Molecular Dynamics of Methyl Rotors and Hydrogen Bonds studied by High Pressure NMR

Submitted for the Degree Doctor of Philosophy

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Abstract

The dynamics of molecular groups in solids continues to stimulate great interest. At low temperature, the reorientations of small molecular groupings are governed by quantum mechanics. A transition to a regime describable using classical mechanics takes place when the temperature is increased.

In this thesis, two types of molecular dynamics are examined: The rotational reorientation of methyl (CH$_3$) groups and hydrogen bond dynamics of carboxylic acid dimers. Both types of motion involve a large hindering barrier which, at low temperatures, inhibits classical reorientation. At liquid Helium temperatures (4 K) the reorientation consists of almost pure quantum mechanical tunnelling through the barrier and Nuclear Magnetic Resonance (NMR) techniques are employed to measure the very small energies ($\approx 100$kHz, $\approx 10^{-4}$µeV) associated with these transitions.

In this work, the shape and height of the hindering potential barrier is systematically varied by applying hydrostatic pressure. This unique combination of NMR and pressure forms a very powerful toolset for the study of molecular dynamics.

Several new results are presented for both methyl- and hydrogen bond dynamics. The unprecedented observation of sideband of tunnelling sideband transitions, seen in Dimethyl Sulphide, has provided evidence in support of strong coupling between methyl groups in that material. An extensive analysis of the NMR data using different models assuming weakly and strongly coupled methyl groups is presented. Systems which do not exhibit any coupling between methyl groups are also examined. Additionally, the crystal structure of Dimethyl Sulphide and Benzoic Acid has been determined very accurately by neutron powder diffraction (using HRPD at the ISIS facility, RAL) in the search for a correlation between molecular structure and dynamics. In the case of hydrogen bond dynamics in Benzoic Acid derivatives, a strong correlation between the hydrogen bond length and the dynamics has been found and is presented. Finally, preliminary investigations of hydrogen bond dynamics in DNA base pairs are described.
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I dedicate this thesis to my dear parents, Regine and Walter, to express my gratefulness for the many ways in which they supported me during this period.
Chapter 0: Thesis Background and Overview

Methyl groups (CH₃) may exhibit rotational reorientation about their symmetry axis in a crystal lattice. The study of methyl reorientation has attracted great interest for more than 30 years, for two main reasons.

Firstly, the relative simplicity of a methyl rotor as a quantum mechanical rotational system makes methyl groups an attractive candidate for investigating molecular reorientation. The simplicity originates from the 3-fold symmetry of the group and the fact that its rotational dynamics can be described by just one coordinate, namely the rotational angle ϕ.

Secondly, the transition from quantum mechanical behaviour at very low temperatures to a system which is better described by classical mechanics makes the investigation of methyl rotation at different temperatures particularly exciting. The character of methyl reorientation changes from coherent quantum mechanical tunnelling through a hindering potential barrier at very low temperatures ( < 4K ) to incoherent, thermally assisted, classical hopping over the barrier as the temperature is raised. Interest in this particular aspect is maintained because the transition between the two regimes is not yet fully understood.

The investigation of molecular reorientation exhibited by methyl systems began in the late 1950s. Continuous wave NMR line shape analysis techniques were employed to deduce the tunnel splittings associated with the reorientation of highly hindered methyl groups at low and intermediate temperatures.¹

In this temperature range, methyl groups exist in the form of three proton spin symmetry species, denoted by A, Eᵦ and Eᵧ, having a total spin of 3/2, 1/2 and 1/2, respectively. The energy separation between the A and E ground states corresponds to the tunnel splitting ℏω₀.

¹ Stejskal EO and Gutowsky HS, J Chem Phys 28 (1958), 388
It was observed that with increasing temperature the measured tunnel splittings decreased. Allen explained this decrease with the Allen Model in 1974 \(^2,3\) which takes the thermal average of all tunnel splittings into consideration and thereby accounts for the observed temperature dependence of the measured tunnel splitting. Since the ascending order of energy levels is A,E,E,A,A,E,..., each successive pair of (E,A) levels is reversed in order. As a result, successive state splittings alternate in sign. A thermal average over all states tends to zero with increasing temperature.

One main difficulty at the time was the inability to account for changes in the symmetry species of the methyl rotor associated with the observed rotational transitions. These symmetry conversions cannot be caused by the lattice phonons, which are only of A-type symmetry. This problem was addressed but not satisfactorily resolved by A Hueller \(^4,5\).

The next milestone in the history of the investigation of methyl reorientation was the Methyl Thermometer Model proposed by Clough et al\(^6\) which described a universal correlation between the tunnel splitting observed at low temperatures and the temperature at which the NMR spin-lattice relaxation time \(T_1\) has a minimum value. The \(T_1\) minimum occurs at a temperature at which the incoherent hopping rate is of order the NMR measurement frequency. This correlation has been subsequently verified with more than 50 samples which exhibit tunnel splittings ranging over eight orders of magnitude.

\(^3\) Allen PS and Taylor DG, J Phys C : Solid State Phys. 8 (1975), 3036
The problem of spin symmetry conversion was re-addressed by Clough et al in 1993 and attempts made to explain it by the introduction of gauge potentials \(^7\).

Conceptually, it was proposed that it is insufficient to consider the methyl group as existing in a fixed rigid lattice. Rather each methyl rotation leads to a slight lattice recoil, therefore adding conceptual complexity to the lattice as a host environment for the methyl rotor. The gauge potential was a convenient means of describing the average effects of the lattice interaction. It was proposed that the simplest environment of a methyl group accessible experimentally is another methyl rotor, leading to great interest in studying systems of coupled methyl rotors.

There was some evidence that long range coupling of chains of methyl groups occurs in \(\gamma\)-Picoline, which has therefore attracted great interest in the recent past\(^8\). These long range effects were not explicable by earlier models.

These results, in addition to the existing interest in studying coupled methyl rotors, provided the main motivation to examine a system of coupled methyl groups as part of this work, and Dimethyl Sulphide has been chosen as a model system. Dimethyl Sulphide has been a focus of attention in the past \(^9\) since there have been indications that the methyl groups in that material exhibit coupling. In particular, two tunnel splittings are observed, but unlike other systems, not two \(T_1\) minima. Rather, the temperature dependence of the NMR spin-lattice relaxation time \(T_1\) shows an unusually broad minimum at atmospheric pressure.

The application of hydrostatic pressure as a means to systematically alter the molecular potentials affecting the rotational tunnelling spectrum has been utilised in this work in combination with NMR techniques employed to measure the small reorientational tunnel splittings. A motivation for using pressure is that it is

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\(^8\) Fillaux F, Carlile CJ and Kearley GJ, Physica B 180&181 (1992), 642

\(^9\) McDonald PJ et al, Molec.Phys. 57 (1986), 901
able to subtly change molecular potentials in a smooth fashion, not possible by any other method. Consequently, detailed study of the dependence of the tunnel splitting on the barrier become possible.

The application of hydrostatic pressure is potentially able to bring different tunnel splittings originating from methyl groups facing different lattice environments closer together by increasing one and decreasing the other. Such tuning effects and possible observation of anti-level crossings could provide strong evidence of coupling. An example of pressure causing the tunnel splitting to increase as well as decrease is given in 10 where the observed tunnel splitting initially increases and then decreases as the applied pressure is increased.

This phenomenon of applied pressure potentially equalising different tunnel splittings has constituted the main motivation for examining methyl acetate and dimethyl urea as part of this work.

As the project progressed, attention was also given to a different type of molecular reorientation, namely hydrogen bond dynamics of carboxylic acid dimers. Carboxylic acids typically form dimers which are held together by two parallel hydrogen bonds. The protons forming such a double hydrogen bond may reorientate in a translational fashion along each bondline, leading to the formation of a different tautomer.

This type of hydrogen bond represents a more complicated system exhibiting molecular reorientation, since the energy minima associated with the two stable tautomer configurations are of unequal depth.

Two different hydrogen bond systems with different orders of magnitude of the parameters describing their dynamics have been investigated as part of this work, namely benzoic acid and terephthalic acid.

In addition to results deduced from NMR spin-lattice relaxation time measurements aimed to obtain a measure of the parameters describing the

10 McDonald PJ et al, J Phys Condens. Matter 1 (1989), 2441
dynamics, exciting results emerged from accurate structural measurements of the hydrogen bond lengths by high resolution neutron powder diffraction. Strong evidence is presented indicating that the hydrogen bond dynamics appear to be strongly correlated with the geometry of the hydrogen bond. In particular, the rate of incoherent tunnelling associated with the proton transfer in the double hydrogen bond increases exponentially with decreasing hydrogen bond length.
Chapter 1

Introduction

1.1 Molecular Dynamics

The quantum mechanical dynamics of small particles at low temperatures are currently the focus of attention of many solid state physicists. In particular, the dynamics of atomic and molecular particles under the influence of a potential energy surface continue to attract great interest in condensed matter science.

