A Theoretical and Experimental Study of Water Proton Spin Relaxation in liquid, hexagonal-ice and the Paramagnetic Gd$^{3+}$(H$_2$O)$_8$ Complex.

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Abstract

The project is a combination of theoretical and experimental works for understanding the spin relaxation properties of water molecules and the effect of paramagnetic source Gd (III) ions in ice and pure water sample. At the theory part relaxation equations is derived by using relevant theory. Experimentally paramagnetic source has been used to study enhanced spin relaxation.

It is found that paramagnetic source gives obviously improvement of signal intensity compare to pure water sample at normal room temperature (283.15K to 293.15K). And 0.1mM Gadolinium (III) chloride hexahydrate is enough to see the enhancement, which in the range at 0.2mM to 0.4mM gives good result. The limit is around 0.01mM. Results with normalization of concentration also present in nice way.

In ice sample with paramagnetic source wasn’t enhance spin relaxation too much compare to ice sample of pure water. However with the simulation it is obviously to see that the correlation time is reduced. A similar size compound (CaCl2•2H2O) with no paramagnetic effect is used in the experiments in the purpose for comparison to Gadolinium (III) chloride hexahydrate. Generally reduce of correlation time in ice is comes from the changes of ice structure and the effect from paramagnetic sources is limited.

EPR experiments is performed for a sample of 130mM Gd-aqua complex at 293.15K (20 °C) in three different experimental conditions. And it is found that higher microwave power gives stronger intensity while keep the other parameters no change. Solid state of EPR is also tested. However with the limitation of instrument it is only possible to test a mixture of water and ice. In this condition the intensity is much reduced compare to in pure water experiments.

Keywords: NMR, T1, relaxation, spin-1/2, Liouville equation, perturbation theory, NMRD, field cycling relaxometer, paramagnetic source, EPR
Veritati et sapientiae semper studeamus.
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The aim of thesis
The project is a combination of theoretical and experimental works for understanding water with three aims:

First, it is to study water proton spin-lattice relaxation in hexagonal ice and liquid water.

And the effect of paramagnetic source Gd (III) ions in ice and water.

Programming of FORTRAN is also carried out in the purpose of theoretical simulation.

After introduce the background of NMR (nuclear magnetic resonance) and water molecular, at the theory part will start to discuss the way of derive relaxation equations by using relevant theory. In order to describe the paramagnetically enhanced spin relaxation, the effect of paramagnetic species will also be considered when derive relaxation equations.

By experimental part, measurement of proton NMRD (nuclear magnetic relaxation dispersion), relaxation is presented for liquid water, ice and paramagnetically doped ice. Derived equations from theory part are used for analysis proton T1 NMRD results.

Also, for theoretical part the thesis uses a step-to-step way on present equations. Hence most books related to the topic is too advanced on math, therefore it can also be used as an introduction of this topic for those non-mathematical background students at graduated level.

A Quick NMR Experiment Guide for ‘Spinmaster FFC2000 1T C/DC’ (The fast field cycling NMR relaxometer) is also available in the appendix.

1. Introduction

1.1 General background of relaxation
The study of NMR (nuclear magnetic resonance) related topic is very exciting. Beside of ‘pure science’ (mathematical calculations, complex theory which difficult to understand, etc.), MRI (magnetic resonance imaging) has been well known for the society. Due to the advantageous such as easy to use, no harm to patient (compare to X ray or CT which use ionizing radiation), etc., one has no doubt to say that we get much benefit from this technique.

Although it can be difficult, generally the main idea is easy to talk. As we all known, spin is a fundamental and characteristic property of particles (proton and neutron, etc.) It is the same as for example one proton can have property as charge. A spin system is orderless and randomly until an external magnetic field ($B_0$) is added. For a simply example, consider spin-$1/2$ which gives two states. Random spin system is ‘forced’ by the magnetic field and the number of spins for each state will be equilibrium with Boltzmann distribution.

After short review of spin, we can introduce a term called magnetic moment ($m$), and it is defined as

$$m = \gamma P \quad (1-1)$$

, where $\gamma$ is gyromagnetic ratio (or magnetogyric ratio), and $P$ is the spin angular momentum. The value of $\gamma$ for hydrogen is $267.522 \times 10^6 \text{ rad s}^{-1} \text{T}^{-1}$. [1.1]

When $B_0$ is added, the spinning nucleus will also experience processing. (Figure 1.1) It is similar to the image of the Earth orbit: spinning of itself, also around another object. However here we have magnetic field instead, in case it is not visible.

![Figure 1.1](image)

Figure 1.1 A figure shows how a nucleus is processing in magnetic field.

The resonance angular frequency depends on the magnetic field is given by

$$\omega = \gamma B_0 \quad (1-2)$$

, and it is called Larmor frequency after the name who found it. The unit of frequency can be in rad s$^{-1}$ or in Hz.
If an extra external magnetic field (RF pulse, $B_1$; RF stands for radio frequency) is added perpendicular to $B_0$ and they have the same frequency as $\omega$, the nucleus at low energy level will transition to high energy level by absorbing energy. This is the basic idea of nuclear magnetic resonance.

![Diagram](image.png)

**Figure 1.2** Energy levels of spin-$1/2$. The magnetization vector is shown from the view of longitudinal direction ($M_z$). (a) With $B_0$, (b) after extra external magnetic field $B_1$ is added.

If the number of protons at two states is equal, we can name it as a $90^\circ$ pulse.

After $B_1$ is removed, the whole system would like to ‘return’ the state before, it is called relaxation. With difference ways of energy exchange process between a nucleus and its environment we can divide them into two groups: spin-lattice relaxation and spin-spin relaxation.

Spin-lattice relaxation or longitudinal relaxation is normally called $T_1$-process; another is on transverse direction we named as $T_2$-process. Measurements of dependence of spin relaxation (both $T_1$ and $T_2$) and magnetic field is done by using field cycling relaxometer, and such kind of experiments is called nuclear magnetic resonance dispersion (NMRD). Relaxometry can be used to study dynamics and structure of molecules in biochemistry (such as protein function), material science and medical science (paramagnetic source for MRI).

### 1.2 The water molecule

Water (chemical formula: $H_2O$) might be the most well-known inorganic compound, hence we need it every day. In human body about 70% is water; for a jellyfish it is up to 95% and
70-75% of our planet is covered by water (include both solid and liquid states). We have a long history to understand how it works related to our life and to the world. Back to ancient Greece it has been considered as one or four (sometimes five) elements. In China, on the *Classic of History* (simplified Chinese: *Shang Shu*, presented by the bamboo slips texts from the tombs of Guodian in Hubei Provence, dated to the 300 BC.) also present water as a basic element which form the world.

Naturally it is not pure; however the impurities can be removed by distillation. Table below shows some basic properties of water. [1.2]

Table 1.1 some properties of water [1.2]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>18.01528(33) g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>1000 kg/m³ at 4°C, liquid</td>
</tr>
<tr>
<td>Melting point</td>
<td>273.15K (0°C)</td>
</tr>
<tr>
<td>Boiling point</td>
<td>373.13K (99.98°C)</td>
</tr>
<tr>
<td>pK_a</td>
<td>15.74</td>
</tr>
<tr>
<td>pK_b</td>
<td>15.74</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.001 Pa s at 293.15K (20°C)</td>
</tr>
</tbody>
</table>

The structure of water molecule is simple. The OH bond has length as approximately 96pm, and the angle of H-O-H is 104.5°. Each of them bound to the oxygen atom by a covalent bond. (Figure 1.3) [1.2]

![Figure 1.3](image)

*Figure 1.3* Structure of a water molecule.

One might have seen from other articles the angel is presented as 109.5°. Here, we must consider that an Oxygen atom has six outer shell electrons and only two of them have been used by bond to Hydrogen atoms. The rest two pairs of non bonding state would like to ‘push’ each other because of the negative charge between them. Of course they are not able to leave from the Oxygen atom, therefore the repulsion is also effect the H-O bonds. This twist of tetrahedral structure gives the angle of H-O-H is 104.5°. [1.3] And two Hydrogen atoms in water is chemical equivalence.

As present, the two non bonding pairs on Oxygen side is more negative compare to Hydrogen side. Although the water molecule is neutral but the distribution of charges are not ‘on average’.
Each Oxygen atom has six outer shell electrons (in red), the covalent bond is shown with blue colour, and non-bonding pairs show with colourless.

As property of magnetism: negative charge attracts positive charge, we could imagine in a glass of water the ‘positive’ Hydrogen always would like to attract ‘negative’ Oxygen (hydrogen bonding). And due to hydrogen bonding, the attraction of water molecules is increased. [1.3]

When water freeze to ice, the volume will increase. Now water molecules are not chaotic but more ordered. Each one is ‘bonded’ with other neighbour water molecules by hydrogen bonds, so the crystal structure is mainly hexagonal. Figure 1.4 shows ice of pure water in both three dimensional and molecule structure.

1.3 An introduction to EPR [1.5]
EPR stands for the abbreviation of electron paramagnetic resonance, and can also be called as electron spin resonance (ESR). EPR has similar physical background to NMR, and the difference is compare to NMR which measure protons but EPR measures electron spins. However only unpaired electron will effect and has resonance.

Figure 1.5 shows a block diagram of an EPR spectrometer. The blue parts offer magnetic field, between them there is a cavity where one can insert sample. Here can also supply cooling system if it is need. Intensity and field are collected and link to the computer. With specific software EPR spectra will be seen on the screen.

\[ \hbar \nu = g \beta B \Rightarrow g = \frac{\hbar \nu}{\beta B} \]  

(1-3)  

[1.6]

Here \( h \) is Planck constant (\( h=6.62620*10^{-34} \) JS); \( \nu \) is microwave frequency (in Hz); \( \beta \) stands for Bohr magneton (\( \beta=9.27410*10^{-28} \) JG^{-1}) and \( B \) stands for magnetic field (in mT).

Mainly there are three kind of microwave frequency have been used: X-band, K-band and Q-band. (In this thesis X-band is used in experiments.)

2. Theoretical method
In this chapter, we will focus on main concepts of spin relaxation. (Reference books can be found at [2.1-2.8]) The thesis is based on water relaxation therefore the topic will only focus on discussion of spin -1/2.

