the water furthest from a silicate surface would melt first followed by more strongly bonded water closer to the silicate surface at higher temperatures, which is what is observed when C-S-H is subjected to heating in a TGA[15].

5.4 Experimental Methods

Conventional tools including Vicat needle, X-ray diffraction, isothermal calorimetry, and SEM were used to study the kinetics of setting and hardening of C₃S + (H₂O or D₂O) pastes maintained at 23°C. In parallel with these measurements, NMR was used to collect static ²H NMR powder patterns and T₁ relaxation times for complimentary D₂O pastes run in sealed capsules in real time at three different magnetic fields.

How does one determine if the water is in the solid state? One way is to use D₂O hydrated samples and NMR to determine relaxation times of the deuteron. In bulk liquid D₂O T₁s are nominally in the 400 ms range at room temperature and in the extreme narrowing motional regime, independent of the magnetic field. In kanemite, zeolite A, and in the solid water fraction of hydrating cement pastes at room temperature, the T₁s are nominally in the 3-10 ms range with magnetic field dependence.
In the solid state, the dynamics of the D$_2$O molecules (or the O-D bond vector) are limited to jumps at rates comparable to the Larmor frequency on the tetrahedral lattice of the solid water in addition to a C$_2$ type of motion for those water molecules coordinated to ions. This mixture of solid state motions produces the observed 3-10 ms $T_1$ values. In the liquid state, D$_2$O molecules experience isotropic rotational diffusion with a rotational rate constant $= 6D_{rot} \sim 10^{12}$ sec$^{-1}$, two or more orders of magnitude faster than the Larmor frequency. This produces the observed $T_1$ value of 400 msec.

Tricalcium silicate was synthesized from reagent grade silicic acid and CaCO$_3$. These were mixed in stoichiometric proportions, ball milled in absolute ethyl alcohol with alumina/zirconium balls until homogeneous (typically 24 hours). The mixture was poured into a Pyrex dish allowing the alcohol to evaporate at room temperature. The resulting powder was pressed into one inch diameter pellets, stacked on a zirconia plate and repeatedly fired (after grinding between firings) in a SiC furnace at 1400-1500°C. The sample was X-rayed and found to be single phase tricalcium silicate (M$_1$ polymorph). No evidence of CaO was observed.

The sample was ground by hand in an agate mortar and then ball milled dry with zirconium balls. The Blaine surface area of the powder was measured as 3400 cm$^2$/g. The powder served as the starting material. It was mixed at one D$_2$O/C$_3$S ratio (0.40). The well mixed paste was placed in NMR sample tubes and sealed with epoxy for analysis as a function of hydration time. The NMR spectrometers used to investigate the $T_1$’s were a Chemagnetics CMX-300, a Chemagnetics Infinity 500, a Bruker DRX-400, a Bruker Dpx-300, a Bruker AMX2-500, and a Bruker DRX-600. The inversion-recovery pulse sequence was implemented to measure the $^2$H $T_1$’s at 3 different magnetic fields. The
resulting $T_1$ data were fit to a monoexponential decay function (validated by a stretched exponential evaluation of the data, Kohlrausch equation in which $\beta > 0.95$)

$$
\phi(t) = \exp\left(-\frac{t}{T_1}\right) \quad 5.1
$$

It is nothing more than a regular exponential expression with one extra parameter, $\beta$, the stretching parameter.

The $T_1$ values at the 3 different fields were used to calculate the mole ratio of liquid water to solid water present as a function of time based on the equation

$$
\frac{1}{T_1}_{\text{observed}} = f_{\text{liquid}} \frac{1}{T_1}_{\text{liquid}} + f_{\text{solid}} \frac{1}{T_1}_{\text{solid}} \quad \text{(Eq. 5.2)}
$$

The total must be 1, and the $T_1 = T_2$ liquid at all 3 fields is 400 msec. At any given time of hydration, the $f_{\text{liquid}}$ and $f_{\text{solid}}$ values must be fixed and independent of the magnetic field. With these stipulations, the magnetic field dependent $T_1$ solid values were found to converge to the same values that were found for kanemite and zeolite A at the same temperatures. [17] This allows one to calculate the liquid to solid water ratio as a function of time (Fig 5.7).

Corresponding paste samples made with D$_2$O and DI water were also tested using a Vicat needle that penetrated into the paste cast into a small paste filled mold (2” in diameter and 2” tall). The mold was covered with plastic wrap to prevent evaporation in as much as setting took close to 24 hours when D$_2$O rather than H$_2$O was used to hydrate
the sample (See Fig. 5.1). Penetration would become less as the sample set and finally hardened so that the needle no longer penetrated the sample. Interestingly, this was a reversible process. By placing the hardened C₃S in the microwave for a given amount of time, the Vicat needle would again penetrate the material suggesting destruction of hydrogen bonds.

The paste was also studied using a Thermonetics isothermal conduction calorimeter maintained at about 23°C over the same time periods. In this case paste samples were mixed externally and then placed in a square stainless steel tightly lidded sample holder that fit snugly into the calorimeter cup. Data were collected via a computer data logger.

Finally, small subsamples of paste made with DI H₂O were allowed to hydrate at 23°C as a function of time in tightly sealed glass vials. Using Vicat needle penetration for DI water mixed pastes as a sign of setting for the H₂O system, glass vial samples of the same age (w/s =0.36) were freeze dried and used to examine microstructural characteristics (via SEM) as a function of time. See Fig. 5.3 for the actual samples studied (1-8).

5.5 Results and Discussion

A compilation of C₃S+D₂O paste data is given in Figure 5.4. T₁ relaxation times were measured on the same set of sealed samples using different magnetic fields (9.39, 7.02 and 11.74 Tesla) at their Larmor frequencies. Vicat data were obtained using a
Fig. 5.2: Vicat traces of C₃S/H₂O (w/s=0.36) versus C₃S/D₂O (w/s=0.40). Penetration times for pastes at 23°C. Times are approximately 3X as long when hydration is carried out using D₂O versus H₂O. D₂O is a retardant.
Fig. 5.3: Vicat trace with numbered sampling points. Samples in glass vials were freeze dried to stop hydration. Hydration times are what one normally expects when hydrating C₃S with H₂O.
modified ASTM C 191 [2] procedure using a 2” diameter by 2” high sample cup. Isothermal calorimetry was measured at 23°C using a Thermonetics isothermal conduction calorimeter.

This plot contrasts the behavior of three data sets plotted on a common time axis. One can see the interrelation of penetration depth, heat flux, and T₁ relaxation times for hydrating C₃S + D₂O paste. There are major changes occurring in the paste at ~1000 minutes. The paste is thickening, it is warming and the T₁ relaxation times are decreasing at an exponential rate. All these measurements indicate that the paste is well on its way to becoming solid. The new observation here is that the T₁ times are leaving the realm of liquid water and approaching those attributed to a mixture of solid state and liquid state water. It was observed that T₁ times decreased from a high of 400 ms (typical of bulk liquid heavy water) to a low of 10-40 ms (typical of solid water) with time at all three frequencies measured. It is likely that a few layers [5] of solid water exist on all solid surfaces in the paste, but it is the solid water that covers the surfaces of nucleating and growing foils of C-S-H and Ca(OH)₂ crystals that are responsible for the initial joining of solid particles during the early stages of the acceleratory period. All surfaces are covered with several layers of solid state water. When solid state water covered surfaces come in contact they form the solid water bridges. These bridges comprise the initial network contacts that form at an increasing rate during the setting process. The heat evolved is thus partly due to the heat of fusion of the water and in part due to the formation of stable C-S-H and Ca(OH)₂ hydrates.
Fig. 5.4: Data Compilation for D₂O-hydrated C₃S.
Microstructures of selected DI water hydrated samples are in Fig. 5.4. These reflect an increase in the number of foils that are seen forming on the surfaces of the C$_3$S grains with time. The increase in the number of foils parallels the decrease in $T_1$ and Vicat needle penetration. The heat evolution indicates that reaction rates are increasing as more foils are produced.