The reorientation of methyl groups (CH$_3$) represents a simple example system of rotational dynamics. Each methyl group may be envisaged as a three-bladed molecular propeller rotating about its carbon-bond axis. Neighbouring atoms in the lattice give rise to a potential barrier hindering the methyl group rotation.

A common example for molecular dynamics of translational rather than rotational nature is the motion of hydrogen atoms along hydrogen bonds. These hydrogen bond dynamics typically involve a correlated pair-wise proton exchange along a pair of hydrogen bonds resulting from the formation of carboxylic acid dimers. This proton exchange along the double hydrogen bond causes the formation of a different tautomer. The correlated translational dynamics may be described by a one-dimensional transition of the protons from one potential well into another. These two potential minima correspond to the two distinct tautomeric configurations.

For both translational and rotational molecular reorientation, there are two main parameters which are the most important factors influencing the dynamics.

The first is temperature. At very low temperatures (around 4 K) the dynamics of methyl groups and hydrogen bonds are of almost purely quantum mechanical character. Methyl reorientation and tautomer exchange correspond to quantum mechanical tunnelling transitions. As the temperature is raised, a transition into the regime of classical mechanics takes place. The dynamics are now better described by classical hopping over the potential barrier. This transition between
quantum- and classical mechanics continues to be of particular interest since it is not yet fully understood.

The second important factor governing molecular dynamics is the potential the methyl rotors or hydrogen bond protons are subjected to. Minima in this potential correspond to equilibrium orientations and their width and depth determine the energies involved in the molecular dynamics.

1.2 Altering the Potential - Hydrostatic Pressure

In this project, a very powerful tool for systematically altering the shape of the molecular hindering potential has been utilised: Hydrostatic pressure. The application of pressure forms an advantageous alternative to the conventional method of changing the sample in order to achieve an alteration of the molecular potential in a smooth systematic fashion.

In combination with hydrostatic pressure to influence the shape of the potential seen by the reorientating molecular groups, Nuclear Magnetic Resonance (NMR) techniques have been employed to sense the effect of these potential alterations on the molecular dynamics by measuring the associated tunnel splittings. Measurements of the NMR spin-lattice relaxation time, and in particular its temperature dependence, also provide valuable information about the molecular dynamics, especially with respect to the transition between the quantum mechanical regime at low temperatures and the classical regime at higher temperatures.

This project on molecular dynamics includes the study of the rotational reorientation described by methyl groups and the translational relocation of protons exhibited by hydrogen bond dynamics by employing the unique combination of NMR techniques and application of hydrostatic pressure.

1.3 Thesis Overview

This thesis consists of two main parts. Firstly, the reorientation of methyl groups is discussed. Chapter 2 is dedicated to introducing the theory of the molecular dynamics of a single methyl rotor and the NMR techniques employed to detect the very small tunnel splittings associated with this reorientation. Experimental results on various methyl tunnelling systems are then presented in chapter 3, firstly describing the experimental instrumentation and procedures and
then moving on to present results from NMR measurements aimed to sense the reorientational
dynamics. Structural considerations are also presented. Additionally to systems of independ-
ent methyl rotors, the phenomenon of strong coupling between methyl groups is observed and
examined in detail.

The second part of the thesis is concerned with the other type of molecular dynamics, namely
hydrogen bond dynamics exhibited by carboxylic acid dimers. The theory of this type of molecu-
lar reorientation along double hydrogen bonds is discussed in chapter 4. Chapter 5 describes
NMR measurements carried out for different hydrogen bond systems and also presents high
resolution neutron diffraction measurements carried out in order to determine the structure of
these systems for various hydrostatic pressures. The effect of pressure on the hydrogen bond
lengths is correlated with its effect on the hydrogen bond dynamics - this correlation is discussed
in chapter 5 as well. A brief account of an idea to observe proton exchanges along hydrogen
bonds between DNA base pairs concludes chapter 5.
Chapter 2

Theory of Methyl Systems

2.1 Single Methyl Rotor

Methyl (CH$_3$) groups in a lattice may exhibit rotational reorientation about their carbon-bond axis. This rotation is normally strongly hindered by a potential barrier originating from neighbouring atoms, as schematically shown in figure 2.1.

![Figure 2.1: Single methyl rotor subjected to a rotational barrier](image)

Due to the symmetry of the group methyl reorientation may be described as a single particle moving in a three-fold potential [1],[2]. This simple description assumes a rigid rotor in a static hindering environment and does not account for possible variations in the C-H bond angles or any recoiling motion of neighbouring atoms. However, this model has been adopted over the last 30 years as the conventional description of the system, providing sufficient accuracy to account for observed tunnelling phenomena [3]-[18]. Within this description the hindering
potential is modelled as a simple three-fold cosine term

\[ V = \frac{V_0}{2}(1 - \cos 3\phi) \]  

(2.1)

where \( V_0 \) is the barrier height and \( \phi \) the rotational angle of the methyl group. At low temperature, in the quantum mechanical regime, the rotor levels can be determined by solving the stationary Schroedinger equation

\[ \mathcal{H}\Phi = E\Phi \]  

(2.2)

with the Hamiltonian

\[ \mathcal{H} = B\nabla^2 + V \]  

(2.3)

where \( B = -(\hbar^2/2I) \) is the rotational constant of a methyl group with moment of inertia \( I = 5.31 \times 10^{-47} \text{[kg m}^2]\). The rotational tunnelling eigenvalues can be obtained by diagonalising the Hamiltonian matrix using a basis of free rotor states, \((2\pi)^{-\frac{1}{2}} \exp(\text{i}m\phi)\), where \( m \) is an integer. The kinetic term is diagonal, with elements \((\hbar^2m^2/2I)\), whilst the potential term has off-diagonal elements linking free rotor states with \( m \) values differing by \( \pm 3 \) [19]. Hence the matrix can be separated into three non-interacting parts, which correspond to the three proton spin symmetry species shown in the table below.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>0, ( \pm 3, \pm 6, \ldots )</td>
</tr>
<tr>
<td>( E^a )</td>
<td>1, (1 ( \pm 3 )), (1 ( \pm 6 )), \ldots</td>
</tr>
<tr>
<td>( E^b )</td>
<td>-1, (-1 ( \pm 3 )), (-1 ( \pm 6 )), \ldots</td>
</tr>
</tbody>
</table>

The \( E^a \) and \( E^b \) levels are degenerate. A schematic energy level diagram for a highly hindered methyl rotor is shown in figure 2.2. The highest energy levels above the barrier are free-rotor states. The two lowest-lying energy states correspond to the ground state levels of \( A \) and \( E \)-type symmetry. The states of intermediate energy are torsional rotor levels. At low temperature, usually only the ground state levels are populated. Their energy difference defines the tunnel splitting \( \hbar\omega_t \) [19]. The eigenfunctions associated with the ground states overlap in between the potential minima, leading to a non-zero tunnelling probability.

For a methyl group, the tunnel splitting \( \hbar\omega_t \) can be calculated for a given barrier height \( V_0 \) by diagonalising the Hamiltonian matrix for the \( A \) and \( E \) species and subtracting the lowest-lying
A and E energy levels. Caution has to be exercised to include a sufficiently large number of \( m \) values in the matrix such that the resulting eigenvalues are independent of the matrix size. Figure 2.3 shows a graph of the methyl tunnel splitting against barrier height, calculated using a sufficiently large matrix of 101x101 elements.

The value at \( V_0 = 0 \) is the free rotor splitting \( (h^2/2I) \) which is equal to \( 1.584 \times 10^{11} \) Hz for a methyl group.

2.2 NMR techniques

2.2.1 Introduction to NMR Basics

Various Nuclear Magnetic Resonance (NMR) techniques form a tool-set for sensing the characteristics of molecular dynamics. Therefore a brief outline of the basics of NMR is given here. We are mainly concerned with hydrogen nuclei. These consist of single protons and have an intrinsic nuclear spin \( I = 1/2 \). The presence of this spin means that each hydrogen nucleus
Figure 2.3: Tunnel splitting $\hbar \omega$ of a methyl rotor subjected to a hindering barrier of height $V_0$ possesses an angular momentum $p$ given by

$$p = \hbar I$$  \hspace{1cm} (2.4)

where $\hbar = h/2\pi$, $h$ being Planck's constant and $p$ and $I$ are the angular momentum and spin operators, respectively. Due to the electric charge associated with each proton, the presence of angular momentum gives rise to a non-zero magnetic dipole moment for each nucleus,

$$\mu_i = \gamma p_i$$  \hspace{1cm} (2.5)

where $\gamma$ is constant for a given type of nucleus and known as the magnetogyric ratio. $\gamma = 42.58 \text{ [MHz/T]}$ for hydrogen nuclei.