2.1 Density Matrix and Liouville equation

It is not very difficult to think about ‘the ensemble of isolated spin-1/2’ easily through to look at into a cup of pure water. Those rare isotopes can be neglected hence $^1$H has NA = 99.985%.

Figure 2.1 Ensemble of isolated spin-1/2; notice that each individual has different state.

All of those protons have different polarization states, so it is difficult to treat each one individually and quantify them by sum the results (though principally possible). However, with the help of density operator we could try to perform calculation in a much more convenient way [2.2] (equation 10.7):

$$\hat{\rho} = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix} = \begin{pmatrix} c_\alpha c_\alpha & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix}$$

Without count interaction, the density operator in the form of a matrix (right part (⋅⋅) of the equation) is shown by 2-1. The bar over quadratic product of the superposition coefficients means average over the ensemble states. We can also write it in the following term:

$$\rho(t) \equiv \sum_{m,n} c_{m,n} |m\rangle \langle n|$$

(2-2)

where $c_{m,n} = \rho_{m,n}$, and the multiplied column vector and row vector $|m\rangle <n|$ for spin-1/2 with all possible combinations are $|1/2><1/2|$, $|1/2><-1/2|$, $|-1/2><1/2|$ and $|-1/2><-1/2|$.

The Time dependent equation of motion for a density matrix can be written as:

$$\frac{d}{dt} \rho(t) = -\frac{i}{\hbar} [\hat{H}, \rho(t)]$$

(2-3)

Time evolution operator $\mathcal{L}$ is defined by:
\[ \hat{L}_Q = \frac{1}{\hbar}[\hat{H}, \hat{Q}] \quad (2-4) \]

So now the equation presented before can be rewritten with Liouville operator:

\[ \frac{d}{dt} \rho(t) = -iL \rho(t) \quad (2-5) \]

By expansion the density operator in the form of matrix, the Liouville equation has transformed to:

\[
\frac{\partial}{\partial t} \begin{bmatrix}
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\end{bmatrix} = \begin{bmatrix}
\frac{1}{2} \sqrt{2} \\
\frac{1}{2} \sqrt{2} \\
\frac{1}{2} \sqrt{2} \\
\frac{1}{2} \sqrt{2} \\
\end{bmatrix}
\begin{bmatrix}
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\rho_{\frac{1}{2}, \frac{1}{2}} \\
\end{bmatrix}
\]

We can solve the \((\cdots)\) term by introduce the norm on the Liouville space*. It is defined as

\[
<\hat{Q}_N|\hat{Q}_m> = Tr\left\{\hat{Q}_N^* \hat{Q}_m \right\} = \sum_\mathcal{N} \langle N|t\rangle \langle k|m\rangle \langle n|N\rangle
\]

\[
= \sum_\mathcal{N} \langle N|t\rangle \langle k|m\rangle \langle n|N\rangle
\]

\[
(2-7)
\]

, where \(\delta_{N,l}, \delta_{k,m} \) and \(\delta_{n,N} \) are satisfied with Kronecker function:

\[
\delta_{ij} = \begin{cases}
1, & i = j \\
0, & i \neq j
\end{cases} 
\]

(* Liouville space is a vector space which basis are operators.)

Notice that for any \(Q\) we have

\[
\hat{Q}_k = |k\rangle \langle l| 
\]

, where \(|k\rangle \langle l|\) is called projecting operator. The equation becomes

\[
<\hat{Q}_N|\hat{L}_Q|\hat{Q}_m> = \frac{1}{\hbar}\left\{\hat{Q}_k \left[\hat{H}, \hat{Q}_m \right] \right\} = Tr\left\{\hat{Q}_k^* \left(\hat{H} \hat{Q}_m - \hat{Q}_m \hat{H} \right) \right\}
\]

\[
= Tr\left\{\hat{Q}_k^* \hat{H} \hat{Q}_m \right\} - Tr\left\{\hat{Q}_k^* \hat{Q}_m \hat{H} \right\} = \sum_P \langle P|\hat{Q}_k^* \hat{H} \hat{Q}_m |P\rangle - \sum_P \langle P|\hat{Q}_k^* \hat{Q}_m \hat{H} |P\rangle
\]

\[
(2-10)
\]
We can rewrite the Hamiltonian operator with geomagnetic ratio, static field and operator for nuclear spin angular momentum for the z component.

\[ \hat{H} = \hat{H}_z = -\gamma \hbar B^z \hat{I}_z \quad (2-11) \]

Use equation 2-11 into last equation, we can get the norm as

\[ (\hat{Q}_{mz} | \hat{Q}_{m'} ) = -i\gamma B^z \left( \langle \mathcal{N}| \hat{I}_z | m \rangle \langle m | \mathcal{N}' \rangle - \langle \mathcal{N}' | \hat{I}_z | m \rangle \langle m | \mathcal{N} \rangle \right) \]

Now consider a real condition with \(|1/2><1/2|\),

\[ \hspace{1cm} \]

We can get the same result for \(|-1/2><-1/2|\), because the final terms cancel to each other.

Continue with the calculation with \(|1/2><-1/2|\):

\[ \hspace{1cm} \]

As mentioned before (2-11), we also know that

\[ \hat{I}_z \left| \frac{1}{2} \right> = \frac{1}{2} \left| \frac{1}{2} \right> \quad ; \quad \hat{I}_z \left| -\frac{1}{2} \right> = -\frac{1}{2} \left| -\frac{1}{2} \right> \quad (2-15) \]

, simple put the numbers in to the equation we can get the solution:

\[ \hspace{1cm} \]

It is the same way to calculate (\(|-1/2><1/2|\),\(|-1/2><-1/2|\)\), and the only difference of the result is a minus sign. Now our matrix has become:
Now we could analysis the result into equation 2-3, we will get

\[
\frac{d}{dt} \rho_{\frac{1}{2} \downarrow} (t) = i \omega \rho_{\frac{1}{2} \downarrow}(t) \Rightarrow \frac{d}{dt} \rho_{\frac{1}{2} \downarrow} (t) = \left( i \omega - \frac{1}{T_2} \right) \frac{d}{dt} \rho_{\frac{1}{2} \downarrow} (t)
\]

(2-18)

The differential equation can be solved and give result as

\[
\rho_{\frac{1}{2} \downarrow} (t) = \rho_{\frac{1}{2} \downarrow} (0) e^{(i \omega - \frac{1}{T_2})t}
\]

(2-19)

, which indicate the free induction decay (FID).

So far the equation is time-dependent. By apply Fourier-Laplace transform (FT) we can transfer it into frequency dependent:

\[
\tilde{f}(\omega) = \int_{-\infty}^{\infty} f(t) e^{i \omega t} dt \Rightarrow \tilde{\rho}_{\frac{1}{2} \downarrow}(\omega) = \tilde{\rho}_{\frac{1}{2} \downarrow} (0)(-) \frac{1}{i(\omega - \omega_0) + \frac{1}{T_2}}
\]

\[
= \tilde{\rho}_{\frac{1}{2} \downarrow} (0)(-) \frac{T_2}{i(\omega - \omega_0)T_2 + 1}
\]

(2-20)

Notice that \( \omega \) and \( \omega_0 \) is not the same, first is frequency (in units of rad s\(^{-1}\)) and the latter is the Larmor frequency.

\[
(-) \frac{T_2}{i(\omega - \omega_0)T_2 + 1} = (-) \frac{T_2[-i(\omega - \omega_0)T_2 + 1]}{[i(\omega - \omega_0)T_2 + 1][-i(\omega - \omega_0)T_2 + 1]} = \text{Re(\(\cdots\))} + \text{Im(\(\cdots\))}
\]

\[
= \frac{T_2}{(\omega - \omega_0)^2 T_2^2 + 1} + \frac{-i(\omega - \omega_0)T_2 + 1}{(\omega - \omega_0)^2 T_2^2 + 1}
\]

(2-21)

By this we could separated it into two terms: the first part (real part), this term presented the energy absorption in the sample that we could measured; and the second part (imaginary part) shows the dynamic frequency shift. The value of that is very small so we ignore it here.
Now we have shown the way from theoretical calculation to real. By using FT we could plot measured result from FID into spectrum (the Lorentzian line shape).

![Diagram](image)

**Figure 2.2** An example of spectrum, peak width of half height has been indicated. And $2T_{2}^{-1}$ is the full width at half height (FWHH).

As presented clearly from figure 2.2, we could rearrange the equation 2-20 we’ve got from FT:

$$\rho_{1\rightarrow2}(\omega) = \rho_{1\rightarrow2}(0) \frac{T_{2}}{(\omega - \omega_{0})^{2}T_{2}^{2} + 1} \Rightarrow (\omega - \omega_{0})^{2}T_{2}^{2} + 1 = 2$$

$$(\omega - \omega_{0})^{2}T_{2}^{2} = 1$$

$$\Delta \omega^{2} = \frac{1}{T_{2}} \Rightarrow |\Delta \omega| = \frac{1}{T_{2}}$$

(2-22)

We could see that the final result actually is the decay rate constant of a coherence, or transverse magnetization.
2.2 The pure dephasing relaxation model

We will see that the measured $T_2$ actually is expressible in terms of the combination of correlation time and the fluctuation, by the related calculation of the pure dephasing relaxation model.

Let’s back to a cup of water. Water molecules do not stable but moving around chaotically all the time. They must interact to each other, so instead take $\omega_0$ we should add an extra amount to cover the effect from interaction. It is very small and time depended. We name it as $\Delta \omega(t)$. (Figure 2.3 (a))

![Figure 2.3 (a) many water molecules interact to each other. (b) Plot of delta function.](image)

As we have mentioned before (see equation 2-18):

\[
\frac{d}{dt} \rho_{\frac{1}{2} \frac{1}{2}}(t) = -i\omega_s \rho_{\frac{1}{2} \frac{1}{2}}(t) \quad (2-23)
\]

(It is doesn’t matter for the minus sign before $i\omega_0$, here use the value from matrix form 2-17 in order to maintain the unitary and compactness in writing.)