Quantitative analysis of the $T_1$ data for D$_2$O containing samples hydrated for more than 80 days presented in Fig. 5.5 allows one to observe the amount of solid versus liquid water present in the sample at a given time. A SEM image of the C-S-H final product can be seen in Fig. 5.6.

These data differ from the earlier data in as much as they cover the entire range of hydration terminating at a point in time where one might normally consider the sample fully cured.

**5.6 Conclusions**

It is concluded that hydrated tricalcium silicate pastes that are beginning to set contain enough solid state water to coat growing C-S-H foils and fibrils and at the same time form solid water bridges between grains that are close enough that the solid water surfaces join together. At zero penetration the sample appears to contain roughly 10% solid water and 90% liquid water. Given the amount of surface area the sample has at this point, the solid water would form a film ~3 molecular layers thick. Also the amount of heat given off during setting is close to the amount of heat one would expect if an
Fig. 5.5: Microstructures of C₃S pastes. A = anhydrous. B = 240 min.
C = 385 min. D = 485 min. Massive foils present 385 minutes and later. A and B are top row left to right respectively. Bottom row are C and D left to right respectively.
Fig. 5.6: SEM of close to fully hydrated C-S-H showing the growth of fibrils on the surface of the inner-product C₃S.
Fig. 5.7: Analysis of the T₁ data as a function of time. The fractions of liquid and solid water were calculated for a C₃S +D₂O paste hydrated in a sealed SiO₂ tube using Eq. 5.1.
equivalent amount of water was frozen (a.k.a. the heat of fusion of that amount of water could account for a similar magnitude of heat evolution). Undoubtedly, there is a certain amount of heat evolution due to the formation of C-S-H and Ca(OH)_2, but the free energy, ΔG°, of formation of the compounds themselves may be too high in light of the solid state water forming on and between adjacent surfaces..

It is suggested that the heat evolution during the acceleratory period has two sources: one is related to the chemical reaction as solid C-S-H and Ca(OH)_2 precipitate and grow from solution. Surface area measurements by Wieker [18] suggest that the growth curve due to C-S-H is similar to the heat evolution curve. A second source of heat is the conversion of adsorbed water films to the solid state. As more silicate surfaces are formed, the molecular films of water on their surfaces are converted to the solid state.

Based upon the it is proposed that the initial setting one observes when C_3S pastes begin to thicken is due to the formation of solid state water bridges between foils and fibrils. There is initially no mechanical intergrowth of foils because each foil is covered with a molecular layer or two of solid water. What comes in contact first are these solid water surfaces. Because the bonds that form are hydrogen bonds, strength is relatively small. As a result, pastes can be stirred and liquefied, or heated and penetrated, but once they are allowed to rest they regain their so called Bingham liquid behavior. When setting occurs networks are more strongly hydrogen bonded. There are more solid-solid water bridges as well as particle to particle contacts. Setting is due to the intergrowths of layers of solid water and ultimately foils and fibrils. The solid water on silicate surfaces in the system also provides a pathway for diffusion of hydrated Ca^{2+} and SiO_4^{4-} ions through the “open” tetrahedrally coordinated array of water molecules that make up solid state water.
This makes it possible to form a silicate network in situ. Ca\textsuperscript{2+} ions can diffuse through the developing silicate structure and form additional solid C-S-H. The deuterons will migrate into the underlying C\textsubscript{3}S to form inner product. O-D bond vectors jump between lattice sites, both tetrahedral and C\textsubscript{2} site to site via Bjerrum, ionic, and lattice defects [19]. If this model is correct, it may in fact begin to shed some light on the nature and state of water during setting and hardening and the cause of the associated exothermic reaction of setting cement paste.

After reaching high levels of saturation with respect to both Ca\textsuperscript{2+} and SiO\textsubscript{4}\textsuperscript{4-} during the induction period, the solution phase becomes less concentrated with respect to SiO\textsubscript{4}\textsuperscript{4-} as C-S-H begins to nucleate and grow. Ca remains more or less in steady state equilibrium with the developing C-S-H and Ca(OH)\textsubscript{2} during the induction period. If one considers the effect of Ca\textsuperscript{2+} on the solid structure of water it is assumed that the ions are octahedrally coordinated and exhibit C2TET type motion, the same case as in zeolite-A and kanemite. For sake of discussion it is assumed that this is the case and that the amount of Ca\textsuperscript{2+} present does not adversely affect the formation of solid state water films and bridges and in fact contributes as Na\textsuperscript{+} does in both kanemite and zeolite A [17].
References


14. Unpublished results, BVO, AJB, MWG.


Appendix A

$T_1$ Kohlrausch Relaxation Examples

Above is an example of a $T_1$ inversion recovery experiment of zeolite-A.

The x axis is time in msec and the y axis is arbitrary intensity units.
Fit

(* No problem in fitting regular T1 fit, done below for D2O-hydrated Zeolite A at 418 K *)

\[ \text{ftest} = \text{FindFit}\{\text{test2}, a + b \times \exp\left(-x/c\right), \{a, b, c\}, x\} \]

\[ \{a \rightarrow 0.985029, b \rightarrow -1.74311, c \rightarrow 0.103091\} \]

\[ C = T_1 = 103 \text{ msec at } \sim 400 \text{ K} \]

Below a Kohlrausch stretched exponential analysis to determine the exponentiality of the data. From the analysis one can determine singular or multiple processes contributing to the overall relaxation. That said it is well established that there are 2 motions contributing to the overall relaxation values. Because the two motions are in fast exchange with one another over a wide range of temperatures, the Kohlrausch analysis still shows exponential behavior (i.e. \( \beta > 0.97 \)).
The Kohlrausch Equation

\[ f_{test3} = \text{FindFit}[\text{test2}, a + b \times \exp[-\text{Re}\left(\left(\frac{x}{104}\right)^\beta\right)], \{a, b, \beta\}, x] \]

(* Now we plot the data against the curve calculated for the stretched exponential at 418 K *)

Plot[f[10^x], {x, -6, 0}, AxesOrigin -> {-6, -1}, PlotRange -> {Automatic, {-1, 1.1}}, Epilog -> Prepend[Point/@test3, PointSize[0.01]];]

Here we find \( \beta > 0.97 \) indicating a monoexponential decay. The denominator of the exponential is the \( T_1 \) value from the earlier fit. \( A \) and \( B \) are fit parameters and \( \beta \) is the exponential fit value.