Hence every hydrogen nucleus in the sample may be envisaged as a tiny bar magnet. Once an external magnetic field $B_0$ is applied, it will have an energy $E$ given by

$$E = -\mu_i B_0$$  \hspace{1cm} (2.6)

and according to equations 2.4 and 2.5, we get

$$E = -\gamma \hbar I B_0$$  \hspace{1cm} (2.7)
For hydrogen nuclei, I can either be $+1/2$ or $-1/2$, corresponding to an alignment with or against the external magnetic field $B_0$, which leads to an energy difference between the two different orientations of

$$\Delta E = \gamma \hbar B_0$$

(2.8)

$\Delta E$ is also known as the Zeeman splitting $\hbar \omega_Z$ where $\omega_Z = \gamma B_0$. Transitions between the two Zeeman states may be induced by the application of electromagnetic radiation of angular frequency equal to $\Delta E/\hbar$. Although the lower energy level is the preferred one, thermal motion induces transitions to occur naturally - leading to only a small excess of spins in the lower energy state.

Strictly speaking, the quantum mechanical description should be used to investigate all NMR phenomena. However, it is easier to visualise most concepts using the classical model in which all orientations of the nuclear spin with respect to the applied magnetic field are allowed. All of the predictions of the classical model normally agree exactly with those of the quantum theory for a macroscopic system [20].

In the classical model, the interaction of the magnetic moment with the applied magnetic field tries to align the two. This turning force $L = \mu_i \times B_0$ constitutes a torque on each hydrogen nucleus, causing it to precess about $B_0$. The precession frequency is known as the Larmor frequency and is equal to $\frac{1}{2\pi} \omega_L = \frac{1}{2\pi} \omega_Z = \gamma B_0$.

When considering the observable bulk magnetisation $M$ in a macroscopic sample given by the combined effect of all nuclear magnetic moments $M = \sum_i \mu_i$ there is no component perpendicular to the applied magnetic field at equilibrium since the individual magnetic moments precess out of phase. Instead, some net magnetisation parallel to $B_0$ is present due to the different populations of the two Zeeman states. The application of an electromagnetic pulse of the Larmor frequency will perturb the bulk magnetisation $M$ and cause it to precess about $B_0$ with the Larmor frequency since it introduces phase coherence between the nuclear magnetic moments $\mu_i$. As stated above, this RF pulse will also provide the energy $\Delta E$ needed to induce transitions between the Zeeman states, leading to a reduction in the population difference and hence minimizing the parallel component in the bulk magnetisation $M$. If the duration of the RF pulse is chosen such that the populations of the two Zeeman levels are equalized and the precession of all nuclei is in phase, the RF pulse is referred to as a 90-degree pulse since it effectively “flips” the bulk magnetisation vector $M$ by 90 degrees into the $xy$-plane perpendicular to the applied field $B_0$. As a result, the observable bulk sample magnetisation $M$ will precess about $B_0$ in
the xy-plane with the Larmor frequency.

After a 90-degree pulse has been applied, the precessing magnetisation $M$ is able to induce a current in a coil of wire wound in a plane parallel to $B_0$ (usually the same coil used to apply the 90-degree pulse). The signal induced in the coil will be a sine wave at the Larmor frequency and with decaying amplitude, as shown in figure 2.4.

![90-degree pulse](image)

Free Induction Signal

![Free Induction Signal](image)

Figure 2.4: Free Induction Decay (FID) following a 90-degree RF pulse

The decay in amplitude, referred to as Free Induction Decay (FID), is due to a loss of phase coherence with time, resulting in a decrease of the magnetisation component in the xy-plane (perpendicular to $B_0$).

There are two main types of relaxation which are only briefly described here. One relaxation mechanism is caused by interactions between the nuclear magnetic moments. Although the local magnetic field seen by a nucleus is dominated by the applied field $B_0$, neighbouring nuclei will also contribute a small perturbation. This dipole-dipole interaction is dominant in $^1$H solids and causes a slight local variation of the precession frequency for individual nuclei. This leads to a loss of phase coherence and hence a reduction in the transverse component of $M$ (perpendicular to $B_0$). This type of relaxation is known as spin-spin relaxation and the time constant of the decay in the transverse component of $M$ is known as $T_2$, the spin-spin relaxation time.

The other mechanism is known as spin-lattice relaxation. Transitions between the two Zeeman levels will cause some nuclei to "fall back" into the lower energy state, resulting in an increase in the population difference until it reaches equilibrium again. This leads to a growth of the component of $M$ parallel to $B_0$ (longitudinal component) towards its equilibrium value. The spin-lattice relaxation occurs in a time characterized by the spin-lattice relaxation time $T_1$. Both
relaxation times $T_2$ and $T_1$ can be measured and give valuable information about the dynamic environment of the nuclei of interest.

We shall now consider the NMR techniques employed to determine the characteristics of molecular dynamics of methyl rotors.

### 2.2.2 Field Cycling and Stir-Scan

#### Thermodynamic Considerations

In order to understand the low-field Nuclear Magnetic Resonance (NMR) techniques employed to measure small tunnel splittings of highly hindered methyl groups it is appropriate to firstly consider the thermodynamics involved. Assuming a large number of methyl groups arranged in a lattice at low temperature subjected to an external magnetic field $B_0$, we can identify three distinct thermal reservoirs. These are the lattice, methyl and nuclear Zeeman reservoirs. The important concept is that a temperature may be defined for each reservoir. The temperature of the lattice $\Theta_L$ is considered constant by assuming the lattice reservoir to be very much larger than the other two. The methyl tunnelling temperature $\Theta_t$ is defined by the relative population of methyl groups of symmetry E to those of A-type symmetry [21]:

$$\frac{p(E)}{p(A)} = \exp[-\left(\frac{\hbar h}{k_B \Theta_t}\right)\omega_t]$$

where $\hbar \omega_t$ is the tunnel splitting and $k_B$ is the Boltzmann constant. The nuclear Zeeman temperature $\Theta_Z$ is inversely proportional to the nuclear magnetisation present in the sample and defined in terms of the relative population of protons of spin $+\frac{1}{2}$ to those of spin $-\frac{1}{2}$

$$\frac{p(+\frac{1}{2})}{p(-\frac{1}{2})} = \exp[-\left(\frac{\hbar}{k_B \Theta_Z}\right)\omega_Z] = \exp[-\left(\frac{\hbar \gamma B_0}{k_B \Theta_Z}\right)]$$

where $\hbar \omega_Z$ is the Zeeman splitting which is proportional to the magnetic field $B_0$. The Boltzmann constant $k_B$ and the gyro-magnetic ratio $\gamma = 42.58$ [MHz/T] for protons form the proportionality constants. As shown schematically in figure 2.5, the transfer of heat (=energy) between the reservoirs is restricted to certain conditions.

There is only very weak direct contact between the lattice and the methyl tunnelling reservoir. This is due to the lattice phonons being exclusively of A-type symmetry whilst interactions with the methyl tunnelling reservoir are required to be of E-type symmetry [22]. The lattice is “weakly” linked to the Zeeman reservoir through the spin-lattice relaxation mechanism, characterized by the NMR parameter $T_1$, the spin lattice relaxation time which can be measured. $T_1$ at
low temperature (∼ 4 Kelvin) is usually of considerable duration of order minutes, imposing a
narrow bottleneck to the tendency of the two reservoirs to reach thermal equilibrium by growing
magnetisation in the direction of the external magnetic field. The Zeeman reservoir is normally
isolated from the methyl tunnelling reservoir. Only in the special case of matching the tunnel
splitting $\hbar \omega_t$ with the nuclear Zeeman splitting $\hbar \omega_Z$ or $2\hbar \omega_Z$ can energy be rapidly exchanged,
potentially leading to a great change in $\Theta_Z$ resulting in an alteration in the total magnetisation
present.

Therefore, an experiment can be designed to find values of $\hbar \omega_Z$ where the condition for energy
exchange between the tunnelling and Zeeman reservoirs ($\hbar \omega_t = \hbar \omega_Z$ or $\hbar \omega_t = 2\hbar \omega_Z$) is ful-
filled. These values of $\omega_Z$ correspond to distinct values of the magnetic field $B_0 = (\hbar \omega_Z / \gamma)$. An
experiment can therefore be designed in which the magnetic field is continuously altered until a
distinct value is found for which there is a significant change in overall sample magnetisation.
This is accomplished by field cycling [23].
CHAPTER 2. THEORY OF METHYL SYSTEMS

Field Cycling

Firstly, all existing magnetisation is destroyed by applying a train of 90-degree pulses (providing a reproducible starting condition). At this stage the Zeeman temperature $\Theta_Z$ has a maximum value - the associated Zeeman reservoir is hot. Then the magnetic field is rapidly switched to a relaxation value $B_r$, allowing magnetisation to grow (the Zeeman reservoir to cool) during a fixed time period $\tau$, and then rapidly switched back to the NMR field where the magnetisation in the sample is measured using a single 90-degree pulse by integrating the resulting FID. This process is repeated as a function of $B_r$. The resulting spectrum will show the proportional growth of recovered magnetisation with relaxation field, but may show additional features for distinct values of $B_r$ which will correspond to a match between the tunnel splitting $\hbar \omega_t$ and the Zeeman splitting $\hbar \omega_Z$ or $2\hbar \omega_Z$ where $\hbar \omega_Z = \hbar \gamma B_r$ is known. An example field cycling scan of Methyl Urea is shown in figure 2.6, where the symbols represent the individual magnetisation measurements and the solid line is an 8-point running average.