If we do not have the $\Delta \omega(t)$ term, the solution of 2-18 will follow the delta function. Instead of a spectral peak we will got a ‘line’ (actually it is not a line, accurately, it is a very sharp line shape which the area is equal to one.) as shown in figure 2.3 (b), indicated with the red colour. When the $\Delta \omega(t)$ term has been considered we will get a spectral peak (blue colour) with separated bandwidth. After added $\Delta \omega(t)$ term equation 2-23 becomes:

\[
\frac{d}{dt} \rho_{\frac{1}{2} \frac{1}{2}}(t) = -i(\omega_s + \Delta \omega(t))\rho_{\frac{1}{2} \frac{1}{2}}(t) = (-i\omega_s - i\Delta \omega(t))\rho_{\frac{1}{2} \frac{1}{2}}(t) = -i\omega_s \rho_{\frac{1}{2} \frac{1}{2}}(t) - i\Delta \omega(t)\rho_{\frac{1}{2} \frac{1}{2}}(t) \quad (2-24)
\]
Mathematically we have this simple transform as
\[
\rho_{\frac{1}{2}}(t) = e^{-i\omega t} \rho_{\frac{1}{2}}(t) \Longleftrightarrow e^{i\omega t} \rho_{\frac{1}{2}}(t) = \rho_{\frac{1}{2}}^*(t)
\]  
(2-25)

So we could rearrange 2-24 into
\[
\frac{d}{dt} \rho_{\frac{1}{2}}(t) = (-i \omega) e^{i\omega t} \rho_{\frac{1}{2}}^*(t) + e^{i\omega t} \frac{d}{dt} \rho_{\frac{1}{2}}^*(t) \Rightarrow \frac{d}{dt} \rho_{\frac{1}{2}}(t) = (-i \omega) \rho_{\frac{1}{2}}(t) + e^{-i\omega t} \frac{d}{dt} \rho_{\frac{1}{2}}^*(t)
\]  
(2-26)

Let’s summarize the result from equation 2-25 and 2-26 together, we get
\[
-i \omega \rho_{\frac{1}{2}}(t) - i \Delta \omega(t) \rho_{\frac{1}{2}}(t) = (-i \omega) \rho_{\frac{1}{2}}(t) + e^{-i\omega t} \frac{d}{dt} \rho_{\frac{1}{2}}^*(t)
\]  
(2-27)

So the first term (both left and right side of the equation) cancels to each other, which left
\[
-i \Delta \omega(t) \rho_{\frac{1}{2}}(t) = e^{-i\omega t} \frac{d}{dt} \rho_{\frac{1}{2}}^*(t) \Rightarrow \frac{d}{dt} \rho_{\frac{1}{2}}^*(t) = -i \Delta \omega(t) e^{i\omega t} \rho_{\frac{1}{2}}(t) = -i \Delta \omega(t) \rho_{\frac{1}{2}}^*(t)
\]  
(2-28)

With the help of the sample transform 2-25, now we could get an equation with \( \rho^* \) only, proceeding the equation with Redfield theory, we could get
\[
\int d\rho_{\frac{1}{2}}^*(t) = \int_{t_0}^t -i \Delta \omega(s) \rho_{\frac{1}{2}}^*(s) ds
\]  
(2-29)

With the result of 2.28 it is immediately seen that
\[
\frac{d}{dt} \rho_{\frac{1}{2}}^*(t) = -i \Delta \omega(t) \left[ \rho_{\frac{1}{2}}^*(t_0) + \int_{t_0}^t -i \Delta \omega(s) \rho_{\frac{1}{2}}^*(s) ds \right]
\]
\[
= -i \Delta \omega(t) \left[ \rho_{\frac{1}{2}}^*(t_0) - i \int_{t_0}^t \Delta \omega(s) \rho_{\frac{1}{2}}^*(s) ds \right] = -i \Delta \omega(t) \rho_{\frac{1}{2}}^*(t_0) - i \Delta \omega(t) \Delta \omega(s) \rho_{\frac{1}{2}}^*(s) ds
\]  
(2-30)

As \( t = 0, t = \infty \), consider \( \Delta \omega(t) \) is much faster compare to (s) depended term, we introduce Markov approximation that \( \rho^*(s) \approx \rho^*(t) \). With this approximation we could get
\[
\frac{d}{dt} \rho^* \left( t \right) \approx -i \Delta \omega(t) \rho^* \left( t \right) - \int \Delta \omega(t) \Delta \omega(s) ds \rho^* \left( s \right) = - \int \Delta \omega(t) \Delta \omega(s) ds \rho^* \left( t \right) \tag{2-31}
\]

The bar means take average value. Now we introduce a new term called \( R_2 \), it defined as
\[
R_2 = \int \Delta \omega(t) \Delta \omega(s) ds \tag{2-32}
\]

\( \Delta \omega(t) \Delta \omega(s) \) is a correlation function, which only depends on \((t-s)\). Apply it into last equation we get
\[
\frac{d}{dt} \rho^* \left( t \right) = -R_2 \rho^* \left( t \right) \tag{2-33}
\]

also with the help of the simple transform from equation 2-25 gives
\[
\frac{d}{dt} \left( \rho_{1, \frac{1}{2}}(t) e^{i\omega t} \right) = -R_2 \left( \rho_{1, \frac{1}{2}}(t) e^{i\omega t} \right) \tag{2-34}
\]

By solve the differential equation, it becomes
\[
(i\omega) e^{i\omega t} \rho_{1, \frac{1}{2}}(t) + e^{i\omega t} \frac{d}{dt} \rho_{1, \frac{1}{2}}(t) = -R_2 e^{i\omega t} \rho_{1, \frac{1}{2}}(t) \tag{2-35}
\]

Here \( e^{i\omega t} \) is cancelled from both sides, also with the help of math formula
\[
\frac{d}{dt} f(t) = kf(t) \Rightarrow f(t) = \text{const.} \cdot e^{kt} \tag{m-1}
\]

(* Mathematical equations from math hand book with have separate numbers)

We then have a new equation as
\[
\rho_{1, \frac{1}{2}}(t) = \rho_{1, \frac{1}{2}}(0) e^{-R_2 \cdot i\omega t} \tag{2-36}
\]

Again, Fourier transform (FT) (2-20) has been applied to it in order to change the time depend equation to frequency depend
\[
\tilde{\rho}_{1, \frac{1}{2}}(\omega) = \int \rho_{1, \frac{1}{2}}(t) e^{i\omega t} dt = \int \rho_{1, \frac{1}{2}}(0) e^{(-R_2 - i\omega, +i\omega)^t} dt \tag{2-37}
\]

If we assume that \( \omega - \omega^0 = \Delta \omega \), we will have
\[
\tilde{\rho}_{1, \frac{1}{2}}(\omega) = \int \rho_{1, \frac{1}{2}}(0) e^{(-R_2 + i\Delta \omega)^t} dt \tag{2-38}
\]
The result from last equation is

\[ \rho_{11}^{\pm}(\omega) = \frac{\rho_{11}^{\pm}(\omega)}{R_z + i\Delta \omega} \quad (2-39) \]

We now define \( R_z \) as

\[ R_z = \frac{1}{T_z} \quad (2-40) \]

Rewrite equation 2-39 with the new defined term it gives

\[ \rho_{11}^{\pm}(\omega) = \rho_{11}^{\pm}(\omega) \frac{T_z}{1 + i\Delta \omega T_z} = \text{Re}(\cdots) + \text{Im}(\cdots) = \rho_{11}^{\pm}(\omega) \frac{T_z}{1 + \Delta \omega^2 T_z^2} \quad (2-41) \]

Here we take the real parts only.

Back to the figure 2.3 (b), in order to ‘count’ the variance, we need to take the square of \( \Delta \omega \) (the amplitude). We can plot the \( <\Delta \omega(0)^2> \) term and it can be described as an exponential function as shown in the figure 2.4:

![Figure 2.4](image-url)

\( <\Delta \omega(0)^2> \) can be described as a memory function.

It is possible to replace \( ds \) with \( d\tau \) from equation 2-32:

\[ R_z = \int_0^{\infty} \langle \Delta \omega(t) \Delta \omega(t+\tau) \rangle e^{-t/\tau_c} d\tau = <\Delta \omega(0)^2> \tau_c \quad (2-42) \]

The exponential function is called ‘memory function’. By variable substitution we got \( \tau_c = t-s \), and with the definition of \( R_z \) we could see the reason for name it as ‘memory’. However here it is the condition for spin-1/2 and for spin-1 (or the others) may need several memory functions. Hence we are dealing with water so the other condition will not be discussed here.

Obviously, from equation 2-39, we found \( R_z \) is only related to the variance term \( <\Delta \omega(0)^2> \) and the correlation time \( \tau_c \).
2.3 Dipolar interactions for spin like system

It is not difficult to see from the previous discussion that the essential part of nuclear magnetic relaxation is the interaction of nuclear spins, either inter- or intra-molecular.

The mutual potential energy of two magnets is given by [2.1] (equation 4.17)

\[ \Phi = \hbar G(t) = -\left(\frac{6}{5} \pi \right)^2 \gamma_1 \gamma_2 h^2 \sum_{q=2}^2 (-)^q r(t)^3 Y_q^2(\theta(t), \phi(t)) A_{q,q} \]  

(2.40)

The \( hG(t) \) is perturbing Hamiltonian. \( r(t)^3 Y_q^2(\theta(t), \phi(t)) \) is the random motion where \( r \) and angle \( \theta \) and \( \phi \) are all time-depend functions. \( A_{q,q} \) is called spin dependent operator. By cancelled the Planck constant for both sides it is easily to see that

\[ G(t) = -\left(\frac{6}{5} \pi \right)^2 \gamma_1 \gamma_2 h^2 \sum_{q=2}^2 (-)^q r(t)^3 Y_q^2(\theta(t), \phi(t)) A_{q,q} = \sum_{q=2}^2 (-)^q \hbar T_{q,q}(t) \eta_{q,q} \]  

(2.41)

Then we found that the interaction Hamiltonian is a component of a spherical tensor of rank 2, the first part contains only constant numbers is called the strength constant.

\[ H_q(t) = -(\frac{6}{5} \pi)^2 \gamma_1 \gamma_2 h^2 \sum_{q=2}^2 (-)^q r(t)^3 Y_q^2(\theta(t), \phi(t)) = -(\frac{6}{5} \pi)^2 \gamma_1 \gamma_2 h^2 r(t)^3 Y_q^2(\theta(t), \phi(t)) \]  