The data was plotted against an exponential fit (solid line).
Kanemite $T_1$ Experiment

Regular $T_1$ fit of the data yields $c = T_1 = 19.4$ msec at 367K

(*) For the stretched exponential we fix the $a$ and $b$ values, and use the regular $T_1$ *)

\[
\text{ftestkan367b} = \text{FindFit}[\text{testkan367b}, 0.9898976068418308^* -1.7377577193923608^* \text{Exp}[\text{Re}\left[\left(\frac{x}{0.019446156759784478}\right)^2\right]], \{\beta}, x]
\]

[\beta \rightarrow 0.984596]

\[
\text{ftestkan367} = \text{FindFit}[\text{testkan367b}, a+b^* \text{Exp}[-x/c], \{a, b, c\}, x]
\]

\{a \rightarrow 0.989898, b \rightarrow -1.73776, c \rightarrow 0.0194462 \text{ is the } T_1\}
\[ \beta > 0.98 \text{ again indicating a monoexponential decay.} \]
Appendix B

Correlation Functions and Spectral Densities for \( C_2 \) Jumps

The following is direct output from Mathematica showing the calculations of pertinent correlation functions and their corresponding spectral densities which lead to the calculated \( T_1 \) and \( T_2 \) values.

(* This notebook calculates the eigenvalues, eigenvectors, \( C_{aa'}(t) \), \( C_m(t) \), \( J_m(\omega) \), and \( T_1 \) for a deuterium experiencing \( C_2 \) symmetry jumps in the solid state. See Torchia and Szabo, J. Magnetic Resonance, 49, pp. 107-121, 1982 *)

(* The matrix for tetrahedral jumps is (see eqns. 18,19 of Torchia/Szabo *)
\[
R = \begin{bmatrix}
-k & k \\
  k & -k \\
\end{bmatrix}
\]

(* The eigenvalues and orthonormalized eigenvectors are calculated below *)
\[
\lambda = \text{Eigenvalues}[R] \\
\{0, -2k\} \\
X = \text{Eigenvectors}[R] \\
\{\{1,1\},\{-1,1\}\}
\]

<<LinearAlgebra`Orthogonalization`
GramSchmidt[X]
\[
\left\{\left\{\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right\}, \left\{-\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right\}\right\}
\]

X=%;
(* We can check the eigenvalues/eigenvectors using equation 20 of Torchia/Szabo *)
\[
R.X[[1]] \\
\{0,0\} \\
\lambda[[1]]*X[[1]] \\
\{0,0\} \\
R.X[[2]] \\
\left\{\frac{2k}{\sqrt{2}}, \frac{-2k}{\sqrt{2}}\right\} \\
\lambda[[2]]*X[[2]] \\
\left\{\sqrt{2}k, \sqrt{2}k\right\}
\]

FullSimplify[%%]
\[
\{\sqrt{2} \ k, -\sqrt{2} \ k\}
\]

(* Open wigrot.nb for wigner rotation tables *)

(* The \(\theta\) values for the two jump sites (for the PAS in the Crystal frame) are *)
\[\theta = \{57.5^\circ/180, 57.5^\circ/180\}\]
\[\{1.00356, 1.00356\}\]

(* The \(\phi\) values for the four jump sites are *)
\[\phi = \{0, \pi\}\]
\[\{0, \pi\}\]

(* The \(\theta\) or \(\phi\) value of a jump site can be extracted as follows: *)
\[\theta[[2]]\]
1.00356

(* Here we revise equation 23 from Torchia and Szabo, which has a sign error in the argument of the first exponential that is corrected below, and make it general to deal with nonzero \(\eta\) (see equations 12-14) *)
\[dd1[n_, \omega_] := -1* (\lambda[[n]]/ (\lambda[[n]]^2 + \omega^2))\]
\[dd2[n_, \omega_] := -1* (\lambda[[n]]/ (\lambda[[n]]^2 + (2*\omega)^2))\]

\[c1[a_, aa_] := \]
\[\sum_{n=1}^{2} \sum_{j=1}^{2} \sum_{q=-2}^{2} \sum_{r=-2}^{2} (apas[2, q]*apas[2, r]/(apas[2, 0]^2)) * dd1[n, \omega] *\]
\[X[[1, 1]] * X[[n, 1]] * X[[1, j]] * X[[n, j]] * Conjugate[(D2[q, a] /. \{\beta \to \theta[[1]], \alpha \to 0, \gamma \to \pi - \phi[[1]]\})] * (D2[r, aa] /. \{\beta \to \theta[[j]], \alpha \to 0, \gamma \to \pi - \phi[[j]]\})\]

\[c2[a_, aa_] := \]
\[\sum_{n=1}^{2} \sum_{j=1}^{2} \sum_{q=-2}^{2} \sum_{r=-2}^{2} (apas[2, q]*apas[2, r]/(apas[2, 0]^2)) * dd2[n, \omega] *\]
\[X[[1, 1]] * X[[n, 1]] * X[[1, j]] * X[[n, j]] * Conjugate[(D2[q, a] /. \{\beta \to \theta[[1]], \alpha \to 0, \gamma \to \pi - \phi[[1]]\})] * (D2[r, aa] /. \{\beta \to \theta[[j]], \alpha \to 0, \gamma \to \pi - \phi[[j]]\})\]

\[c1[1,1] \]
\[0.616045 \ k/4 \ k^2 + \omega^2 + 0.410697 \ k \eta/4 \ k^2 + \omega^2 + 0.0684495 \ k \eta^2/4 \ k^2 + \omega^2\]

FullSimplify[%]
The lab frame autocorrelation function is given by equation 13 from Torchia and Szabo. In this case it must be modified because $\eta$ is nonzero. *)

<<Algebra`ReIm`

$\alpha/: \text{Im}[\alpha] = 0$

$\beta/: \text{Im}[\beta] = 0$

$\gamma/: \text{Im}[\gamma] = 0$

$C1 = \sum_{a=-2}^{2} \sum_{aa=-2}^{2} \text{Conjugate}[(D2[a, 1] /. \gamma \to 0)] \ast (D2[aa, 1] /. \gamma \to 0) \ast \text{FullSimplify}[c1[a, aa]]$

$C2 = \sum_{a=-2}^{2} \sum_{aa=-2}^{2} \text{Conjugate}[(D2[a, 2] /. \gamma \to 0)] \ast (D2[aa, 2] /. \gamma \to 0) \ast \text{FullSimplify}[c2[a, aa]]$

(* The spectral densities are given by *)

$J1[\omega, k, \alpha, \beta, \eta] :=$

$N[\frac{1}{4. k^2 + \omega^2} (k (0.30802267681622597^\omega + (0.20534845121081732^\omega + 0.03422474186846957^\omega) \eta + (0.01711237093423479^\omega (2.999999966719964^\omega + \eta) (3.0000001332800394^\omega + \eta) - 0.01711237093423479^\omega (2.999999999999982^\omega + \eta)^2 \text{Cos}[2\alpha] \text{Cos}[2\beta] + (2.99999970197678^\omega + \eta) (3.00000002902323^\omega + \eta) - 0.01711237093423478^\omega + 0.01711237093423478^\omega \text{Cos}[2\alpha] \text{Cos}[4\beta])]$
\[ J_2[\omega, k, \alpha, \beta, \eta] := \]
\[ \text{N}\left[ \frac{1}{k^2 + \omega^2} (k (2.99999970197678^\omega + \eta) (3.00000029802323^\omega + \eta) \right. \]
\[ \left. \left( 0.00855618546711739 + 0.00855618546711739 \cos[\beta]^2 + \cos[2\alpha] (-0.004278092733558695 + 0.004278092733558695 \cos[2\beta]) \right) \right) \]
\[ \sin[\beta]^2 \right] \]
\[ J_1[2\pi 45.6*10^6,1.0*10^9,0,0,1] \]
\[ 2.68292 \times 10^{-10} \]
\[ J_2[2\pi 45.6*10^6,1.0*10^9,0,0,1] \]
\[ 0. \]