Although low-field NMR field cycling is a common technique to measure tunnel splittings it was not the primary technique employed in this project. Field cycling experiments can behave very randomly, sometimes the features are clearly seen, sometimes not. This is mainly due to the thermodynamics involved. The entire history of what happened to the methyl reservoir after cooling may affect the temperature $\Theta_t$ and therefore determine the outcome of a field cycling experiment. There is a modified technique which allows a more consistent clarity of the features of interest: Stir-Scan.

Stir-Scan

Stir-Scan has been developed at Nottingham University [21] and involves two low frequency RF signals being applied at low magnetic field.

Reorientational transitions of a methyl rotor correspond to transitions between the A and E methyl symmetry species. An applied RF signal cannot drive such transitions at high magnetic field since an RF field (which has A-type symmetry) cannot directly induce a change in symmetry of the state function [22]. At low field, however, the dipole-dipole interaction [24],[25] becomes more dominant and causes mixing of the symmetry states [22]. This results in a partial transfer of applied RF energy to drive methyl tunnelling transitions provided that there is an energy match between the applied RF signal and a tunnelling transition.

Since the dipole-dipole interaction is of only small significance at higher fields, methyl tunnel-
Figure 2.6: Field cycling scan of methyl urea at 4K temperature. The arrows show changes in the recovered magnetisation which are attributed to a match of the tunnel splitting and the Zeeman splitting (at \( \approx 18000 \) G) and twice the Zeeman splitting (at \( \approx 9000 \) G).
ling experiments cannot be carried out at high field - this would lead to a problem due to the very low signal/noise ratio attainable in low-field NMR. Two solutions to this problem are either to use a superconducting quantum interference device (SQUID) detector [26] or to cycle the field such that the experiment is carried out at low field and only the final measurement is obtained at high field. Field cycling is employed during a stir-scan cycle which is schematically illustrated in figure 2.7.

![Diagram](attachment:figure27.png)

Figure 2.7: Low field stir-scan NMR combines field cycling with the application of low RF signals

A stir-scan experiment consists of several identical cycles where only one of the applied RF frequencies is incremented. After an initial train of 90-degree pulses applied to eliminate any existing magnetisation in the sample and therefore creating a reproducible starting condition, the magnetic field is changed to a high preparation field \( B_{\text{prep}} \approx 2 \text{ T} \). After a fixed preparation time \( (t_{\text{prep}} \approx 1 \text{ min}) \) the magnetic field is rapidly switched to a very low relaxation field \( B_{\text{relax}} \approx 13 \text{ mT} \) where the sample is irradiated with two alternating low frequency RF signals. This irradiation lasts for about 20 seconds during which the frequency is switched between a fixed “stir” frequency \( \nu_{\text{stir}} \) applied to initiate transitions in the tunnelling reservoir and the current value of a “scan” frequency \( \nu_{\text{scan}} \) to probe for further tunnel splittings. Both applied low frequency RF signals are of order \( \approx 100 \text{ kHz} \). \( \nu_{\text{scan}} \) is incremented for different stir-scan cycles during the experiment whilst \( \nu_{\text{stir}} \) remains constant. After the low field RF irradiation the magnetic field is cycled back to the NMR field \( B_{NMR} \approx 0.56 \text{ T} \) and the sample magnetisa-
tion measured using a single 90-degree pulse. The whole cycle is repeated for different values of the scan frequency $\nu_{\text{scan}}$ and the recovered magnetisation is plotted against $\nu_{\text{scan}}$.

Effectively the Zeeman reservoir is heated (corresponding to a loss of magnetisation grown during the preparation period) for distinct energies of the applied RF signal which correspond to tunnelling transitions. Therefore, we expect a stir-scan spectrum to show a constant amount of magnetisation for a range of applied RF signal frequencies $\nu_{\text{scan}}$, with "holes" appearing for distinct frequencies corresponding to energy level transitions. As shown in figure 2.8, central Larmor transitions are typically accompanied by sideband transitions at $\pm \nu_t$, the tunnel frequency ($\omega/2\pi$).

![Diagram](image)

Figure 2.8: Typical features seen in a stir-scan spectrum consist of central Larmor troughs accompanied by sidebands at $(\nu_{\text{Larmor}} \pm \nu_t)$.

A clear example of observed tunnelling sidebands is shown in figure 2.9. This data was taken of Methyl Acetate at atmospheric pressure and a temperature of 4 K. The experimental results on Methyl Acetate are discussed in more detail in chapter 3.

### 2.2.3 Spin-Lattice Relaxation Time $T_1$

Another parameter which may provide some information about the molecular reorientation of methyl groups is the spin-lattice relaxation time $T_1$ which can be measured by standard
CHAPTER 2. THEORY OF METHYL SYSTEMS

NMR techniques. Of particular interest is the temperature dependence of $T_1$ since each methyl rotor will follow a transition from purely quantum mechanical tunnelling at low temperatures to thermally assisted classical “hopping” at higher temperatures. The parameter linking the observable spin-lattice relaxation time $T_1$ with the molecular dynamics is $\tau_c$, the correlation time of the methyl reorientation. It is usually of sufficient accuracy to express $T_1$ as a function of $\tau_c$ according to modified BPP theory [19]:

\[
T_1^{-1} = C_0 \left[ \frac{\tau_c}{(1 + \omega_0^2 \tau_c^2)} + \frac{4 \tau_c}{(1 + 4 \omega_0^2 \tau_c^2)} \right] + C_1 \left[ \frac{\tau_c}{(1 + (\omega_0 - \omega_1)^2 \tau_c^2)} + \frac{\tau_c}{(1 + (\omega_0 + \omega_1)^2 \tau_c^2)} + \frac{4 \tau_c}{(1 + (2\omega_0 - \omega_1)^2 \tau_c^2)} \right]
\]

(2.11)

where $\omega_0/2\pi$ is the proton NMR frequency and $C_0, C_1 \approx 10^9 \text{[s}^{-2}]$ are constants corresponding to the lattice sum of proton dipole-dipole matrix elements. The term in $C_1$ corresponds to transitions between two $E$ species while the $C_1$ term takes account of the transitions between $A$ and $E$ species [19]. According to the semi-phenomenological methyl thermometer model [19], the reorientation rate $\tau_c^{-1}$ can be calculated by evaluating the expectation value of the modulus of the angular momentum $<\Omega>$ of the excited states and subtracting that of the ground state.

Figure 2.9: Observed stir-scan spectrum of Methyl Acetate. The three “troughs” correspond to the Larmor transition (center) accompanied by tunnelling sidebands.
Since A states have no angular momentum hence only the E states $E^a$ and $E^b$ are considered and their angular momenta have equal and opposite values. Therefore, $\tau_c^{-1}$ is given by

$$\tau_c^{-1} = \frac{3}{4\pi^2} \sum_p (|<\Omega|_{1+3p} - |<\Omega|_{1}|) \exp\left(-\frac{E_{1+3p}}{k_B\Theta}\right) \sum_p \exp\left(-\frac{E_{1+3p}}{k_B\Theta}\right)$$

(2.12)

where

$$<\Omega|_p = \hbar \sum_m c_{pm}^2 m$$

(2.13)

$<\Omega|_p$ and $E_p$ are the angular momentum expectation value and energy of the $p_{th}$ level, respectively. The $p_{th}$ level has the eigenfunction with coefficients $c_{pm}$.

Figure 2.10 shows $T_1$ as a function of $\tau_c$, following equations 2.11 to 2.13 above.

![Graph](image)

Figure 2.10: NMR spin-lattice relaxation time $T_1$ as function of molecular reorientation rate $\tau_c$, with proton NMR frequency of 24 MHz and constant $C_0 = 10^9$[s$^{-2}$].

We can clearly see that, for a proton NMR frequency of 24 MHz, the spin-lattice relaxation time $T_1$ has a minimum when $\tau_c^{-1} = 2.5 \times 10^8$s$^{-1}$.

In order to measure the NMR spin-lattice relaxation time experimentally, the saturation-recovery technique has been employed in this project. The magnetisation recovered after a time interval
\( \tau \) is measured by subjecting the sample to a train of 90-degree pulses in order to eliminate all existing magnetisation, then leaving the sample magnetisation to recover for a period \( \tau \), and then obtaining the FID by a single 90-degree pulse. The sample is continuously subjected to the NMR field of 0.56 T during the process. The relaxation period \( \tau \) is incremented exponentially and the recovered magnetisation is plotted against \( \tau \), yielding a curve which can normally be fitted by a single-exponential function. Figure 2.11 shows an example set of measured recovered magnetisation values obtained for Methyl Acetate.

\[ M = M_0[1 - \exp\left(\frac{-\tau}{T_1}\right)] + C \]  

where \( C \) is a baseline constant. For the data set presented in figure 2.11, \( M_0 = 1.57 \times 10^5 \), \( C = 4.8 \times 10^3 \) and \( T_1 = 0.294 \) secs.
Chapter 3

Experimental Results of Methyl Systems

3.1 Instrumentation and Experimental Procedures

Description of the Apparatus

The apparatus consists of a helium gas intensifier, a high pressure sample cell and a feed capillary, a superconducting magnet in a He cryostat and a home-made spectrometer along with a digital storage oscilloscope and a BBC microcomputer for data acquisition. The intensifier consists of a three-stage helium gas compressor supplied by Unipress, Poland. A beryllium copper sample cell with sample volume 0.15 ml contains a small NMR coil consisting of three parallel wires with three loops each. The cell is sealed by metal gaskets and the coil wires are fed through a pyrophillite powder seal and connected to a coaxial feed cable inside the main probe stick. The probe is lowered into the cryostat where the sample can be cooled down to 4.2 K. The probe arrangement is shown in figure 3.1.