(2.42)

The spectral density is given by [2.1] (equation 2.43)

\[ j_n(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} \langle H_q(0) H_q(\tau) \rangle e^{i\omega \tau} d\tau; (n = q) \]  

(2.43)

We can rewrite it with the interaction Hamiltonian presented before by simply put it into the equation, it is looks like:

\[ j_n(\omega) = j(\omega) = \frac{1}{2} \left[-\left(\frac{6}{5} \pi \right)^2 \gamma_1 \gamma_2 \hbar \right] \int_{-\infty}^{\infty} \langle r(0)^3 Y_q^2(\theta(0), \phi(0)) r(t)^3 Y_q^2(\theta(t), \phi(t)) \rangle e^{-i\omega t} dt \]  

(2.44)

How does the term \( j_n(\omega) \) becomes \( j(\omega) \)? According to the symmetry theory that by the isotropic reorientation condition all the correlation functions are equally, then \( j_n(\omega) \) becomes \( j(\omega) \). Also, as \( -q \) (in equation 2.42) have values as \(+/2,+/-1\) and 0, normally we write a zero.
The ensemble average for correlation function is shown as \[ \langle A'(0)B(t) \rangle = \int A'(0)B(t)p[S(0),0,S(t),t]ds(0)ds(t) \] (2.45)

where \( P \) is the joint probability, and \( S \) variable from \( S(0) \) at time 0 to \( S(t) \) at time \( t \). Also the \( P \) terms is defined as

\[ p[S(0),0,S(t),t] = p[S(0),0]w[S(0),0,S(t),t] \] (2.46)

Therefore the ensemble average can be expressed as

\[ \langle A'(0)B(t) \rangle = \int p[S(0),0]A'(0)ds(0)w[S(0),0,S(t),t]B(t)ds(t) \] (2.47)

Now consider equation (2.44) again, we can use the way discussed before to expand it as

\[ \langle r(0)^{-3}Y_0^3(\theta(0),\phi(0))r(t)^{-3}Y_0^3(\theta(t),\phi(t)) \rangle \]

\[ = \int p[r(0),0]r(0)^{-3}Y_0^3(\theta(0),\phi(0))dr^2(0) \int w[r(0),0;r(t),t]r(t)^{-3}Y_0^3(\theta(t),\phi(t))dr^2(t) \]

\[ = \int \int p[r(0),0]w[r(0),0,r(t),t]r(0)^{-3}Y_0^3(\theta(0),\phi(0))r(t)^{-3}Y_0^3(\theta(t),\phi(t))dr^2(0)dr^2(t) \] (2.48)

Consider it is formed by a rigid bond, then the distance between is just equals to \( r \).

\[ r(0)^{-2} = r(t)^{-2} = r^{-2} \] (2.49)

Summarize a little bit of what has been presented so far, we will have

\[ j(\omega) = \frac{1}{2} \left[ \frac{6}{5} \pi \frac{1}{r} \gamma \frac{\gamma}{2} \frac{1}{h} \right] \int_{-\infty}^{+\infty} r(0)^{-3}Y_0^3(\theta(0),\phi(0))r(t)^{-3}Y_0^3(\theta(t),\phi(t)) >e^{-\omega}dt \]

\[ = \frac{1}{2} \left[ \frac{6}{5} \pi \frac{1}{r} \gamma \frac{\gamma}{2} \frac{1}{h} \right] \int_{-\infty}^{+\infty} e^{-\omega}dt \int p[r(0),0]w[r(0),0,r(t),t]r(0)^{-3}Y_0^3(\theta(0),\phi(0))r(t)^{-3}Y_0^3(\theta(t),\phi(t))dr^2(0)dr^2(t) \]

\[ = \frac{3}{5} \pi \gamma \frac{\gamma}{2} \frac{1}{h} \int_{-\infty}^{+\infty} e^{-\omega}dt \int p[r(0),0]w[r(0),0,r(t),t]r^2Y_0^3(\theta(0),\phi(0))Y_0^3(\theta(t),\phi(t))dr^2(0)dr^2(t) \] (2.50)

The angel term can be expressed as the following way [2.1] (equation C.31)

\[ \langle Y_{iq}^*(\theta(0),\phi(0))Y_{tq}(\theta(0),\phi(0)) \rangle = \frac{\delta_{qq}}{2l+1} \sum_{n,m}^l Y_{n,m}(\theta',\phi') \langle R^n(t) \rangle_{n,m} Y_{n,m}^*(\theta',\phi') \] (2.51)

By putting numbers in the equation we get

\[ \langle Y_{2q}(\theta(0),\phi(0))Y_0^3(\theta(t),\phi(t)) \rangle = \frac{1}{5} \sum_{n,m}^q Y_{n,m}(\theta',\phi') \langle R^n(t) \rangle_{n,m} Y_{n,m}^*(\theta',\phi'); (l = 2, q = 0 = q', \delta_{qq} = 1) \] (2.52)
Now we are ready to introduce the equation of spectral density, it can be written as

\[
j(\omega) = \left( \frac{3}{5} \pi \gamma^2 \hbar^2 \right) \left( \frac{1}{r^6} \right) \sum_{m,n} \sum_{\theta, \phi} Y_{2m}^{*}(\theta, \phi) Y_{2n}^{*}(\theta, \phi) \langle R(t) \rangle_{m,n} e^{-i\omega t} dt
\]

\[
= \frac{3\pi \gamma^2 \hbar^2}{25r^6} \sum_{m,n} \sum_{\theta, \phi} Y_{2m}(\theta, \phi)Y_{2n}(\theta, \phi) \langle \hat{R}(t) \rangle_{m,n} e^{-i\omega t} dt
\]

\[
= \left( \frac{3\gamma^2 \hbar^2}{25r^6} \right) \left( \frac{5}{4\pi} \right) \left( \frac{2\tau_{\alpha}}{1 + \omega^2 \tau_{\alpha}^2} \right) \left( \frac{3\gamma^2 \hbar^2}{10r^6} \right) \left( \frac{\tau_{\alpha}}{1 + \omega^2 \tau_{\alpha}^2} \right)
\]

(2-53)

We could see that the spectral density is a combination of constant and only related to the correlation time and frequency.

Now we can try to derive $T_1$ and $T_2$. First let’s consider a self-adjoint operator $\mathbf{O}$, the ensemble average of $\mathbf{O}$ is shown as [2.1] (equation 3.64, with modification) (related to both 2-54 and 2-55)

\[
\langle \hat{O} \rangle = \text{tr} \left( \rho \hat{O} \right) = \sum_{\alpha} \langle \rho \hat{O} \rangle = \sum_{\alpha} \rho_{\alpha \alpha} \hat{O}_{\alpha \alpha}
\]

(2-54)

Also we have

\[
\frac{d}{dt} \langle \hat{O} \rangle = \sum_{\alpha} \frac{d}{dt} \rho(t)_{\alpha \alpha} \hat{O}_{\alpha \alpha}
\]

(2-55)

Use density matrix instead of operator $\mathbf{O}$, we have

\[
\frac{d}{dt} \rho(t)_{\alpha \beta} = -\frac{i}{\hbar} \left[ \rho(t), \hat{H}_0 \right]_{\alpha \beta} + \sum_{\alpha'} P_{\alpha \beta \alpha'} \rho(t)_{\alpha' \beta'}
\]

(2-56)

$P_{\alpha \beta \alpha'}$ is called transition probability. It is easily to see the equation 2-54 can be rewritten as

\[
\frac{d}{dt} \langle \hat{O} \rangle = -\frac{i}{\hbar} \sum_{\alpha} \left[ \rho(t), \hat{H}_0 \right]_{\alpha \alpha} \hat{O}_{\alpha \alpha} + \sum_{\alpha \beta} P_{\alpha \beta \alpha'} \rho(t)_{\alpha' \beta'} \hat{O}_{\alpha \alpha}
\]

(2-57)

Here we can define $\mathbf{O}$ as $I_\alpha$ instead of the expression of $\mathbf{O}$ we could get [2.1] (equation 3.72)

\[
\frac{d}{dt} \langle I_\alpha \rangle = \sum_{\alpha \beta \alpha'} \left\{ j(\omega_\alpha - \omega_\beta) \sum_{q r} A^{(q)}_{\alpha \beta} A^{(q)*}_{\beta \alpha'} + j(\omega_\alpha - \omega_\beta) \sum_{q r} A^{(q)*}_{\beta \alpha} A^{(q)}_{\beta' \alpha'} \right\} \times \rho(t)_{\beta' \beta} \langle I_\alpha \rangle -
\]

\[- \frac{\delta_{\alpha \beta}}{2} \sum_{\nu} \left[ j(\omega_\nu - \omega_\beta) \sum_{q r} A^{(q)}_{\alpha \beta} A^{(q)*}_{\beta \nu} + \delta_{\alpha \beta} - \delta_{\alpha \beta} \sum_{q r} j(\omega_\nu - \omega_\beta) \sum_{q r} A^{(q)*}_{\beta \nu} A^{(q)}_{\beta} \right] \times \rho(t)_{\beta' \beta} \langle I_\alpha \rangle \]

(2-58)

Thus it is looks like a very completed equation, the relaxation equations are shown in a reduced way [2.1] (equation 4.46, 4.47, with modification):
\[
\frac{d}{dt} \langle I_x + S_x \rangle = -I(I+1) \left[ \frac{4}{3} f(\omega_0) + \frac{16}{3} f(2\omega_0) \right] \langle I_x + S_x \rangle = -\frac{4}{3} I(I+1) \left[ f(\omega_0) + 4 f(2\omega_0) \right] \langle I_x + S_x \rangle \quad (2-59)
\]

\[
\frac{d}{dt} \langle I_z + S_z \rangle = -I(I+1) \left[ 2 f(0) + \frac{10}{3} f(\omega_0) + \frac{4}{3} f(2\omega_0) \right] \langle I_z + S_z \rangle \quad (2-60)
\]