(* For deuterium in a hydrate, e^2 qQ/h ~ 220 kHz, so \( \omega_q \)

\[ \text{Clear}[\omega_q] \]
\[ \omega_q = 2\pi (3/4) * 220*10^3 \]
\[ 330000 \pi \]

(* The inverse of \( T_1 \) is given by *)
\[ T_1^{-1}[\omega, k, \alpha, \beta, \eta] := (\omega_q^2 / 3) \times (J_1[\omega, k, \alpha, \beta, \eta] + 4 \times \right) \]
\[ J_2[\omega, k, \alpha, \beta, \eta] \]

(* The \( T_1 \) (in seconds) is given by *)
\[ T_1[\omega, k, \alpha, \beta, \eta] := \text{N}[1 / T_1^{-1}[\omega, k, \alpha, \beta, \eta]] \]

(* The Larmor frequency for H2 on the CMX-300 solid state spectrometer is ~ 45.6 MHz *)
\[ T_1[2\pi 45.648*10^6,1.0*10^7,0,0,0] \]
\[ 0.0374534 \]

\[ \text{Tint}[\omega, k, \eta] := \frac{1}{(1 / (4\pi)) \int_0^{2\pi} \int_0^{\pi} \text{Sin}[\beta] T_1^{-1}[\omega, k, \alpha, \beta, \eta] d\beta d\alpha} \]

\[ \text{General::spell1: Possible spelling error: new symbol name "Tint" is similar to existing symbol "Tinv".} \]

\[ \text{Tint}[45.648*10^6*2\pi,1.0*10^7,0] \]
\[ 0.0467316 \]
\[ \text{Tint}[76.78*10^6*2\pi,1.0*10^7,0] \]
\[ 0.131951 \]
\[ \text{Tint}[2\pi*45.648*10^6,2.0*10^8,0] \]
\[ 0.00460197 \]
\[ \text{Tint}[2\pi*76.778*10^6,2.0*10^8,0] \]
\[ 0.00911553 \]
\[ \text{Plot}[\text{Tint}[45.648*10^6*2\pi,1.0*10^7,\eta],\{\eta,0,1\}] \]
Graphics
Clear[\(\omega q\)]
\(\omega q=2\pi\times (3/4)\times 193\times 10^3\)
289500 \(\pi\)
Appendix C

Tetrahedral Jump Correlation Functions and Relaxation Calculations

The following is direct output from Mathematica showing the calculations of pertinent correlation functions and their corresponding spectral densities which lead to the calculated $T_1$ and $T_2$ values.

(* This notebook calculates the eigenvalues, eigenvectors, $C_{aa'}(t)$, $C_m(t)$, $J_m(\omega)$, and $T_1$ for a deuterium experiencing tetrahedral jumps in the solid state. See Torchia and Szabo, J. Magnetic Resonance, 49, pp. 107-121, 1982. Note that this calculation includes the effect of $\eta$ on the relaxation times, and therefore differs a bit from the Torchia/Szabo paper where $\eta$ was assumed to be zero. *)

(* The matrix for tetrahedral jumps is (see eqns. 18,19 of Torchia/Szabo *)

\[ R = \begin{pmatrix} -3k & k & k & k \\ k & -3k & k & k \\ k & k & -3k & k \\ k & k & k & -3k \end{pmatrix} \]

(* The eigenvalues and orthonormalized eigenvectors are calculated below *)

\[ \lambda = \text{Eigenvalues}[R] \]
\[ \{0, -4k, -4k, -4k \} \]

\[ X = \text{Eigenvectors}[R] \]
\[ \{\{1,1,1,1\},\{-1,0,0,1\},\{-1,0,1,0\},\{-1,1,0,0\}\} \]

(* Are the eigenvectors normalized?? No, as we see below *)

\[ X[[1]].X[[1]] \]
\[ 4 \]

<<LinearAlgebra`Orthogonalization`

(* We need to make sure that the eigenvectors are orthonormalized *)

\[ \text{GramSchmidt}[X] \]
\[\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}, \{-\frac{1}{\sqrt{2}}, 0, 0, \frac{1}{\sqrt{2}}\}\]

\[\{-\frac{1}{\sqrt{6}}, 0, \sqrt{\frac{2}{3}}, -\frac{1}{\sqrt{6}}\}, \{-\frac{1}{2 \sqrt{3}}, \frac{\sqrt{3}}{2}, -\frac{1}{2 \sqrt{3}}, -\frac{1}{2 \sqrt{3}}\}\]

\[
X = \%
(* Now they are normalized, as shown below *)
\]

\[\text{Table}[X[[n]].X[[n]],\{n,1,4\}]\]
\[\{1,1,1,1\}\]

(* We can check the eigenvalues/eigenvectors using equation 20 of Torchia/Szabo *)

\[\text{R.X[[1]]}\]
\[\{0,0,0,0\}\]
\[\lambda[[1]]*X[[1]]\]
\[\{0,0,0,0\}\]

(* \(\lambda[[1]] = 0\) is the eigenvalue corresponding to \(n=0\)—See text between equations 20 and 21 of Torchia/Szabo *)

\[\text{R.X[[2]]}\]
\[\left\{\frac{4k}{\sqrt{2}}, 0, 0, -\frac{4k}{\sqrt{2}}\right\}\]

\[\lambda[[2]]*X[[2]]\]
\[\{2\sqrt{2}k, 0, 0, -2\sqrt{2}k\}\]

\[
\text{FullSimplify}[%]\]
\[\{2\sqrt{2}k, 0, 0, -2\sqrt{2}k\}\]

\[\text{R.X[[3]]}\]
\[\left\{\sqrt{\frac{2}{3}}k + \sqrt{\frac{3}{2}}k - \frac{k}{\sqrt{6}}, \sqrt{\frac{2}{3}}k - \frac{2k}{\sqrt{6}}, -\frac{2k}{\sqrt{6}}, \sqrt{\frac{2}{3}}k + \frac{3}{2}k - \frac{k}{\sqrt{6}}\right\}\]

\[
\text{FullSimplify}[%]\]
\[\{2\sqrt{\frac{2}{3}}k, 0, -4\sqrt{\frac{2}{3}}k, 2\sqrt{\frac{2}{3}}k\}\]

\[\lambda[[3]]*X[[3]]\]
\[\{2\sqrt{\frac{2}{3}}k, 0, -4\sqrt{\frac{2}{3}}k, 2\sqrt{\frac{2}{3}}k\}\]

\[\text{R.X[[4]]}\]
\[\left\{-\frac{k}{\sqrt{3}} + \sqrt{3}k, -\frac{3k}{2\sqrt{3}} - \frac{3\sqrt{3}k}{2}, -\frac{k}{\sqrt{3}} + \sqrt{3}k, -\frac{k}{\sqrt{3}} + \sqrt{3}k\right\}\]

\[
\text{FullSimplify}[%]\]
(* Open wigrot.nb for wigner rotation tables *)
(* The tetrahedral angle is calculated below *)
\[ \text{ArcCos}\left[-\frac{1}{3}\right] \]

\[ \text{N[\%]} \]

1.91063
\%*180/Pi
109.471

(* The \( \theta \) values for the four jump sites (for the PAS in the Crystal frame) are *)
\[ \theta = \{0, \text{ArcCos}[-1/3], \text{ArcCos}[-1/3], \text{ArcCos}[-1/3]\} \]

\[ \{0, \text{ArcCos} \left[-\frac{1}{3}\right], \text{ArcCos} \left[-\frac{1}{3}\right], \text{ArcCos} \left[-\frac{1}{3}\right]\} \]