The sample cell is connected to the intensifier through a beryllium copper feed capillary. Several thermo sensors and heaters are arranged along the main probe. The NMR coil is tuned by the self-capacitance of the central coaxial cable forming the RF down-feed. The NMR fine-tuning components are external at the top end of the central coaxial cable, together with a high-gain preamplifier. The amplified signal is then taken to the fixed-frequency spectrometer which in turn is connected to the digital storage oscilloscope to produce the FID. The oscilloscope samples the FID data for both real and imaginary channels and sends the digital data to the BBC microcomputer which integrates the FID to obtain a measure of the total magnetisation. Other than storing the magnetisation data, the BBC computer is dedicated to perform all the relay-switching and magnetic field cycling as well as controlling the low-RF signal. The magnetic
Figure 3.1: The main probe consists of the high pressure cell with its feed capillary, a copper coax cable connected to the NMR coil and thermal control/sensor devices.
field is controlled by a digital to analog converter (DAC) connected to the magnet power supply. Later during the project the BBC was linked to a local UNIX host by a serial cable, allowing the current magnetisation data to be plotted and analysed during the experiment. The overall hardware setup is illustrated in figure 3.2.

![Diagram of experimental equipment]

**Figure 3.2:** The experimental equipment consists of a superconducting magnet in a He-cryostat, a He-gas intensifier, standard NMR components and a dedicated BBC microcomputer

**Preparation**

Prior to each set of experimental runs the cryostat had to be cooled down after pumping the insulation spaces in order to create a good thermal insulation vacuum. The vacuum pumping usually takes a week and the cooling is done in stages over two days. Before each experiment the sample was loaded into the pressure cell after carefully mounting all pressure seals and then the probe was inserted into the cryostat. Whilst operating the intensifier care had to be taken to avoid solidifying of the Helium and a careful cooling (heating) procedure was adopted to ascertain that the Helium solidified (melted) first (last) in the main pressure cell rather than in the feed capillary. For this purpose a heater was mounted along the feed capillary. The Helium melting curve is shown in figure 3.3.
CHAPTER 3. EXPERIMENTAL RESULTS OF METHYL SYSTEMS

Figure 3.3: The Helium Melting Curve for pressures up to 10 kBar

Once the sample was cooled to LHe temperature (4.2 K) and a stable desired pressure obtained, the experiment could begin after powering up the superconducting magnet and leaving it at high field to minimise its cycling hysteresis. Except for spin-lattice relaxation time ($T_1$) measurements the temperature was kept stable at 4.2 K.

3.2 Methyl Acetate: Uncoupled Methyl System

Methyl Acetate is a liquid at room temperature and its molecular structure is schematically shown in figure 3.4.

There are two independent methyl rotors in Methyl Acetate which face different hindering potentials, giving rise to two distinct tunnel splittings. The larger splitting has previously been determined at atmospheric pressure by neutron scattering [27] and found to be equal to 322 MHz (1.33 $\mu$eV), which is outside the observable range of NMR field cycling techniques. The smaller splitting has also been previously measured at atmospheric pressure, using field cycling [27] and
its value was found to be 84 kHz (equivalent to $3.47 \times 10^{-4}$ eV).

3.2.1 Methyl Acetate NMR measurements

The stir-scan technique has been employed to measure the smaller tunnel splitting of Methyl Acetate as a function of hydrostatic pressure. Also, the temperature dependence of the spin-lattice relaxation time $T_1$ has been determined for various hydrostatic pressures.

**Stir-Scan Data**

The stir-scan technique (discussed in section 2.2.2 above) has been employed whilst the sample temperature was kept constant at 4.2 K. All stir-scan data is inverted and normalised for presentation, showing points of maximum magnetisation loss as peaks and allowing an easy assessment and qualitative comparison between different data sets. The normalisation is done by taking the maximum measured magnetisation (a number with arbitrary units) within a data set as a reference and plotting the entire spectrum as percentages in lost magnetisation. Each magnetisation measurement is hence converted to a percentage according to

$$M_L[\%] = 100 \times \left(1 - \frac{M_{\text{measured}}}{M_{\text{maximum}}}\right)$$  \hspace{1cm} (3.1)

resulting in a value representing the magnetisation loss in percent. A 5-point running average line is commonly displayed as well for clarity.

Figure 3.5 shows a stir-scan spectrum of Methyl Acetate at atmospheric pressure. During each stir-scan cycle, the sample was initially prepared at 0.7 T for 60 seconds. Then the magnetic field was cycled down to the relaxation field of 13 mT where the sample was alternately irradiated with the scan frequency $\nu_{\text{scan}}$ and the stir frequency $\nu_{\text{stir}} = 85$ kHz for 12 seconds. The NMR field was 0.55945 T and the scan frequency resolution 4 kHz. The total time needed for this scan was 11.5 hours.

The two main peaks labelled A and B correspond to $\Delta m = 1$ and $\Delta m = 2$ transitions, respect-

*The scan and stir frequencies were switched every second during this relaxation process.*
Figure 3.5: Methyl Acetate stir-scan spectrum at 4.2 K, atmospheric pressure. The thin solid line represents a 5-point average of the data.

Each of these transitions causes a very substantial 60% loss in recovered magnetisation after applying the matching scan frequency $\nu_{\text{scan}}$ for a total of 6 seconds. The sidebands labelled $b-$ and $b+$ are clearly visible and are separated from their central $\Delta m = 2$ peak $B$ by ±70 kHz, which is the smaller of the two distinct tunnel splittings present in Methyl Acetate. This splitting of 70 kHz has been observed a total of nine times at atmospheric pressure and due to the very high quality of the data the error in this observation is relatively small ($\nu_t = 70 \pm 5$ kHz). Hence the previously reported value of 84 kHz [27] has to be slightly adjusted. The additional weak peak labelled $H$ occurs in the spectrum at half the frequency of $A$ and corresponds to a harmonic in the frequency oscillator and not to a tunnelling transition.

Reducing the Zeeman splitting by choosing a lower relaxation field of 11 mT causes a shift of all peaks to lower values of $\nu_{\text{scan}}$ as expected. This is demonstrated in figure 3.6, the relaxation field is reduced to 11 mT.

The application of hydrostatic pressure causes an alteration of the molecular potentials seen by the methyl groups, hereby changing the tunnel splittings. This in turn will cause the observed tunnelling sidebands to shift to more narrow or wide positions with respect to their central peak. Figure 3.7 shows a stir-scan spectrum obtained at 2.5 kBar pressure. The relaxation field for this scan is 13 mT and the stir frequency was set to 50 kHz. The relaxation time was shortened
Figure 3.6: Methyl Acetate stir-scan spectrum similar to figure 3.5, but with a reduced relaxation field $B_{relax} = 11 \text{ mT}$

Figure 3.7: Methyl Acetate stir-scan spectrum at 2.5 kBar pressure. The observed tunnel splitting $\nu_t = 60 \text{ kHz}$
to 5 seconds. As a result of the increase in pressure, the sidebands $b-$ and $b+$ have shifted and their frequency separation from the main Larmor peak $B$ is reduced to 60 kHz. One can also notice a lower signal to noise ratio for this high-pressure data set. That is mainly because the atmospheric data has been taken in a different, larger sample cell. Also, the application of pressure often deforms the NMR coil, leading to a degradation of the obtained NMR signal. Increasing the hydrostatic pressure further resulted in a continued decrease in the measured tunnel splitting $v_t$. The highest pressure applied to this sample was 4.3 kBar, where $v_t = 35$ kHz, as shown in figure 3.8. This tunnel splitting is one of the smallest molecular splittings observed to date. This data set has identical acquisition parameters to the 2.5 kBar data presented in figure 3.7 above.