The equations presented above give the description of relaxation process, when this ‘spin like’ system (simply two protons) only influenced by the perturbing Hamiltonian---as shown before it is \( hG(t) \). Replace \( I_x + S_x \) as \( \langle I_x + S_x \rangle - \langle I_x + S_x \rangle_0 \) [2,1], then we will have

\[
\frac{d}{dt} \langle I_x + S_x \rangle = -\frac{1}{T_1} \left( \langle I_x + S_x \rangle - \langle I_x + S_x \rangle_0 \right), \quad \frac{d}{dt} \langle I_z + S_z \rangle = -\frac{1}{T_2} \left( \langle I_z + S_z \rangle - \langle I_z + S_z \rangle_0 \right) \quad (2-61) & (2-62)
\]

Where the relaxation rate ‘R’ is shown in the following way, the unit is \( \text{s}^{-1} \). (In result it is written as \( R_1 \text{s}^{-1} \).)

\[
R_1 = \frac{1}{T_1} = -\frac{4}{3} I(I+1) \left[ f(\omega_0) + 4 f(2\omega_0) \right] \quad (2-63)
\]

\[
R_2 = \frac{1}{T_2} = I(I+1) \left[ 2 f(0) + \frac{10}{3} f(\omega_0) + \frac{4}{3} f(2\omega_0) \right] \quad (2-64)
\]

We can define a new term \( \tilde{j}(\omega_0) \) related to the spectral density,

\[
\tilde{j}(\omega_0) = \frac{\tau_\omega}{1 + \tau_\omega \omega^2} \quad (2-65)
\]

Rewrite \( R_1 \) and \( R_2 \) with new defined term \( \tilde{j}(\omega_0) \),

\[
R_1 = \left( \frac{3}{10} \right) \left( \frac{\gamma_x^2 \gamma_z^2 \hbar^2}{r^2} \right) \frac{4}{3} I(I+1) \left[ \tilde{j}(\omega_0) + 4 \tilde{j}(2\omega_0) \right] = \left( \frac{2 \gamma_x^2 \gamma_z^2 \hbar^2}{5 r^2} \right) I(I+1) \left[ \tilde{j}(\omega_0) + 4 \tilde{j}(2\omega_0) \right] \quad (2-66) & (2-67)
\]

Hence we are working with spin \( \frac{1}{2} \) therefore it is convenient to put constant numbers into the equation. In order to use SI system we should introduce the magnetic field constant \( \mu_0 \). (Here N is Newton, A is Ampere, H stands for Henry and m is simply meter.) Also we should account normalization of the equation for spectral density \( (2-53) \):

\[
I = \frac{1}{2}, \quad I(I+1) = \frac{3}{4}, \quad \gamma_x = \gamma_z = \gamma, \quad \mu_0 = 4\pi \times 10^{-7} \text{N} / \text{A}^2 = 4\pi \times 10^{-7} \text{H} / \text{m};
\]

\[
\sum_{n,m=-2}^{2} Y_{n,m}(\theta', \phi') Y_{n,m}^*(\theta, \phi') = \frac{1}{4\pi};
\]

Finally we summarize all and get
Form the equations present above it is obviously to see that the relaxation rate is depends on some constant numbers (such as gyromagnetic ratio $\gamma$, distance $r$ and Planck constant $\hbar$), and the rewritten spectral density. On the other way to say, the relaxation rate is depends on correlation time $\tau_c$. 

\[
R_1 = \frac{3\pi}{25r^6} \gamma^2 \hbar^2 \left\{ \frac{\gamma}{j(\omega_b)} + 4 \frac{\gamma}{j(2\omega_b)} \right\} = \frac{3}{160} \frac{\mu_e}{\pi^2 r^6} \gamma^2 \hbar^2 \left\{ \frac{\gamma}{j(\omega_b)} + 4 \frac{\gamma}{j(2\omega_b)} \right\} 
\]

\[
R_2 = \frac{3\pi}{25r^6} \gamma^2 \hbar^2 \left\{ \frac{3}{2} \frac{\gamma}{j(0)} + \frac{5}{2} \frac{\gamma}{j(\omega_b)} + \frac{5}{2} \frac{\gamma}{j(2\omega_b)} \right\} = \frac{3}{160} \frac{\mu_e}{\pi^2 r^6} \gamma^2 \hbar^2 \left\{ \frac{3}{2} \frac{\gamma}{j(0)} + \frac{5}{2} \frac{\gamma}{j(\omega_b)} + \frac{5}{2} \frac{\gamma}{j(2\omega_b)} \right\} 
\]
3. Experiments

3.1 Chemical agent:

\[
\begin{array}{c}
\text{H}_2\text{O} \\
\text{H}_2\text{O} \quad \text{Cl} \quad \text{Gd} \quad \text{Cl} \quad \text{H}_2\text{O} \\
\text{H}_2\text{O} \quad \text{Cl} \quad \text{H}_2\text{O} \\
\text{H}_2\text{O}
\end{array}
\]

*Figure 3.1* The structure of \( \text{GdCl}_3 \cdot 6\text{H}_2\text{O} \). [3.1]

1) Gadolinium (III) chloride hexahydrate (\( \text{GdCl}_3 \cdot 6\text{H}_2\text{O} \)), from Sigma-Aldrich Company. [3.2]

2) Pure water, from Millipore water purification system of the department.

3) Calcium chloride dehydrate (\( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \)), from Sigma-Aldrich Company. Donate from Dr. Guangye Han’s lab.

**Sample preparation:**

For gadolinium (III) chloride hexahydrate, a stock solution of 40mM has been prepared. Samples are dilution made of the stock solution. The same for calcium chloride dehydrate.

There are five samples have been used in the NMR experiments:

Sample1: pure water, 2ml.

Sample2: pure water + \( \text{GdCl}_3 \cdot 6\text{H}_2\text{O} \) (0.1mM), 2ml.

Sample3: pure water + \( \text{GdCl}_3 \cdot 6\text{H}_2\text{O} \) (0.2mM), 2ml.

Sample4: pure water + \( \text{GdCl}_3 \cdot 6\text{H}_2\text{O} \) (0.4mM), 2ml.

Sample5: pure water + \( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \) (0.4mM), 2ml.

3.2 Instrument:

The fast field cycling NMR relaxometer: ‘SPINMASTER FFC2000 1T C/DC’, from STELAR (STELAR s.r.l. via Enrico Fermi, 427035 Mede (PV) - ITALY). ([www.stelar.it](http://www.stelar.it))

Max field \( B_0 \) is 1 Telsa +/- 5%. More details can be found at the webpage or see Appendix B, a commercial of the instrument from the STELAR Company*. EPR X-band (9.5GHz) experiments were performed by using Bruker 300 E spectrometer. A sample with 130mM concentration has been use.

*Appendix B is from STELAR Company, this commercial is only for the convenient of reader who is not possible to visit the file online while reading this thesis.*
4. Result and discussion

The experiments were carried out by using ‘Spinmaster FFC2000 1T C/DC’ (The fast field cycling NMR relaxometer) from Stelar Company, Italy. Ethanol is used for cooling system.

Limit of instrument: The switching time (the time between BPOL (polarisation field) and BRLX (polarisation field)) is only 0.003s; due to the limitation it is not possible to collect date at very low relaxation field.

Experiments for each sample at different temperatures have been performed. Each test tube contains 2ml sample. A smaller volume as 0.8ml has also been tested, and there is no sufficiently difference with the bigger volume one.

For liquid samples experiments were taken at 283.15K (10°C) and 293.15K (20°C); solid state experiments were taken at 269.15K (-4°C), 265.15K (-8°C) and 261.15K (-12°C). This chapter will start from pure water samples, and then with paramagnetic source. The third part will discuss the comparison of them. EPR lineshapes will be shown finally.

* When presented as ‘experimental’ for figures, means no modification. It is directly plot of original data from experiments.

4.1 Pure water sample (in ice form) at three different temperatures

4.11 Experimental proton H-T1 NMRD profiles

*Figure 4.1 Experimental proton H-T\textsubscript{1} NMRD profiles of the same water sample (ice) at three different temperatures.*
First we will start with pure water sample. Figure 4.1 shows the logarithm plot of relaxation field against the correlation rate. Here the temperature unit is in Kelvin (K). (°C = [K] - 273.15)

From the figure it is clear to see that at higher temperature the sample gives a higher relaxation rate at lower field.

By theory part relaxation equations are derived and found that the correlation rate is depends on spectral density (or let’s say the correlation time $\tau_c$). A FORTRAN program is used to calculate the theoretical value and plot it in the same figure with experimental data.

### 4.12 Theoretical line fitting

Several theoretical line fitting have been performed by changing the correlation time in the program. Figure 4.2 shows the best simulation result.

![Theoretical line fitting](image)

**Figure 4.2** Experimental proton H-NMRD profiles of water sample (ice) at three different temperatures compare with theoretical line fitting. Small figure on the right side is a partial the original.

The theoretical correlation time of experiment at 269.15K (-4°C) is 2.6 μs (microsecond), for experiment at 265.15K (-8°C) is 3.7 μs and for experiment at 261.15K (-12°C) is 5.0 μs.
Some articles [4.1] may present different values (shorter or longer); this is due to how ice sample has been made. In this thesis first leave the sample in ice bath for several hours until one could see ice in the surface. Then place the sample at -35°C liquid ethanol for approximately 20 to 30 seconds until it is totally frozen. Notice that in the second step it is important to keep the sample in a stable condition (that means do not remove it from the cooling system). With this way it is possible to get better formation of ice (with no air bubble and looks like crystal). Sun’s group [4.2] has presented a more scientific way on ice formation, and discussed the effects of dipole polarization on format ice under processing electrostatic field.

It is clearly to see that the simulation is successful. However it does not fit exactly at very low field, this might comes from the limit of instrument as mentioned in the beginning of this chapter.

So the theoretical model for water relaxation looks like very ‘convenient’. It is possible to fit the experiment data via only change several parameters. Here the theoretical line shapes are changing by set up \( \tau_c \) and one will see the difference immediately. On the other way, it might say that it is also a ‘sensitive’ model.

### 4.13 Calculation of the activation energy

From a theoretical proton H-NMRD profile (figure 4.3a), on the left side of the figure is called ‘extreme narrowing limit’, where \( \omega \tau_c \) is much smaller than 1. The right side is ‘dispersion limit’ where \( \omega \tau_c \) is much larger than 1. On this plot there will be one point which has relationship between correlation time \( \tau_c \) and the relaxation field is just equal to 1.