(* The \( \phi \) values for the four jump sites are *)
\[ \phi = \{0, 0, 2 \pi/3, 4 \pi/3\} \]

\[ \{0, 0, \frac{2 \pi}{3}, \frac{4 \pi}{3}\} \]

(* The \( \theta \) or \( \phi \) value of a jump site can be extracted as follows: *)
\[ \theta[2][2] \]

\[ \text{ArcCos} \left[-\frac{1}{3}\right] \]

(* Here we revise equation 23 from Torchia and Szabo, which has a sign error in the argument of the first exponential that is corrected below, and make it general to deal with nonzero \( \eta \) (see equations 12-14) *)
apas[2,1]
0

apas[2,0]
\[ \sqrt{\frac{3}{2}} \delta_{zz} \]
apas[2,2]
\[ \frac{\eta \delta_{zz}}{2} \]
\[
\sqrt{\frac{3}{2}} e^{-i \gamma} \cos[\beta] \sin[\beta]
\]

(* Since the time dependence is given by \(e^{-\lambda[[n]] t}\), and the angular dependence has no bearing on the Fourier transform, we calculate the nonangular part of the spectral densities that are part of \(J_1\) and \(J_2\) (T/S equation 8,10) as follows *)

\[
\begin{align*}
dd1[n_, \omega_] &:= -1*(\lambda[[n]]) / (\lambda[[n]]^2 + \omega^2) \\
\dd2[n_, \omega_] &:= -1*(\lambda[[n]]) / (\lambda[[n]]^2 + (2\omega)^2)
\end{align*}
\]

Clear[c1]
Clear[c2]

(* Equation 23

(after Fourier transformation to get the spectral densities from the correlation function time dependence) can be written as follows. Note that we need to sum over \(q\) and \(r\), which correspond to \(n\) and \(n'\) from T/S eqn. 12. Also note that since there are two different spectral densities we need to calculate (eqn. 8), the T/S \(C_{aa'}\) term calculated in equation 23 has to be divided into two parts, \(C_{1aa'}\) and \(C_{2aa'}\). This is because the integral in eqn 10 needs to be evaluated twice---once for \(J_1\) and once for \(J_2\)*)

\[
c1[a_, aa_] := \sum_{n=1}^{4} \sum_{l=1}^{4} \sum_{j=1}^{4} \sum_{q=-2}^{2} \sum_{r=-2}^{2} (apas[2, q] \astapas[2, r] / (apas[2, 0]^2)) \ast\dd1[n, \omega] \ast
\]

\[
X[[1, 1]] \ast X[[n, 1]] \ast X[[1, j]] \ast X[[n, j]] \ast
\]

Conjugate[(D2[q, a] /. \{\beta \to \theta[[1]], \alpha \to 0, \gamma \to \pi - \phi[[1]]\})] \ast

(D2[r, aa] /. \{\beta \to \theta[[j]], \alpha \to 0, \gamma \to \pi - \phi[[j]]\})
(* The lab frame autocorrelation function is given by equation 13 from Torchia and Szabo. In this case it must be modified because \( \eta \) is nonzero. *)

\[
\sum_{n=1}^{4} \sum_{l=1}^{4} \sum_{q=-2}^{2} \sum_{r=-2}^{2} (\text{apas}[2, q] \cdot \text{apas}[2, r] / (\text{apas}[2, 0]^2)) \cdot \text{dd2}[n, \omega] \cdot \text{X}[[1, 1]] \cdot \text{X}[[n, 1]] \cdot \text{X}[[1, j]] \cdot \text{X}[[n, j]] \cdot \text{Conjugate}[(\text{D2}[q, a] /. \{\beta \rightarrow \theta[1], \alpha \rightarrow 0, \gamma \rightarrow \pi - \phi[[1]]\})] \cdot \text{Conjugate}[(\text{D2}[r, aa] /. \{\beta \rightarrow \theta[[j]], \alpha \rightarrow 0, \gamma \rightarrow \pi - \phi[[j]]\})]
\]

\[\text{C1}[1,1] = \]

\[\sum_{a=-2}^{2} \sum_{aa=-2}^{2} (\text{Conjugate}[(\text{D2}[a, 1] /. \gamma \rightarrow 0)] \cdot (\text{D2}[aa, 1] /. \gamma \rightarrow 0) \cdot \text{Conjugate}[(\text{D2}[a, 1] /. \gamma \rightarrow 0)] \cdot (\text{D2}[aa, 1] /. \gamma \rightarrow 0) \cdot \text{FullSimplify}[\text{C1}[a, aa]] \]

\[\text{C2} = \]

\[\sum_{a=-2}^{2} \sum_{aa=-2}^{2} (\text{Conjugate}[(\text{D2}[a, 2] /. \gamma \rightarrow 0)] \cdot (\text{D2}[aa, 2] /. \gamma \rightarrow 0) \cdot \text{Conjugate}[(\text{D2}[a, 2] /. \gamma \rightarrow 0)] \cdot (\text{D2}[aa, 2] /. \gamma \rightarrow 0) \cdot \text{FullSimplify}[\text{C2}[a, aa]] \]

(* The spectral densities \( J_1 \) and \( J_2 \) are given by \( \text{C1} \) and \( \text{C2} \) because we have already FT'ed them!!! *)
\[ J_1[\omega, k, \alpha, \beta, \eta] := \]
\[ \frac{1}{10368 (16k^2 + \omega^2)} \left( k \left( -4 (288 + \eta (-672 + 149 \eta)) \cos[2 \beta] - (2016 + \eta (480 + 341 \eta)) \cos[4 \beta] - 256 \sqrt{2} (3 + \eta) (-12 + 5 \eta) \cos[3 \alpha] \cos[\beta] \sin[\beta]^3 + 9 (864 + \eta (96 + 161 \eta)) + 24 \eta (-3 \eta \cos[4 \alpha] \sin[\beta]^4 + 4 (3 + \eta) \cos[2 \alpha] \sin[2 \beta]^2)) \right) \]
\[ J_2[\omega, k, \alpha, \beta, \eta] := \]
\[ \frac{1}{165888 (4k^2 + \omega^2)} \left( k \left( 9 (3744 + \eta (-864 + 871 \eta)) + (2016 + \eta (480 + 341 \eta)) \cos[4 \beta] + 64 \eta^2 \cos[4 \alpha] \sin[\beta]^4 + 4 \cos[2 \beta] (288 + \eta (-5856 + 851 \eta)) - 432 \eta (3 + \eta) \cos[2 \alpha] \sin[\beta]^2 + 64 (3 + \eta) \sin[\beta]^2 (-81 \eta \cos[2 \alpha] + 2 \sqrt{2} (-12 + 5 \eta) \cos[3 \alpha] \sin[2 \beta]) \right) \]
\[ J_1[2\pi 45.6*10^6, 1.0*10^9, 0, 0, 1] = 4.91306 \times 10^{-11} \]
\[ J_2[2\pi 45.6*10^6, 1.0*10^9, 0, 0, 1] = 2.61796 \times 10^{-11} \]

(* The inverse of T1 is given by *)
\[ T_1^{-1}[\omega, k, \alpha, \beta, \eta, qcc] := ((2\pi* (3/4)*qcc)^2/3) * (J_1[\omega, k, \alpha, \beta, \eta] + 4 J_2[\omega, k, \alpha, \beta, \eta]) \]