![Figure 3.8: Methyl Acetate stir-scan spectrum obtained at 4.3 kBar pressure, showing the main Larmor peak $B$ and its tunnelling sidebands with a reduced frequency separation of ±35 kHz. This represents one of the lowest molecular tunnel splittings observed to date](image)

In total 31 stir-scan data sets of Methyl Acetate were taken at pressures between atmospheric pressure and 4.3 kBar. Figure 3.9 shows the tunnelling sidebands of the Larmor peak $B$ at 3.0 kBar. All parameters are still identical to the 2.5 kBar data shown in figure 3.7 and the observed tunnel splitting is now 55 kHz.
Figure 3.9: Methyl Acetate at 3.0 kBar. The measured tunnel splitting $\nu_t$ is 55 kHz

Figure 3.10: Methyl Acetate at 2.0 kBar pressure. The measured tunnel splitting $\nu_t$ is 80 kHz
A spectrum obtained at 2.0 kBar is shown in figure 3.10. The relaxation took place for 12 seconds at 13 mT. There are several facts that should be pointed out about this data set. The observed tunnel splitting is 80 kHz, which is larger than the atmospheric tunnel splitting of 70 kHz. If we expect the tunnel splitting to decrease with increasing pressure, we would not expect to observe a larger tunnel splitting at 2.0 kBar. We shall return to this point when discussing the pressure dependence of \( v_t \) below. Another feature is that the maximum magnetisation loss achieved in this scan is 30%, well below the typical 60-70% in the previously presented data sets. Some effect caused a degradation in the variation of the recovered magnetisation with the applied RF frequency \( \nu_{\text{scan}} \), leading to less contrast in \( M_{\text{measured}} \) between a match and mismatch of \( \nu_{\text{scan}} \) and a molecular energy transition. Also, this degradation apparently is time-dependent. As time after pressurising and cooling the sample elapses, subsequent spectra taken with identical acquisition parameters show less and less contrast in the recovered magnetisation, until the peaks disappear in noise after about 40 hours. This effect is illustrated in figure 3.11, where three spectra taken subsequently at different times after cooling the sample are shown. All parameters for this 2.0 kBar data are constant. During the time in between the three stir-scan runs no experiments were carried out, the sample remained at the low relaxation field at 4.2 K temperature. As one can see by inspecting figure 3.11, the features disappear as time progresses. This effect has been seen twice at pressures around 2 kBar.

At pressures below 1.5 kBar this loss of contrast in magnetisation as function of \( \nu_{\text{scan}} \) becomes more dominant and no features could be resolved at any pressures between atmospheric and 1.5 kBar. Figure 3.12 shows a scan taken at 0.5 kBar to demonstrate this fact.

The possible reasons for this effect remain unclear. Quite likely, an accelerated low-field spin-lattice relaxation may cause a faster interchange of energy between the nuclear Zeeman and lattice reservoirs at the relaxation field, leading to a loss of magnetisation irrespectively of the applied RF frequency \( \nu_{\text{scan}} \). This would explain the resulting smaller variation in recovered magnetisation with \( \nu_{\text{scan}} \). An explanation for the time dependence of this effect is not apparent, although one may argue that a change in molecular structure at that pressure may be responsible. To illustrate this hypothesis, the pressure dependence of the observed smaller tunnel splitting \( v_t \) is examined in figure 3.13.

An additional tunnel splitting determined by measuring the temperature dependence of the nuclear spin-lattice relaxation time \( T_1 \) at 0.9 kBar pressure has been included in this graph and is shown as a square symbol. This will be discussed later as part of the \( T_1 \) data analysis. The
Figure 3.11: Methyl Acetate at 2.0 kBar pressure in consequent, identical stir-scan experiments. The peaks become less prominent with time after cooling.
observed tunnel splitting increases by 44 kHz between atmospheric pressure and 0.9 kBar. For pressures above 0.9 kBar the observed tunnel splitting decreases exponentially with applied hydrostatic pressure. A possible reason for this discontinuity below 0.9 kBar is a structural phase transition which occurs within that pressure range. This may lead to the coexistence of two slightly different structural forms α and β of Methyl Acetate for pressures between 0.0 and 0.9 kBar. The proportion of Methyl Acetate in β form increases with pressure, until at pressures above about 0.9 kBar the β form is dominant. However, both forms may coexist up to pressures of around 1.5 kBar. The coexistence of both forms in significant proportions may lead to an accelerated spin-lattice relaxation as mentioned above, causing a significant interchange of energy between the Zeeman and lattice reservoirs at the relaxation field which in turn results in the inability to resolve any peak features below 1.5 kBar.

**Spin-Lattice Relaxation Time $T_1$ Measurements**

The temperature dependence of the spin-lattice relaxation time $T_1$ of Methyl Acetate has been investigated for different hydrostatic pressures. The saturation recovery technique outlined in section 2.2.3 has been employed to measure the recovered magnetisation for exponentially
Figure 3.13: Observed tunnel splitting $\nu_t$ as function of applied hydrostatic pressure shows an exponential decrease above 1.5 kBar (diamonds). The square symbol indicates a tunnel splitting of 114 kHz determined by $T_1$ measurements at 0.9 kBar, which are discussed further below.
increasing recovery time intervals $\tau$. As discussed in section 2.2.3, the $T_1$ temperature dependence may provide information about the molecular dynamics since minima may be resolved which correspond to specific methyl tunnelling transitions. In the case of Methyl Acetate, we would expect to observe two minima in the $T_1$ temperature curve, corresponding to the two distinct methyl groups present. The $T_1$ temperature dependence of Methyl Acetate measured at atmospheric pressure is shown in figure 3.14.

![Figure 3.14: Temperature Dependence of the spin-lattice relaxation time $T_1$ for Methyl Acetate at atmospheric pressure. The two minima correspond to the two different methyl groups present in the molecular structure.](image)

The common style of plotting the data on a linear-log scale and taking the inverse temperature as x-axis has been adopted. The two minima are clearly visible at $\Theta_1^{-1} = 0.0085K^{-1}$ and $\Theta_2^{-1} = 0.0224K^{-1}$. Since the NMR frequency is 24 MHz, each minimum corresponds to a reorientation rate $\tau_c^{-1}$ of $2.5 \times 10^8$ Hz for the associated methyl group (see section 2.2.3).

Analysis of the measured temperature dependence of the spin-lattice relaxation time involves modelling the dynamics (correlation times) for the two distinct methyl groups by calculating the energy levels and angular momenta for a set of hindering potentials as described in section 2.2.3 above. The $T_1$ curve resulting from the relaxation contributions of the two rotor types is obtained by adding the individual relaxation rates according to [28]

$$\left[\frac{1}{T_1}\right]_{\text{total}} = R_1 \left[\frac{1}{T_1}\right]_1 + R_2 \left[\frac{1}{T_1}\right]_2$$  \hspace{1cm} (3.2)
where $R_1$ and $R_2$ represent the proportion of the number of rotors 1 to the number of rotors 2, respectively, and $R_1 + R_2 = 1$. Here, as described in section 2.2.3 above, each individual $T_1$ contribution is given by

$$\frac{1}{[T_1]}_i = C_i B(\tau_c)_i$$  \hspace{1cm} (3.3)

where

$$B(\tau_c) = \left[ \frac{\tau_c}{(1 + \omega_0^2 \tau_c^2)} + \frac{4\tau_c}{(1 + 4\omega_0^2 \tau_c^2)} \right]$$  \hspace{1cm} (3.4)

The prefactors $C_1$ and $C_2$ may be different for the two distinct rotors and determine the depth of the corresponding $T_1$ minima. Due to the tunnel splitting of the weakly hindered methyl rotor being of the same order as the nuclear Zeeman splitting at 24 MHz NMR proton frequency, the Haupt term has been introduced as well according to [29]. This term is added to each of the methyl group $T_1$ contributions given in equation 3.4 above and is equal to

$$B_{\text{Haupt}}(\tau_c) = \frac{\tau_c}{(1 + (\omega_0 - \omega_t)^2 \tau_c^2)} + \frac{4\tau_c}{(1 + (2\omega_0 - \omega_t)^2 \tau_c^2)}$$

$$+ \frac{\tau_c}{(1 + (\omega_0 + \omega_t)^2 \tau_c^2)} + \frac{4\tau_c}{(1 + (2\omega_0 + \omega_t)^2 \tau_c^2)}$$  \hspace{1cm} (3.5)

At atmospheric pressure, the more strongly hindered methyl group corresponding to the high-temperature minimum has a tunnel splitting of 70 kHz (measured very accurately using the stir-scan technique, see page 28). We can determine the barrier height $V(70 \text{ kHz})$ corresponding to the splitting $\hbar \omega_t = 70 \text{ kHz}$ by calculating the theoretical tunnel splitting as function of $V$. Figure 3.15 shows the theoretical $T_1$-temperature dependence for $V(70 \text{ kHz})$ for the highly hindered methyl group whilst fitting the observed low temperature minimum of the weakly hindered methyl rotor.