![Diagram](image)

**Figure 4.3(a)** shows proton H-NMRD profile from extreme narrowing limit to dispersion limit by the theoretical model.
Therefore the spectral density (also the correlation rate) can be rewritten as:

\[ j(\omega_0) = \frac{\tau_c}{\tau_c^2 \omega^2} \Rightarrow R_1 = (\text{cons.}) \left( \frac{\tau_c}{\tau_c^2 \omega^2} + \frac{4\tau_c}{4\tau_c^2 \omega^2} \right) = 2(\text{cons.}) \frac{1}{\tau_c \omega^2} \]  

(4-1)

where ‘cons.’ stands for some constants.

So if we choose a certain relaxation field, the difference values between two profiles can be expressed as a constant (called ‘strength constant’) and the temperature-depend correlation time \( \tau_c(T) \). (Figure 4.3b)

![Figure 4.3(b)](insert figure)

**Figure 4.3(b)** The deep green line shows at a certain relaxation field the difference between two values (theoretical and experimental) of different NMRD profiles is equal to some constant and \( 1/\omega^2 \tau_c \).

From Arrhenius equation:

\[ k = A e^{-E_a/RT} \]  

(4-1)

Here \( k \) is the rate constant, therefore the temperature-depend correlation time \( \tau_c(T) \) should be expressed in the form of:

\[ \frac{1}{\tau_c(T)} = \frac{1}{\tau_c(0)} e^{-E_a/RT} \]  

(4-2)

\( T \) is temperature in Kelvin (K), \( E_a \) is the activation energy equation and \( R \) is ideal gas constant \( = 8.314 \times 10^{-3} \text{ kJ/mol K} \).
With the equation it is possible to calculate $E_a$ by using equation 4-3:

$$\ln \frac{\tau_c(T)}{\tau_c(0)} = \frac{E_a}{RT} \quad (4-3)$$

![Graph](image)

**Figure 4.3(c)** Use the given correlation times (2.6 μs, 3.7 μs and 5.0μs) for calculation of activation energy.

By previously simulation we got the correlation time $\tau_c$ equals to 2.6 μs, 3.7 μs and 5.0μs. The plot of given $\tau_c$ is shown in figure 4.3(c). A linear fitting of the plot has been performed with the software. Calculated activation energy $E_a$ is 47.74 kJ /mol. Garn’s group [4.3] invented the activation energy for pure ice is 59.8kJ/mol (they using much lower temperature) and this value depend on the structure of ice. For example, doped ice will have less value compare to pure ice.

It is found that the reorientation correlation time is increase while decrease the temperature. The Arrhenius activation energy for hydrogen bond (H$_2$O) is 21.5 kJ /mol [4.4] and compare to the result it is approximately equal to two hydrogen bonds.
4.2 Samples with paramagnetic source

In order to study the enhancement of paramagnetic source for proton spin-lattice relaxation, first experiments are performed at normal room temperature. Samples with different concentration at two different temperatures have been tested.

4.21 Experiments at room temperature

![Figure 4.4(a)](image1.png) Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water (in different concentration) samples at 283.15K (10 °C). Samples follow concentration of 0.1mM, 0.2mM and 0.4mM GdCl$_3$ in water solution.

![Figure 4.4(b)](image2.png) Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water (in different concentration) samples at 293.15K (20 °C).
It is obviously to see that the sample with paramagnetic source give enhanced proton relaxation rate, especially for the sample with higher concentration. From figure 4.4, we could see that pure water at room temperature gives no noticeable dispersion. We can subtract the water background and only look at the paramagnetic source. (figure 4.5 a,b)

**Figure 4.5(a)** Experimental H-T\textsubscript{1} NMRD profiles from figure 4.4a which subtracted water background at 283.15K (10 °C).

**Figure 4.5(b)** Experimental H-T\textsubscript{1} NMRD profiles from figure 4.4b which subtracted water background at 293.15K (20 °C).
One might notice that for 0.4mM concentration sample (in light green colour), at the high field (right side of the figure) the beginning point is raised. This has been seen from other research group with different samples which using the same instrument. It might come from the relaxometer itself.

In order to find out the limit of using paramagnetic source one experiment with much lower sample (0.01mM) has been tested (figure 4.6). The relaxation rate values are very low therefore in order to see the enhancement one should use sample with concentration higher than 0.01mM. In our case, as the result we presented for Gadolinium (III) chloride hexahydrate 0.1mM is enough to show the effect and 0.2mM to 0.4mM would be a recommended range.

![Figure 4.6](image)

**Figure 4.6** Experimental H-T\textsubscript{1} NMRD profiles of water sample and GdCl\textsubscript{3} + water (0.01mM) samples at 288.15K (15 °C).

The information we get from the previous figures gives the description of molecule dynamics. Kimmich’s group [4.6] has presented that compare to intra-couplings the inter-molecular interaction is much slower therefore mostly the information we get is about the dynamics of intra-molecular range. The inter-molecular fluctuating happens within a molecule, but intra-molecular needs to contact with the orientation (that means the neighbour molecules).

We can then rewrite T\textsubscript{1} as the sum of resulting from both intra- and inter- molecular couplings: [4.6] (4-3)

\[
\frac{1}{T_1} = \frac{1}{T_{1\text{intra}}} + \frac{1}{T_{1\text{inter}}} \quad (4-3)
\]

Hence the molecular dynamics is anisotropic, 1/T\textsubscript{1} (inter-) will be smaller than 1/T\textsubscript{1} (intra-) term. But for ice it will be different.
4.22 Profiles of subtracted water background and normalized concentration

At this part presents the result of enhanced proton spin relaxation rate which subtracted the water background and also with normalized concentration.

**Figure 4.7(a)** Experimental H-T$_1$ NMRD profiles of GdCl$_3$ + water (normalized concentration) samples subtract the water background at 283.15K (10 °C).

**Figure 4.7(b)** Experimental H-T$_1$ NMRD profiles of GdCl$_3$ + water (normalized concentration) samples subtract the water background at 293.15K (20 °C).
The relationship of relaxation rate values between different concentrations is not linear, but follows some numbers (shown on figures).

For example, on figure 4.7(a) means use R₁ values of sample 1 (s₁) multiply by 6.40464 and use R₁ values of sample 2 (s₂) multiply by 2.64676. The relaxation rate of highest concentration sample is kept. Plot the calculated values will get profiles shown in figure 4.7a and b. It is not from the mistaken concentration hence several experiments with different samples have been performed.

4.3 Comparison of pure water and samples with paramagnetic source in ice form

Within this part, it will show the comparison of pure water and samples with Gd (III) ions. They both in ice form for three different temperatures. As in pure water, theoretical line fitting has been performed for each profile. Discussion will be given with experimental results. The sample with CaCl₂•2H₂O will also be discussed.

4.31 Experimental Result at three different temperatures

![Graph showing relaxation rate values for different concentrations](image)

**Figure 4.8(a)** Experimental H-T₁ NMRD profiles of water sample and GdCl₃ + water sample (both in ice form) at the same temperature 269.15K (-4°C). CaCl₂ + water sample at 0.4mM is also included. Small figures shows separately plot between water and GdCl₃ + water sample.
Figure 4.8(b) Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water sample (both in ice form) at the same temperature 265.15K (-8°C). CaCl$_3$ + water sample at 0.4mM is also included.

Figure 4.7(c) Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water sample (both in ice form) at the same temperature 261.15K (-12°C). CaCl$_3$ + water sample at 0.4mM is also included.
Figure 4.7a-4.7c show results from experiments. From those figures we could see that GdCl$_3$ + water sample has higher relaxation rate at a certain field compare to pure water sample, although the difference isn’t very much.

Why it is like this? In ice form water molecules couldn’t be as much active as in room temperature. They have been formed into hexagonal structure (as shown in figure 1.4) therefore the molecular interaction has been reduced. Also the water molecules near by the paramagnetic source cannot ‘transfer’ the relaxation effect to the other neighbours though interaction or random motion as in liquid, and remember that the measurement is the average of all population. So there is no large difference between different profiles.

The effect of paramagnetic spin relaxation is also reduced, so relaxation enhancement isn’t very obliviously.

A sample with CaCl$_2$•2H$_2$O (concentration = 0.4mM) has been tested in order to take a further view. This compound isn’t one of paramagnetic sources, and at room temperature the profile is almost the same as pure water sample (see Appendix D). But in ice form it behaves similar to paramagnetic source. The reason can be: hence the beautiful hexagonal structure of pure water is ‘disturb’ by paramagnetic/similar size molecules. Compare to water molecule Gadolinium, Calcium and chloride have larger size, and this also gives difference to correlation rate. So the difference between two NMRD profiles isn’t all comes from paramagnetic sources (their effects are really limited), but mainly because of the disturbed hexagonal structure of ice.

### 4.3.2 Theoretical line fitting

The theoretical line fitting also been performed for samples with paramagnetic sources in ice form. The simulation profiles look like very similar to figure 4.2. Instead of that, here gives a table and a figure of correlation time against concentration.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Conc.(mM)</th>
<th>$\nu_c$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>269.15K</td>
<td>0</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>2.15</td>
</tr>
<tr>
<td>265.15K</td>
<td>0</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>261.15K</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>3.7</td>
</tr>
</tbody>
</table>

**Table 4.1** Correlation time (in micro second) from the theoretical simulation for four samples (include pure water, concentration as 0) at three different temperature.
Figure 4.7(d) Plot of correlation time against concentration for samples with paramagnetic source and pure water (concentration as 0), both in ice form.

On the table above shows the values of figure 4.7(d). It is obviously to see that the sample with paramagnetic source has shorter correlation time. Generally the higher concentration of adding paramagnetic source, the shorter correlation time it will be. However for high concentration sample at very low temperature, such as 0.4mM sample at 261.15K (-12°C), the enhancement is decreased.