(* The T1 (in seconds) is given by *)
\[ T_1[\omega, k, \alpha, \beta, \eta, qcc] := N[1/T_1^{-1}[\omega, k, \alpha, \beta, \eta, qcc]] \]

(* The Larmor frequency for H2 on the CMX-300 solid state spectrometer is 45.648 MHz *)
\[ T_1[2\pi*45.648*10^6, 1.0*10^7, 0, 0, 0, 0, 193000] = 0.0225929 \]
\[ T_1[2\pi*45.648*10^6, 1.0*10^7, 0, 0, 0, 0, 193000] = 0.0225929 \]
\[ T_1[2\pi*45.648*10^6, 1.0*10^7, 0, 0, 0, 0, 193000] = 0.0178717 \]
\[ T_1[2\pi*45.648*10^6, 1.0*10^7, 0, \pi/2, 0, 0, 193000] = 0.0201147 \]

(* Note that there is a small but real dependence on the latitudinal powder average angle \( \beta \) *)

(* If we choose to ignore the dependence on powder average angles, we can obtain the average T1 value for the powder as *)
(* The liquid state I=1 quadrupolar relaxation (isotropic rotational diffusion) is given below *)

\[
T_{\text{lin}}[\omega, k, \eta, \text{qcc}] := \\
(1 / (4 \pi)) \int_{0}^{2\pi} \int_{0}^{\pi} \sin[\beta] T_{\text{linv}}[\omega, k, \alpha, \beta, \eta, \text{qcc}] \, d\beta \, d\alpha
\]

\[B[\omega_{\text{larmor}}, \tau_{\text{rot}}] := 1 / (1 + (\omega_{\text{larmor}}^2 \times \tau_{\text{rot}}^2)) \]

\[D_{\text{prime}}[\omega_{\text{larmor}}, \tau_{\text{rot}}] := 1 / (1 + (4 + \omega_{\text{larmor}}^2 \times \tau_{\text{rot}}^2)) \]

\[R_{1}[S, \text{qcc}, \eta, \omega_{\text{larmor}}, \tau_{\text{rot}}] := \\
(3 \times (2 S + 3) / (400 \times S^2 \times (2 S - 1))) \times \text{qcc}^2 \times (1 + (\eta^2 / 3)) \times \\
(2 B[\omega_{\text{larmor}}, \tau_{\text{rot}}] + 8 D_{\text{prime}}[\omega_{\text{larmor}}, \tau_{\text{rot}}]) \times \tau_{\text{rot}}
\]

\[R_{1}[1, 260.0 \times 10^3 \times 2 \times \pi, 0, 2 \pi \times 45.648 \times 10^6, 1.0 \times 10^{-12}] = 1.00078 \]

\[T_{\text{liq}}[S, \text{qcc}, \eta, \omega_{\text{larmor}}, \nu_{\text{rot}}] := 1 / R_{1}[S, \text{qcc}, \eta, \omega_{\text{larmor}}, 1/\nu_{\text{rot}}] \]
Plot[{Log[10, T1int[45.84*10^6*2*\[Pi], 1.0*10^n, 0, 193000]],
    Log[10, T1int[61.42*10^6, 1.0*10^n, 0, 193000]],
    Log[10, T1int[76.77*10^6, 1.0*10^n, 0, 193000]],
    Log[10, T1int[92.13*10^6, 1.0*10^n, 0, 193000]],
    Log[10, T1liq[1, 193.0*10^3*2*\[Pi], 0, 45.84*10^6*2*\[Pi], 1.0*10^n]],
    Log[10, T1liq[1, 193.0*10^3*2*\[Pi], 0, 61.42*10^6*2*\[Pi], 1.0*10^n]],
    Log[10, T1liq[1, 193.0*10^3*2*\[Pi], 0, 76.77*10^6*2*\[Pi], 1.0*10^n]],
    Log[10, T1liq[1, 193.0*10^3*2*\[Pi], 0, 92.13*10^6*2*\[Pi], 1.0*10^n]}],
{n, 3, 13}, ImageSize -> 432, DefaultFont -> "Courier", 16.],
Frame -> True, FrameLabel -> {"Log_{10} [\nu]", "Log_{10} [T_1]"},
PlotRange -> {{3, 13}, {\[Minus]3, 3.5}}, GridLines -> Automatic,
PlotStyle -> {{AbsoluteThickness[1], RGBColor[1, 0, 0]},
    {AbsoluteThickness[1], RGBColor[1, 0, 0]},
    {AbsoluteThickness[1], RGBColor[1, 0, 0]},
    {AbsoluteThickness[1], RGBColor[0, 0, 1]},
    {AbsoluteThickness[1], RGBColor[0, 0, 1]},
    {AbsoluteThickness[1], RGBColor[0, 0, 1]}}
-Graphics-
t1graph30=%;
Export["t1plot30.eps",t1graph30]
t1plot30.eps

-Graphics-
t1graph31=%;
Export["t1plot31.eps",t1graph31]
Appendix D

Rigid Powder Pattern Simulation

Calculation of a rigid powder pattern using the conventions of Mehring and real space spin interactions. Rather than calculating the free induction decay the lineshape was evaluated, and then simply mirrored to produce the rigid simulation.

\[
\text{alab}[2,0] = \text{FullSimplify}[\sum_{q=-2}^{2} \text{apas}[2,\ q] \ D[2,\ q,\ 0]]
\]

\[
\frac{1}{4} \sqrt{\frac{3}{2}} (1 + 3 \cos[2 \beta] - 2 \eta \cos[2 \alpha] \sin[\beta]^2) \ \delta_{zz}
\]

\[
% / . \ \delta_{zz} \rightarrow \sqrt{\frac{3}{8}} \ qcc
\]

\[
\frac{3}{16} \ qcc (1 + 3 \cos[2 \beta] - 2 \eta \cos[2 \alpha] \sin[\beta]^2)
\]

\[
\nu1[\alpha_, \beta_, \ qcc_, \ \eta_] = %
\]

\[
\frac{3}{16} \ qcc (1 + 3 \cos[2 \beta] - 2 \eta \cos[2 \alpha] \sin[\beta]^2)
\]

\[
\nu2[\alpha_, \beta_, \ qcc_, \ \eta_] = -1*%
\]

\[
-\frac{3}{16} \ qcc (1 + 3 \cos[2 \beta] - 2 \eta \cos[2 \alpha] \sin[\beta]^2)
\]

\[
\nu1[0, \pi/2, 200000, 0]
\]

\[
\nu2[0, \pi/2, 200000, 0]
\]

\[
\text{gauss}[\nu0_, \ \text{lb}_] := \text{Exp}[(- (\nu - \nu0)^2)/(2 \ \text{lb}^2)]
\]

\[
\text{Plot[gauss[0, 10], \{\nu, -50, 50\}]
\]
boogie1[lb_, qcc_, α_, β_, η_] := gauss[ν1[α, β, qcc, η], lb]
boogie2[lb_, qcc_, α_, β_, η_] := gauss[ν2[α, β, qcc, η], lb]
<<repangwt5253;
intensity[lb_, qcc_, α_, β_, η_] := N[boogie1[lb, qcc, α, β, η] + boogie2[lb, qcc, α, β, η]];

This was added for Gaussian line broadening of the lineshape.

powder[lb_, qcc_, η_] := N[∑_{i=1}^{\text{\text{-length}}}[\text{repang}[i, 3] \times \text{intensity}[lb, qcc, \text{repang}[i, 2], \text{repang}[i, 1], η]]

temp = powder[5000, 200000, 0];
Plot[temp, {ν, -300000, 300000}, PlotRange -> All]
Appendix E