Clearly, in figure 3.15, there is a significant discrepancy between the theoretical high temperature $T_1$ minimum and the experimentally observed one. Since the error bars in the high-temperature $T_1$ measurements are relatively small ($\Delta \Theta^{-1} = \pm 8 \times 10^{-4} \text{ K}^{-1}$ and $\Delta T_1 = \pm 0.015$ secs for $\Theta^{-1} = 0.0085 \text{ K}^{-1}$ and $T_1 = 0.05$ secs) this is a strong indication that the corresponding methyl rotor does not face a simple three-fold hindering potential, but a potential with six- (and possibly higher) -fold contributions as well. This has been observed before [30]. The dynamics are
Figure 3.15: Observed $T_1$-temperature dependence of Methyl Acetate at atmospheric pressure with the theoretical fit. The dynamics of the highly hindered methyl rotor corresponding to the high temperature (leftmost) minimum apparently are not modelled well by a simple 3-fold hindering potential.

hence modelled with a hindering potential consisting of three-fold ($V_3$) and six-fold ($V_6$) contributions, assuming the two to be in phase ($0^\circ$) or out-of-phase ($180^\circ$) by adding or subtracting their terms. Of course, there is an infinite number of shapes of the hindering potential when allowing for intermediate phase differences $\alpha$ between the three- and six-fold contributions. For the quantitative analysis presented here it is sufficient to confine the possible values for $\alpha$ to 0 and $180^\circ$.

Modelling the methyl group dynamics with the modified hindering potential for a range of values of $V_3$ and $V_6$ results in a unique combination of $V_3$ and $V_6$ for which the calculated tunnel splitting $\hbar\omega_t$ matches the observed one and the $T_1$ minima align. For Methyl Acetate at atmospheric pressure, values of $V_3 = 1048$ K and $V_6 = 873$ K correspond to a good fit of the high temperature minimum and yield the measured tunnel splitting $\hbar\omega_t = 70$ kHz. The fit is shown in figure 3.16.

At elevated hydrostatic pressures we expect the $T_1$ minima to shift in temperature since the tunnel splittings of the corresponding methyl rotors are affected by the pressure-induced change in the hindering potential. Whilst fitting the high temperature minimum for higher pressures,
Figure 3.16: Methyl Acetate at atmospheric pressure - the high temperature minimum can be fitted by introducing a 6-fold contribution to the hindering potential.

the ratio of 6-fold to 3-fold contributions in the hindering potential has been kept constant at the same value determined at atmospheric pressure, namely

\[ R_{6:3} = R_{6:3}^{\text{(atmospheric)}} = \frac{873}{1048} = 83.3\% \] (3.6)

Figure 3.17 shows the experimentally obtained \( T_1 \)-temperature dependence at a hydrostatic pressure of 0.9 kBar, together with the theoretical fit indicated by the solid line. The fitting parameters are \( V_3 = 1000 \text{ K} \) and \( V_6 = 833 \text{ K} \) for the highly hindered methyl rotor and \( V_3 = 750 \text{ K} \) for the other methyl group. These correspond to a tunnel splitting of 114 kHz and 66.7 MHz, respectively. We recall that there is a gap in the measured tunnel splittings of the highly hindered rotor for \( \hat{p} \) elevated pressures up to 1.5 kBar due to a fast \( T_1 \) relaxation at low field (as pointed out on page 32) which may probably be attributed to a minor structural phase transition in that pressure range. The splitting of 114 kHz deduced from the \( T_1 \) data at 0.9 kBar is in line with the exponential decrease of \( \hbar \omega_t \) with pressure as measured above 1.5 kBar employing stir-scan techniques (this splitting is included in figure 3.13, page 35 as a square symbol). Hence we may expect the discontinuity (caused by a structural phase transition?) in the pressure dependence of the observed smaller tunnel splitting to be below 0.9 kBar.

Examining the low-temperature fit in figure 3.17, we find an apparently significant deviation of
Figure 3.18: Methyl Acetate at 0.9 kBar pressure: Spin-lattice relaxation time measurements (symbols) and theoretical fit (line).

Figure 3.19: Methyl Acetate at 2.0 kBar pressure: Spin-lattice relaxation time measurements (symbols) and theoretical fit (line).

Figure 3.20: Methyl Acetate at 2.5 kBar pressure: Spin-lattice relaxation time measurements (symbols) and theoretical fit (line).

Figure 3.20: Methyl Acetate at 3.7 kBar pressure: Spin-lattice relaxation time measurements (symbols) and theoretical fit (line).

The fitting parameters for all five data sets are given in the table below.

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<th>$V_6[K]$</th>
<th>$C_1[s^{-2}]$</th>
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<th>$V_3[K]$</th>
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</tbody>
</table>

the theoretical curve and the measured values of $T_1$. This is, however, not of major concern since for very low temperatures ($\Theta < 50$ K) the measured relaxation times commonly appear independent of temperature ("frozen") due to the dominance of relaxation caused by impurities in the sample. Also, one has to realise that a very small temperature range will correspond to a significant variation on the inverse temperature axis for low temperatures, leading to large error bars for those measurements. The main objective is to fit the minima which fortunately occur at temperatures high enough to obtain an accurate fit with relatively small errors.

The $T_1$ data and the theoretical fits are shown for pressures 2.0 kBar (figure 3.18), 2.5 kBar (figure 3.19), and 3.7 kBar (figure 3.20).

The fitting parameters for all five data sets are given in the table below.

<table>
<thead>
<tr>
<th>$P$ [kBar]</th>
<th>$V_2$ [K]</th>
<th>$V_6$ [K]</th>
<th>$C_1$ [s$^{-2}$]</th>
<th>$\hbar\omega_1$ [kHz]</th>
<th>$V_3$ [K]</th>
<th>$C_2$ [s$^{-2}$]</th>
<th>$\hbar\omega_2$ [MHz]</th>
<th>$C_{Hpt}$ [s$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1048</td>
<td>873</td>
<td>$4 \times 10^9$</td>
<td>71</td>
<td>630</td>
<td>1.2 $\times 10^9$</td>
<td>176.5</td>
<td>6 $\times 10^7$</td>
</tr>
<tr>
<td>0.9</td>
<td>1000</td>
<td>833</td>
<td>$4 \times 10^9$</td>
<td>114</td>
<td>750</td>
<td>5.0 $\times 10^8$</td>
<td>66.7</td>
<td>6 $\times 10^7$</td>
</tr>
<tr>
<td>2.0</td>
<td>1035</td>
<td>862</td>
<td>$4 \times 10^9$</td>
<td>81</td>
<td>877</td>
<td>1.5 $\times 10^8$</td>
<td>25.6</td>
<td>6 $\times 10^7$</td>
</tr>
<tr>
<td>2.5</td>
<td>1052</td>
<td>877</td>
<td>$4 \times 10^9$</td>
<td>68</td>
<td>920</td>
<td>2.8 $\times 10^8$</td>
<td>18.6</td>
<td>6 $\times 10^7$</td>
</tr>
<tr>
<td>3.7</td>
<td>1085</td>
<td>904</td>
<td>$4 \times 10^9$</td>
<td>49</td>
<td>990</td>
<td>3.8 $\times 10^8$</td>
<td>11.6</td>
<td>6 $\times 10^7$</td>
</tr>
</tbody>
</table>
CHAPTER 3. EXPERIMENTAL RESULTS OF METHYL SYSTEMS

Figure 3.18: Methyl Acetate at 2.0 kBar pressure: Spin-lattice relaxation time measurements (symbols) and theoretical fit (line).

Figure 3.19: Methyl Acetate at 2.5 kBar pressure: Spin-lattice relaxation time measurements (symbols) and theoretical fit (line).
Figure 3.20: Methyl Acetate at 3.7 kBar pressure: Spin-lattice relaxation time measurements (symbols) and theoretical fit (line).

The error in the fitting parameters associated with the second methyl group is comparatively large since at elevated pressures the corresponding low temperature minimum shifts to a position very close to the high temperature minimum of the other rotor, making it difficult to accurately resolve its position. The inconsistency of the $C_2$ fitting parameters for various pressures is a result of the attempt to fit the depth of the minimum by varying $C_2$. Since the minimum is not well observed for elevated pressures, these values should be treated with caution. Also it can be noticed that at higher pressures the relaxation times for temperatures below 55 K have a constant, but significantly reduced value. This remains unexplained and could be due to the effect of impurities in the sample becoming dominant at very low temperatures or due to effects caused by the Helium (used as the pressure medium) solidifying at higher temperatures for these pressures.

As shown in the table above, the prefactors $C_1$ and $C_2$ which determine the depth of the respective $T_1$ minima show different pressure dependencies. $C_1$ corresponding to the highly hindered methyl rotor is independent of pressure. This can also be clearly seen by examining the depth of the high temperature minimum which is equal for all pressures. The second rotor, however, corresponds to a minimum of varying depth, most probably due to the significant shift in the associated temperature $\Theta_{\text{min}}$. The dependence of the different hindering potential
parameters on pressure is illustrated in figures 3.21 and 3.22.

![Graph](image)

Figure 3.21: The three- and six-fold hindering potential contributions for the highly hindered rotor exhibit linear dependence on pressure for pressures above the range of 0.0 - 0.9 kBar where a phase transition results in a discontinuity of these parameters. The lines are provided as a guide to the eye.