Simulation for sample with CaCl$_2$ is also performed. Result presented in table 4.2. Compare to sample with Gd+ at the same concentration and pure water sample, it is found that the correlation time is similar to the one with paramagnetic source. From this point, the shortening of correlation time mostly comes from the broken structure of hexagonal ice.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Conc.(mM)</th>
<th>Tc (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>269.15K</td>
<td>0.4</td>
<td>2.3</td>
</tr>
<tr>
<td>265.15K</td>
<td>0.4</td>
<td>2.0</td>
</tr>
<tr>
<td>261.15K</td>
<td>0.4</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 4.2 Correlation time (in micro second) from the theoretical simulation for sample with CaCl$_2$•2H$_2$O at three different temperatures
4.33 Linear fitting of ln-ln plot and discussion

Figure 4.8(a) ln(\text{relaxation field})-ln(R_1) plot of Experimental H-T1 NMRD profiles of water sample and GdCl_3 + water sample (both in ice form) at the same temperature 269.15K (-4°C). CaCl_3 + water sample at 0.4mM is also included.

Figure 4.8(b) ln(\text{relaxation field})-ln(R_1) plot of Experimental H-T1 NMRD profiles of water sample and GdCl_3 + water sample (both in ice form) at the same temperature 265.15K (-8°C). CaCl_3 + water sample at 0.4mM is also included.
Figure 4.8(c) ln(relaxation field)-ln($R_1$) plot of Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water sample (both in ice form) at the same temperature 261.15K (-12°C). CaCl$_3$ + water sample at 0.4mM is also included.

Three figures above shows ln-ln plot of NMRD profiles. Except several points, they all look like linear in general. The ln-ln plot for sample with paramagnetic source is always above the water. Linear fitting for each line has been done with the linear function of ‘Origin’ software. The slope is calculated and shown in table 4.3.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Name</th>
<th>Degree</th>
<th>Error</th>
<th>Temp.</th>
<th>Name</th>
<th>Degree</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>269.15K</td>
<td>PURE</td>
<td>-1.08518</td>
<td>0.00791</td>
<td>265.15K</td>
<td>PURE</td>
<td>-1.99382</td>
<td>0.01764</td>
</tr>
<tr>
<td></td>
<td>G1</td>
<td>-2.01917</td>
<td>0.00832</td>
<td></td>
<td>G1</td>
<td>-2.00464</td>
<td>0.01061</td>
</tr>
<tr>
<td></td>
<td>G2</td>
<td>-1.97345</td>
<td>0.01611</td>
<td></td>
<td>G2</td>
<td>-2.00023</td>
<td>0.00971</td>
</tr>
<tr>
<td></td>
<td>G4</td>
<td>-1.994</td>
<td>0.01176</td>
<td></td>
<td>G4</td>
<td>-2.01917</td>
<td>0.0167</td>
</tr>
<tr>
<td></td>
<td>CaG4</td>
<td>-2.00787</td>
<td>0.03785</td>
<td></td>
<td>CaG4</td>
<td>-2.01492</td>
<td>0.00641</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>-1.98510</td>
<td>0.00791</td>
<td></td>
<td>Average</td>
<td>-1.99382</td>
<td>0.01764</td>
</tr>
<tr>
<td>261.15K</td>
<td>PURE</td>
<td>-2.0362</td>
<td>0.01161</td>
<td></td>
<td>G1</td>
<td>-1.95809</td>
<td>0.03107</td>
</tr>
<tr>
<td></td>
<td>G2</td>
<td>-1.93113</td>
<td>0.03572</td>
<td></td>
<td>G2</td>
<td>-1.99859</td>
<td>0.1167</td>
</tr>
<tr>
<td></td>
<td>G4</td>
<td>-2.01917</td>
<td>0.0167</td>
<td></td>
<td>G4</td>
<td>-2.00229</td>
<td>0.02098</td>
</tr>
<tr>
<td></td>
<td>Ca4</td>
<td>-2.00229</td>
<td>0.02098</td>
<td></td>
<td>Ca4</td>
<td>-2.0362</td>
<td>0.01161</td>
</tr>
</tbody>
</table>

‘Temp.’ stands for temperature, and it is in Kelvin (K).

Table 4.3 Slope of linear fitting for each ln(relaxation field)-ln($R_1$) plot from figure 4.8a,b,c.

PURE = pure water
G1 = Gd-aqua 0.1mM
G2 = Gd-aqua 0.2mM
G4 = Gd-aqua 0.4mM
CaG4 = Ca$_2$Cl$_3$+H$_2$O 0.4mM

Average

Table 4.3 Slope of linear fitting for each ln(relaxation field)-ln($R_1$) plot from figure 4.8a,b,c.

‘Temp.’ stands for temperature, and it is in Kelvin (K).
From above table the average value of slope is -1.99859. This value can be named as ‘degree of dispersion’. It has no remarkable relationship with temperature, and no matter the sample with or without adding paramagnetic source. This value is mostly very similar to the average value therefore it can be used as a parameter of NMRD.

4.4 EPR lineshapes

4.41 Experimental Result

EPR experiments are also performed for samples with paramagnetic source, in room temperature (293.15K) and in ice form. However it is difficult to perform it in low temperature hence ice sample in a capillary tube melting very fast. With the limit of the instrument no good result has been collected. But it is found that for mixture of ice and water, in the same setup condition of instruments the intensity is reduced compare to at room temperature. Therefore this part will focus on EPR lineshapes at 293.15K.

![Figure 4.9 EPR lineshapes in three different experimental conditions for sample of 130mM Gd-aqua complex at 293.15K (20 °C).](image)
Figure 4.9 shows EPR lineshapes for a sample of Gd-aqua at 130mM concentration. Different microwave power has been used and it is found that the highest microwave power gives the strongest intensity.

In the figure, all lineshapes look like in nice Lorentzian. Integration for each experimental lineshape has been calculated (figure 4.4 shows the relationship between integration and original experimental data), and the linewidth is shown in the table 4.4.

![Integration of EPR lineshape](image)

**Figure 4.10** Integration of EPR lineshape. Theoretically the linewidth at half height of the integration ($L_1$) is equal to the linewidth in measurement ($L_2$) multiply $\sqrt{3}$.

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>$L_1$ From Int.</th>
<th>$L_2$ From Exp.</th>
<th>$L_1/\sqrt{3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5mW, 5G at 100KHz, 4000G</td>
<td>840</td>
<td>520</td>
<td>485.54913</td>
</tr>
<tr>
<td>5mW, 27G at 100KHz, 4000G</td>
<td>836</td>
<td>496</td>
<td>483.23699</td>
</tr>
<tr>
<td>20mW, 27G at 100KHz, 4000G</td>
<td>785</td>
<td>473</td>
<td>453.75723</td>
</tr>
</tbody>
</table>

**Table 4.4** Values of linewidth for each experimental lineshape in the unit of Gauss. Column $G$ is the values from calculation.

From the table one can see that there is no big difference between the linewidth ($L_2$) from experiment and the calculated value.
4.42 Theoretical line fitting and discussion

Figure 4.11 Theoretical line fitting of experimental lineshape from simulation program.

There are four parameters (in two groups) in the program to be determined, transient ZFS (1/cm, \(\Delta t\)), static ZFS (1/cm, \(\Delta s\)), molecular complex tumbling reorientation time (ps, \(\tau_r\)) and fast reorientation time (ps, \(\tau_f\)). Parameter \(\Delta t\) and \(\Delta s\) are called interaction strength, and \(\tau_r\) with \(\tau_f\) give the correlation time. Here it is assumed that \(\Delta t=\Delta s\) and \(\tau_r=\tau_f\) for a simply model. Theoretical line fitting is performed by changing those parameters. \[4.8\]

Results from different simulation is shown in figure 4.12(a and b).

Figure 4.12(a) Theoretical EPR lineshapes by changing correlation time. The interaction strength \(\Delta t=\Delta s= 0.021(1/cm)\).
The dipole-dipole correlation time $\tau_{c}^{DD}$ is defined as:

$$\tau_{c}^{DD} = \text{Re}(0.1S_{1}^{DD} + 0.3S_{0}^{DD} + 0.6S_{-1}^{DD})$$  \[4.7\]

where $S_{\sigma}^{DD}$ is spectral density function, $\sigma$ can be -1, 0 and 1.

And therefore the paramagnetically enhanced proton spin-lattice relaxation rate $R_{1M}$ will be:

$$R_{1M} = \frac{1}{T_{1M}} = \frac{4}{3} \left( \frac{\mu_0}{4\pi} \right)^2 \hbar \gamma'_{p} \gamma'_{s} \frac{S(S+1)}{\gamma_{p}^2} \tau_{c}^{DD}$$  \[4.7\]

In the equation, one could see that $R_{1M}$ is depends on the term on dipole-dipole correlation time $\tau_{c}^{DD}$ hence the others are constant. In the equation of $\tau_{c}^{DD}$, if it is for pure water model the term $S_{\sigma}^{DD}$ is the Fourier-Laplace transform of the reorientation correlation function at the nuclear Larmor frequency. But for model with paramagnetic source in additional the electron spin correlation function will also be considered. This is how EPR and NMR complementary together.
5. Conclusion

In this thesis we have derive relaxation equations by using relevant theory, and perform experiments as well. Paramagnetic source has been used during experiments in order to take a further study of water relaxation. We have shown the relationship from observable terms to microscopic world. By measure the correlation rate (or $T_1$) we will get information about dynamics of water molecules.

It is obviously to see that at normal room temperature the sample with and without paramagnetic source have big difference. Within liquid water the water molecules around the paramagnetic source will be affected and it will pass to the other water molecules by interaction. So in total ‘the whole environment’ is enhanced, therefore gives shorter correlation time compare to pure water sample. On the other hand, has higher value of correlation rate as we measured.

By concentration, we found that when add 0.1mM Gadolinium (III) chloride hexahydrate ($\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$) is enough to see the enhancement.

From equation 4-1, as we assume that at constant part intra-molecule fluctuation as crucial part (inter-molecule contribution may takes very small count), we will get correlation time in the range of 2 to 6 $\mu$s. And in our experiments we theoretical use 2.5$\mu$s and 4.0$\mu$s, the plot line shapes from theoretical to experimental fit very well.

Compare to ‘paramagnetic’ ice and ‘pure’ ice, they have different structures. In pure it looks like beautiful hexagonal structure, each water molecule is ‘locked’ in this structure. In paramagnetic ice, the structure has been disturbed. We think that within a small area at the surrounding nearby a Gadolinium molecule (also with chlorine molecules) will be liquid water. Gadolinium molecule has a much larger gyromagnetic ratio than protons. If we consider dipole-dipole interaction in this very small area, the relaxation of those protons near paramagnetic is too fast to measure. Hence the other water molecules (those who has no Gadolinium molecule as neighbour) is locked in their structure, so the effect cannot pass by motion. Therefore in ice the enhancement of paramagnetic source (or the intensity of signal) isn’t very strong as in liquid water.