Intermediate Motion Lineshape Calculations

$C_2$ Jump Lineshape calculation also use the real spin space components of Mehring. But here a molecular fast average for the dynamics is used.
amol[2, 0] = \sum_{q=2}^{2} \text{apas}[2, q] D2[q, 0]

\frac{1}{2} \sqrt{\frac{3}{2}} \left(-1 + \text{Cos}[^{\beta}]\right) \delta_{ss} - \frac{1}{4} \sqrt{\frac{3}{2}} e^{i \eta} \text{Sin}[^{\beta}] \delta_{ss}

\eta / \eta \rightarrow 0

\frac{1}{2} \sqrt{\frac{3}{2}} \left(-1 + \text{Cos}[^{\beta}]\right) \delta_{ss}

amol[2, 0] = \emptyset;

amol[2, 1] = \left(\sum_{q=2}^{2} \text{apas}[2, q] D2[q, 1]\right) / \eta \rightarrow 0
\frac{3}{2} e^{-i \eta} \text{Cos}[^{\beta}] \text{Sin}[^{\beta}] \delta_{ss}

amol[2, -1] = \left(\sum_{q=2}^{2} \text{apas}[2, q] D2[q, -1]\right) / \eta \rightarrow 0
\frac{3}{2} e^{i \eta} \text{Cos}[^{\beta}] \text{Sin}[^{\beta}] \delta_{ss}

amol[2, 2] = \left(\sum_{q=2}^{2} \text{apas}[2, q] D2[q, 2]\right) / \eta \rightarrow 0
\frac{3}{4} e^{i \eta} \text{Sin}[^{\beta}] \delta_{ss}

amol[2, -2] = \left(\sum_{q=2}^{2} \text{apas}[2, q] D2[q, -2]\right) / \eta \rightarrow 0
\frac{3}{4} e^{-i \eta} \text{Sin}[^{\beta}] \delta_{ss}

\text{thetastet} = 1.91063323624901055
1.91063

amolfastavg[2, q_] := \text{N[Chop[((amol[2, q] / (\beta \rightarrow \theta, \gamma \rightarrow 0)) and (amol[2, q] / (\beta \rightarrow \theta, \gamma \rightarrow \pi))] / 2)]}

alab[2, 0] = \sum_{q=2}^{2} \text{amolfastavg}[2, q] D2[q, 0]

0. e^{i \theta} \text{Cos}[\theta] + 0. e^{i \theta} \text{Cos}[\theta] \text{Sin}[\theta] + 1.306186 \left(-1 + 3 \text{Cos}[\theta]^2\right) \left(-1 + 3 \text{Cos}[\theta]^2\right) \delta_{ss}
+ 0.459279 e^{i \theta} \text{Sin}[\theta]^2 \delta_{ss}

\text{ExpToTrig[\%] // Expand // Chop // Simplify}

\{0.306186 - 0.918559 \text{Cos}[\theta]^2 + \text{Cos}[\theta]^2 \left(-0.918559 + 2.75656 \text{Cos}[\theta]^2\right) + 0.918559 \text{Cos}[2 \theta] \text{Sin}[\theta]^2 \text{Sin}[\theta]^2 \delta_{ss}\}
\[ \begin{align*} 
\text{lab}[2, 0] &= 0 \\
(0.366186 - 0.918559 \cos[\theta] + \cos[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 6.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 3.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] )) \delta_{\alpha} \\
&\quad \cdot \delta_{\beta} \rightarrow \sqrt{\frac{3}{2}} \, \text{qcc} \\
\frac{1}{2} \sqrt{\frac{3}{2}} \, \text{qcc} \\
(0.366186 - 0.918559 \cos[\theta] + \cos[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 6.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 3.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] )) \gamma_1[\alpha, \beta, \text{qcc}, \theta, \gamma] - \delta \\
\frac{1}{2} \sqrt{\frac{3}{2}} \, \text{qcc} \\
(0.366186 - 0.918559 \cos[\theta] + \cos[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 6.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 3.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] )) \gamma_2[\alpha, \beta, \text{qcc}, \theta, \gamma] - 1 \ast \delta \\
\frac{1}{2} \sqrt{\frac{3}{2}} \, \text{qcc} \\
(0.366186 - 0.918559 \cos[\theta] + \cos[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 6.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] ) + 3.918559 \cos[2 \alpha] \sin[\beta] \gamma ( -0.918559 + 2.75568 \cos[\theta] )) \text{gauss}[v0, \text{lb}, \gamma] := \text{Exp}((-v - v0)^2) / (2 \text{lb}^2) \\
\text{Plot}[\text{gauss}[0, 10], \{v, -50, 50\}] 
\end{align*} \]
<< repangwt5253;

powder[lb_, qcc_, θ_] :=
  N[∑ i repangwt[[i, 3]] * intensity[lb, qcc, repangwt[[i, 2]], repangwt[[i, 1]], θ]]

temp1 = powder[4000, 213000, π * 65/180];
temp2 = powder[4000, 213000, π * 60/180];
temp3 = powder[4000, 213000, π * 55/180];
temp4 = powder[4000, 213000, π * 50/180];
temp5 = powder[4000, 213000, π * 45/180];
temp6 = powder[4000, 213000, π * 40/180];
temp7 = powder[4000, 213000, thetatic/2];

Plot[{temp2, temp3, temp4, temp5, temp7}, {v, -200000, 200000}, PlotPoints -> 120, ImageSize -> 543, Axes -> {True, False}, PlotRange -> {{-300000, 300000}, {-2, 1500}}, DefaultFont -> "Courier", 16.],
PlotStyle -> {{AbsoluteThickness[1], RGBColor[1, 0, 0]}, {AbsoluteThickness[1], RGBColor[0, 1, 0]},
  {AbsoluteThickness[1], RGBColor[0, 0, 1]}, {AbsoluteThickness[1], RGBColor[0, 1, 1]},
  {AbsoluteThickness[1], RGBColor[1, 0, 1]}}]
Appendix F

Tetrahedral Jump Intermediate Exchange
(*) The following derivation for tetrahedral jumps of deuterium is based on Appendix B from the paper by A. J. Vega and E. Luz, J. Chem. Phys., Vol. 86, pp. 1803-1813, 1997, along with the section from Mehring in Encyclopedia of MRI, vol. IV, pp 2596-2598. *)

\[ \delta_{temp} = \frac{1}{\sqrt{2}} \left( (1 - 3 \cos 2\phi) (1 - 7 \eta + (3 + \eta) \cos 2\theta) - e^{-1/2 (\phi - 2) / 2} (3 (1 - \eta) + (3 + \eta) \sin 2\theta) \sin \beta)^2 - e^{-1/2 (\phi + 2) / 2} (3 (1 + \eta) + (3 - \eta) \cos 2\theta) \sin \beta)^2 \right) \]

\[ \delta_{temp} = \frac{1}{\sqrt{2}} \left( (1 - 3 \cos 2\phi) (1 - 7 \eta + (3 + \eta) \cos 2\theta) - e^{-1/2 (\phi - 2) / 2} (3 (1 - \eta) + (3 + \eta) \sin 2\theta) \sin \beta)^2 - e^{-1/2 (\phi + 2) / 2} (3 (1 + \eta) + (3 - \eta) \cos 2\theta) \sin \beta)^2 \right) \]

\[ \theta_{tet} = 1.910633236249018555276423213604402016^\circ \]

\[ 1.910653236249015563 \]