For conclusion, paramagnetic sources has changed the structure of ice, this will gives different on measure water proton $T_1$- NMRD profile. Although isn’t as obvious as in liquid water sample, as it has shorter correlation time we could say that it gives enhancement of spin relaxation by its property (paramagnetism).

It is interesting to think about intra-and inter molecule dynamic in paramagnetic ice hence it is different with in liquid sample, and this will be considered in the further study.
6. Acknowledgement

First, I would like to thanks Prof. Gerhard Gröbner who introduce me to my supervisor. Also he taught me basic concepts of NMR during courses.

Thanks to Dr. Tobias Sparrman and Dr. Guangye Han who give help for instruments set up and share their experience.

Also give many thanks to Prof. Lawrence Berliner for give advises of EPR.

It is always a great pleasure to have discussion with Oleg Opanasyuk on mathematical topics.

As the study counsellor of chemistry department, Dr. Bertil Eliasson gave me many good advises during my master program study.

And above all, as my supervisor Prof. Per-olof Westlund, who introduce and guide me to a very interesting topic.
7. Reference


[1.6] Li, Jeshan et al. *Study of the g-factor in electron paramagnetic resonance*, College of Sciences, China university of mining and technology (http://www.paper.edu.cn/index.php/default/releasepaper/content/200711-337)


[2.8] A private note from discussion with supervisor by author.
Gadolinium (III) chloride hexahydrate from Sigma-Aldrich company; webpage is: http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=203289|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC

[4.1] Weithase, M et al. Proton spin relaxation in hexagonal ice II: The T$\textsubscript{1\rho}$ Minimum. Z.Physik 246, 91-96 (1971) by Springer-Verlag 1971


[4.6] the same as [4.5]


Appendix A

Quick NMR Experiment Guide for ‘Spinmaster FFC2000 1T C/DC’ (The fast field cycling NMR relaxometer)

*Remember to tune the probe before start an experiment.

<Step 1 > NP

Setting the wanted temperature from the instrument panel and connect it to software (‘VTC’ on the figure), then choose experiment ‘NP’.

First, create a file name. It is very simple, just click on FILE (see picture below). Insert recycle delay and delay tau values, BPOL and BRLX values and run (the pistol button on the top.) Remember to save it, and then press F1 button has been shown with the blue cycle.

<Step 2 > ANGLE.FFC

Now we need to determine 90 degree pulse. Choose experiment ‘ANGLE.FFC’.

Follow the picture to set up parameters, notice that the recycle delay shouldn’t be too short.

Save it after running, then press ctrl+F5, choose WAM. The 90 degree pulse value is shown in micro second.
<Step 3> NP/S

Experiment NP/S. First choose ‘Acq.par, Conf’ setup the 90 degree pulse (in micro second). One can read it directly from the top point. Remember to setup the recycle delay and it should be 5 times as T1.

Follow the procedure of the last picture, after correct T1 with the ‘CORRECT T1MX’ button, if the curse does not looks well one can reset up parameters and run it again.
Create a new file name, and use ‘Synchronize with Acq. Parameters’ If one forget to correct T1MX, the value of ‘Initial T1MX’ will not be correct. Setup Polarization time and recycle delay, then it is ready to run!

NOTICE that this has to be 4 or 5 times of T1, and the Recycle delay RD can not be too short. It can even be a little bit longer than the Polar.Time TPOL.
Appendix B

SPINMASTER FFC2000 1T C/DC

The Fast Field Cycling NMR relaxometer

SPINMASTER FFC2000 1T C/DC is a unique NMR instrument designed to measure the field dependence of NMR spin-lattice and spin-spin relaxation time T1 and T2 (Nuclear Magnetic Relaxation Dispersion – NMRD – profiles), from earth field to a maximum operating magnetic field of 42.6 MHz (1H Larmor frequency)

The present Compact system represents the evolution of the previous instruments whose introduction in '97 has given a decisive contribution to the development and the diffusion of the Field Cycling NMR in the last years.

The superb performance offered by Spinmaster FFC2000-1T will further contribute to stimulate new applications in many fields of NMR investigation.

Highlights

- Very compact design and smaller lab space.
- SPINMASTER FFC2000 1T C/DC features the latest research grade versatility, digital NMR console
- PC-NMR and offers new improved performances and new experiments like Field Cycling Spin Echo
- Multi-nuclear operations
- Efficient and accurate temperature control (-140 to +140°C with a 0.1°C resolution)
- Measurements of relaxation times ranging from several seconds to fraction of milliseconds
- Simplicity of use (fully automated acquisition of T1 NMRD)
- Field Cycling Spin Echo Experiments
- Minimum operating costs and effort (no cryogenic gases)
- Short measurement time
- Full-fledged NMR Windows software

Main specifications

MAGNET
- Resistive, low inductivity, 4 layers air-core solenoid, suitable for Fast Field Cycling NMR measurements. The magnet is housed into a special glass-Perspex container and perfused by a special cooling liquid.
- Access bore: 20 mm.
- Max Field B0: 1.1 Tesla +/- 0.5%
- Homogeneity: < 1.5 ppm over 1m3
- Field slew rate: < 150 µs / MHz

POWER SUPPLY
- High stability computer controlled bipolar current source.
- The system is fully software controlled by means of external parallel port and TTL lines.
- Max. Power: 22 kW
- Max. Current: 430 A
- Max voltage: 53 V
- Resolution: < 50 ppm
- Switchable levels: 4 levels (off, Epo, Breax, Back)
- Each level is software controlled
- Switching time: < 150 µs / MHz
- Mains: 400 VAC / 22 kW 50/60 Hz

COOLING SYSTEM
- High efficiency thermally coupled loops. The hermetically closed secondary circuit uses a room temperature cooling fluid.
- The primary circuit uses tap water with regulated + Min water request: < 1000 l/hr at 19°C (0.7bar) 920KW NMR console
- Research grade versatility, digital NMR console PC-NMR (refer to the specific datasheet)
- Digital receiver: with direct detection from 500 kHz to 90 MHz with a maximum spectral width of 10 MHz
- 3 (three) independent RF TX channels individually and separately programmable from DC to 90 MHz.
- 128 bit/20ns/7b/pulse levels pulser.
- 350 W RF linear power pulse transmitter from 500 kHz to 150 MHz
- NMR software package with a large sequence library is supplied for Fast Field Cycling experiment and is very versatile.
- Multi classical NMR, NMR diffusion and NQR applications including mobile NMR.
- VTVC90 Sample temperature controller
- Standard gas flow system
- Range*: -120 to +140°C precision and stability: 0.1°C
- 10 mm probes tunable from 3 to 25 MHz (special probe availability on request)

Please contact Stelar for more detailed specifications.

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The innovation in NMR
The Fast Field Cycling NMR relaxometry

With the ongoing growth of studies of complex systems in biochemistry and materials research, we witness an increasing interest in NMR relaxometry and, in particular, in variable-field relaxometry.

All NMR studies exploiting nuclear relaxation indicate the convenience of measuring nuclear relaxation time (T1) as a function of the magnetic field B, in which they occur (NMRD profile).

Since such "dispersion" curves reflect essentially the distribution of molecular motions in terms of frequency (the so-called spectral densities), they provide an unusually direct way to "sampling" such distributions. Quantitative evaluations lead to important data about the interactions which couple molecular motions with nuclear spins.

In order to fully exploit information of variable field relaxometry, the relaxation field values should cover a range of 4–5 orders of magnitude.

Moreover, measurements in extremely low fields are particularly interesting since they reflect very slow motions, and one would like to cover in a single experiment, field values ranging from a few kHz to tens of MHz (Proton Larmor frequency).

It is evident that no conventional NMR spectrometer can produce such information.

The NMR Field Cycling is the only method capable to acquire T1 dispersion curves as a function of magnetic field strength.

The NMR FC method

In the basic NMR Field Cycling experiment, the Zeeman field Bo, which is applied to the sample, is cycling through three different values. In the first period, a high magnetic field Bpol (polarization field) is applied to pre-polarize the sample in order to boost signal intensity. Thereafter, the sample is allowed to relax in a second field Breax (relaxation field) which can be set to any desired value, including zero. In the last period, the field is set to the detection field Back for signal acquisition.

Fields of application

- **Paramagnetics**: studies of the hydration of paramagnetic metal ions and their organometallic complexes in water solutions.
- **Lipids and lipids in bulk**: studies of lipid dynamics in biological membranes.
- **Membranes**: studies of lipid dynamics in biological membranes.
- **Polymers**: studies of polymer dynamics in solutions.
- **Solids**: studies of solid-state dynamics.

Please contact Stelar for more detailed specifications.
Appendix C Technical Details

Math formulas are written by Visual Tex V8.42.

Figure is made by Microsoft Paint V5.1.

Program uses Compaq Visual Fortran compiler.

Data analysis uses Origin V6.1.

*A reference book for LaTeX (or guide for new user) is:

Appendix D  Extra experimental results

**Figure D1** Experimental proton H-$T_1$ NMRD profiles of the same water sample (ice) at two different temperatures (-5) (-10).

**Figure D2** Experimental proton H-NMRD profiles of water sample (ice) at two different temperatures, compare with theoretical plots.

**Figure D3** Experimental H-$T_1$ NMRD profiles of water sample and GdCl$_3$ + water (in different concentration) samples at the same temperature.

**Figure D4** Experimental H-$T_1$ NMRD profiles of GdCl$_3$ + water (normalized concentration) samples subtract the water background at the same temperature.
Figure D5 Figure 4.4(b) Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water (in different concentration) samples plus CaCl$_2$ + water sample at 293.15K (20°C).

Figure D6 Figure 4.4(b) Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water (in different concentration) samples plus CaCl$_2$ + water sample at 283.15K (10°C).

Figure D7 Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water sample (both in ice form) at the same temperature. (The small figure shows ln(MHz)-ln(R$_1$) plot.)

Figure D8 Experimental H-T$_1$ NMRD profiles of water sample and GdCl$_3$ + water sample (both in ice form) at the same temperature, with theoretical fitting lines.