(*) For \(|\lambda|=1\) the following is true for the relationship of the \(\theta_{tet}\) and \(\delta_{temp}\) *)

\[ \delta_{temp} = \pi \* \theta_{tet} \]

\[ 200000 \]

\[ \eta = 0.0 \]

\[ \theta_{tet} = 1.910633236249018555276423213604402016^\circ \]

\[ 1.910653236249015563 \]

cheetah = [1, 1, 1, 1]

(2, 1, 1, 1)

One = IdentityMatrix[4]

General spell : Possible spelling errors: new symbol name "One" is similar to existing symbol "one". Next:

\[ \{1, 0, 0, 0\}, \{0, 1, 0, 0\}, \{0, 0, 1, 0\}, \{0, 0, 0, 1\} \]

p = \[1/4, 1/4, 1/4, 1/4\]

\[ \left[ \begin{array}{cccc}
\frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4}
\end{array} \right] \]

(*) We need the jump rate matrix. We'll call it \(P\) like Mehring does, but leave out \(T^2\) relaxation to simplify to calculation *)

\[ \Gamma_{[k, l]} := \{(-3k, k, k), (k, -3k, k), (k, k, -3k), (k, k, -3k)\} \]

\[ \Gamma_{[200]} \]

\[ \{(-600, 200, 200, 200), (200, -600, 200, 200), (200, 200, -600, 200), (200, 200, 200, -600)\} \]

\[ \delta s_{[0, 0]} = \text{ahlab20} / (\theta = 0, \phi = 0) \]

\[ 6250 \sqrt{\pi} \left( (1 - 3 \cos 2\phi) (1 - 7 \eta + (3 + \eta) \cos 2\theta) - e^{-1/2 (\phi - 2) / 2} (3 (1 - \eta) + (3 + \eta) \sin 2\theta) \sin \beta)^2 - e^{-1/2 (\phi + 2) / 2} (3 (1 + \eta) + (3 - \eta) \cos 2\theta) \sin \beta)^2 \right) \]

\[ \delta s_{[0, 0]} \]

76530. (* For the second of the tetrahedral sites *)
\[ 62[\alpha, \beta] = \text{alab20} ./ (0 \rightarrow \text{thetatet}, \psi \rightarrow 0) \]
\[ 6250 \sqrt{\pi} \times (-1.33333 (1 + 3 \cos(2 \beta)) + 5.33333 e^{i \frac{2 \pi}{3}} \sin(\beta)^2 + 5.33333 e^{i \frac{4 \pi}{3}} \sin(\beta)^2 + 3.77124 e^{i \frac{2 \pi}{3}} \sin(2 \beta) + 3.77124 e^{i \frac{4 \pi}{3}} \sin(2 \beta)) \]
\[ 62[0, 0] \]
-256519.

(* For the third of the tetrahedral sites *)
\[ 63[\alpha, \beta] = \text{alab20} ./ (0 \rightarrow \text{thetatet}, \psi \rightarrow \frac{2 \pi}{3}) \]
\[ 6250 \sqrt{\pi} \times \left(-1.33333 (1 + 3 \cos(2 \beta)) + 5.33333 e^{i \frac{2 \pi}{3}} \sin(\beta)^2 + 5.33333 e^{i \frac{4 \pi}{3}} \sin(\beta)^2 + 3.77124 e^{i \frac{2 \pi}{3}} \sin(2 \beta) + 3.77124 e^{i \frac{4 \pi}{3}} \sin(2 \beta) \right) \]
\[ 63[0, 0] \]
-256519.

(* For the fourth of the tetrahedral jump sites *)
\[ 64[\alpha, \beta] = \text{alab20} ./ (0 \rightarrow \text{thetatet}, \psi \rightarrow \frac{4 \pi}{3}) \]
\[ 6250 \sqrt{\pi} \times \left(-1.33333 (1 + 3 \cos(2 \beta)) + 5.33333 e^{i \frac{2 \pi}{3}} \sin(\beta)^2 + 5.33333 e^{i \frac{4 \pi}{3}} \sin(\beta)^2 + 3.77124 e^{i \frac{2 \pi}{3}} \sin(2 \beta) + 3.77124 e^{i \frac{4 \pi}{3}} \sin(2 \beta) \right) \]
\[ 64[0, 0] \]
-256519.

(* The diagonal frequency matrix for the four sites is *)
\[ 65[\alpha, \beta] \rightarrow \text{Re}[[61[\alpha, \beta], 0, 0, 0], [62[\alpha, \beta], 0, 0], [0, 0, 63[\alpha, \beta], 0], [0, 0, 0, 64[\alpha, \beta]]] \]

(* Open repulsionangleweights *)
```
<< repangwt5253;
Length[repangwt]
5253
repangwt[[1, 1]]
0.000061333
repangwt[[1, 2]]
-1.1049
```
\[ r[\alpha, \beta, k] = \mathcal{N}(s, \alpha, \beta) \cdot 1(k) \]

\[ r(0, 0, 100) \]

\[ (\cdots \cdot -256510.1, 100., 100., 100.) \cdot (100., -256510.1, 100., 100.) \cdot (100., 100., -256510.1, 100.) \cdot (100., 100., 100., -256510.1) \]

\[ s[\alpha, \beta, k] \rightarrow \text{Chop}[\text{sintran}[r[\alpha, \beta, k]]] \]

\[ \text{sinv}[\alpha, \beta, k] = \text{Chop}[\text{Inverse}[s[\alpha, \beta, k]]] \]

\[ \text{sinv}[\text{repangvt}[11, 22], \text{repangvt}[11, 11], 10^{-3}] \]

\[ A[\alpha, \beta, k] = \text{Chop}[s[0, \alpha, 0] \cdot r[\alpha, 0, 0] \cdot \text{sinv}[0, \alpha, 0] \cdot 10^{-7}] \]

\[ B[\alpha, \beta, k, t] = \text{Chop}[s[0, \alpha, 0] \cdot r[\alpha, 0, 0] \cdot \text{sinv}[0, \alpha, 0] \cdot 10^{-7}] \]

\[ \text{Timing}[\text{echo}[\text{repangvt}[1000, 22], \text{repangvt}[2000, 11], 10^{-3}] \]

\[ \text{Timing}[\text{powdercomplexf}[2.5 \times 10^{-4}, 35 \times 10^{-6}]] \]

\[ \text{Timing}[\text{powdercomplexf}[2.5 \times 10^{-4}, 35 \times 10^{-6}]] \]

\[ \text{Timing}[\text{powdercomplexf}[2.5 \times 10^{-4}, 35 \times 10^{-6}]] \]

\[ \text{Timing}[\text{powdercomplexf}[2.5 \times 10^{-4}, 35 \times 10^{-6}]] \]
Curriculum VITA

Bernie O'Hare

Peer Reviewed Publications


2. “Room-Temperature Icelike Water in Kanemite Detected by 2H NMR T1 Relaxation”, Alan J. Benesi, Bernie O’Hare, Michael W. Grutzeck, and John W. Phair, Langmuir, 21, 527-529, 2005.


Professional Presentations


O’Hare, Bernie; Grutzeck, Michael W.; Kim, Seong H.; Asay, David B.; Benesi, Alan J. “Rapid tetrahedral jumps of 2H nuclei with pseudoisotropic long term rotational diffusion observed in hydrated zeolite A: A case for room temperature solid state water”. Abstracts of Posters, 47th ENC International Meeting, Pacific Grove, CA, United States, April 23-April 28, 2006 (2006).