The hindering potentials associated with the highly hindered rotor I as deduced from the $T_1$ data increase linearly with applied pressure above 0.9 kBar. For the other rotor II the hindering potential also increases with applied pressure but does not exhibit a linear pressure dependence, probably due to simultaneous inter- and intra-molecular contributions. As mentioned above, large error bars are associated with the rotor II results. Nevertheless, it is possible to deduce the effect of increasing hydrostatic pressure on the molecular dynamics of this group. As pressure is increased, the group faces a higher hindering potential and therefore exhibits a smaller tunnel splitting.

It is often possible to relate the variation of the observed tunnel splitting with pressure to structural changes induced by applied pressure. This is discussed in the following section.

### 3.2.2 Structural considerations

At pressures greater than 1.5 kBar the observed small tunnel splitting $\nu_t$ of Methyl Acetate decreases exponentially with increasing pressure, as shown in figure 3.13 above. Hence we can
fit the measured tunnel splitting to the expression

\[ \nu_t(P) = \nu_t(0) \exp \left( -\frac{P}{P_0} \right) \]  

where \( P \) is the hydrostatic pressure in kBar, \( P_0 = 3.1 \text{ kBar}^{-1} \), and \( \nu_t(0) = 140 \text{ kHz} \). Notice that \( \nu_t(0) \) is the extrapolated atmospheric pressure value and not the observed one, since there is a discontinuity in \( \nu_t \) at pressures below 1.5 kBar.

Furthermore, calculation of the energy levels as a function of the hindering potential \( V \) shows that in the highly hindered regime (\( V \gg 0 \)) \( \nu_t \) varies exponentially with \( V \) - as shown in figure 3.23 - which can be accurately fitted by the expression

\[ \nu_t(V) = 1.00 \times 10^6 \text{ kHz} \times \exp \left( -0.00517V \right) \]  

where \( \nu_t \) is in kHz and \( V \) is in Kelvin.

Deducing the corresponding hindering potential \( V \) for each measured tunnel splitting and examining the pressure dependence as shown in figure 3.24 shows a linear relation between the barrier height \( V \) and the applied hydrostatic pressure \( P \) - as one would expect by comparing equations 3.7 and 3.8, showing an exponential decrease of \( \nu_t \) with pressure \( P \) and barrier height.
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Figure 3.23: In the regime of highly hindered methyl reorientation the tunnel splitting $\nu_t$ decreases exponentially with hindering potential $V$

Figure 3.24: For highly hindered methyl groups, the barrier height deduced from the measured tunnel splitting increases linearly with applied pressure $P$ - the solid line is the linear fit referred to in the text $^\star$ $V = V_3 + V_6$
CHAPTER 3. EXPERIMENTAL RESULTS OF METHYL SYSTEMS

$V$, respectively. Therefore, following [13] and [14], we can express the barrier height as function of pressure according to

$$ V(P) = V(0) \times (1 + \alpha P) $$  \hspace{1cm} (3.9)

The parameter $\alpha$ is a structural parameter given by

$$ \alpha = \frac{1}{V(0)} \frac{\partial V}{\partial r} \frac{\partial r}{\partial P} $$  \hspace{1cm} (3.10)

where $r$ represents the distance of the methyl rotor from the source of the three-fold hindering barrier. The solid line in figure 3.24 is a fit of equation 3.9 with $V(0) = 1717.7$ K and $\alpha = 0.0363$ kBar$^{-1}$.

The barrier height is proportional to the first derivative of the inter-atomic potential, which is assumed to be of the form $Kr^{-n}$, leading to

$$ \alpha = -n + 1 \frac{\partial r}{r} \frac{\partial P}{\partial P} $$  \hspace{1cm} (3.11)

Introducing the bulk compressibility $\kappa = -(3/r)(\partial r/\partial P)$ gives

$$ \alpha = \frac{n + 1}{3} \kappa $$  \hspace{1cm} (3.12)

$\kappa$ for Methyl Acetate is unknown. However, values for $\kappa$ of Dimethyl Sulphide and also Terephthalic Acid have been deduced from high-pressure structure determination as part of this project, discussed further below, and the respective values $\kappa_{DMS}$ and $\kappa_{TA}$ are both equal to 0.0092 kBar$^{-1}$, which is in good agreement with the accepted typical value of $\kappa$ for molecular solids of 0.01 kBar$^{-1}$ [31]. Recalling $\alpha = 0.0363$ kBar$^{-1}$ from above, we get $n=9.89$. This value corresponds to intermolecular interactions between the methyl group and neighbouring atoms and is slightly smaller than (but of the same order as) the repulsive part of a Lennard-Jones type interatomic potential. Interactions of intra-molecular nature are usually pressure insensitive.

3.3 Dimethyl Urea - two independent Methyl Rotors

Dimethyl Urea is a symmetric molecule and its molecular configuration is illustrated in figure 3.25.
Although the molecule is symmetric, the arrangement of the molecules in the crystal structure causes the two methyl groups to face quite different hindering potentials. The position of the two corresponding minima in the temperature dependence of the NMR spin-lattice relaxation time $T_1$ suggests tunnel splittings of order 10 and 100 MHz for the two rotors, respectively. Both of these are well out of the energy range accessible by stir-scan techniques, but several attempts have been made to observe the splittings by field cycling procedures. Unfortunately, the results from the field cycling experiments were not conclusive since apparent tunnelling features could not be reproduced in consecutive runs. Hence only $T_1$ data is presented here.

**NMR Spin-Lattice Relaxation Time Measurements**

The temperature dependence of $T_1$ has been measured for hydrostatic pressures of 0.0, 2.5 and 4.0 kBar. The saturation-recovery technique has been employed as for the Methyl Acetate $T_1$-measurements described above. Figure 3.26 shows an attempt to fit the atmospheric data with purely 3-fold hindering potentials for the two distinct methyl rotors, employing a model identical to the one introduced for the two independent rotors of Methyl Acetate in the previous section. The three-fold hindering potential amplitudes $V_3$ for the two groups are 850 and 600 K, respectively.

By inspecting the high temperature $T_1$ minimum in figure 3.26 and its theoretical fit indicated by a solid line, we can see a quite significant difference in the adjacent gradients. The error bars on the high temperature data points are small (due to the experimental error in temperature of ±5 K resulting in very small errors in the inverse temperature plot for high temperatures). Hence we can interpret this discrepancy between the $T_1$ measurements and the theoretical fit as an indication that six-fold contributions to the hindering potentials exist. Figure 3.27 shows the same data fitted with hindering potentials consisting of three- and six-fold contributions. Similarly to the Methyl Acetate data presented in the previous section, we may attribute the poor fit in the low temperature regime to impurity effects "freezing in" the relaxation time at
Figure 3.26: Temperature dependence of the NMR spin-lattice relaxation time $T_1$ for Dimethyl Urea at atmospheric pressure. The solid line represents a fit assuming purely three-fold hindering potentials, showing discrepancies in the shape of the high temperature minimum, suggesting the existence of six-fold contributions as well.

Since the low temperature minimum is not clearly observed at atmospheric pressure, the associated hindering potentials are mainly an extrapolation from high pressure data, where this minimum is resolved much better. This is a nice example of the application of pressure allowing the clearer resolution of tunnelling features.

Figures 3.28 and 3.29 show the experimentally obtained $T_1$ temperature dependences and their theoretical fits at hydrostatic pressures of 2.5 and 4.0 kBar, respectively. The pressure dependence of the three- and six-fold contributions to the hindering potentials of the two distinct methyl rotors is illustrated in figure 3.30 (Methyl Group I) and figure 3.31 (Methyl Group II).
Figure 3.27: Dimethyl Urea at atmospheric pressure - $T_1$-temperature dependence with theoretical fit, now allowing for a six-fold contribution in the methyl rotor hindering potentials.

Figure 3.28: Spin-lattice relaxation time of Dimethyl Urea at 2.5 kBar pressure
Figure 3.29: Dimethyl Urea at 4.0 kBar pressure - $T_1$

Figure 3.30: Pressure dependence of the three- and six-fold contributions, $V_3$ and $V_6$, to the hindering potential of the more highly hindered methyl group I
Figure 3.31: Pressure dependence of the three- and six-fold contributions, $V_3$ and $V_6$, to the hindering potential of methyl group II

We can see that the three-fold hindering contribution increases linearly with hydrostatic pressure for both methyl rotors, whilst the six-fold term decreases linearly.

3.4 Dimethyl Sulphide - System of Coupled Rotors

Dimethyl Sulphide represents one of the main systems investigated in this project. It has attracted great interest in recent years, due to its relatively simple molecular structure (shown schematically in figure 3.32) and the fact that there are two methyl rotors present which may exhibit strong coupling.

Two distinct tunnel splittings of 100 kHz [32] and 750 kHz [33] have been observed previously at atmospheric pressure by NMR techniques. There are two possible explanations for the existence of the two tunnel splittings. The first assumes two distinct uncoupled methyl groups
facing different hindering potentials within the crystal structure and hence giving rise to two different tunnel splittings. The second allows for strong coupling between pairs of methyl rotors (which are either of the same molecule or not) and the resulting paired system gives rise to two observed tunnel splittings.

These two possibilities have been investigated in this project by extending the theory to account for possible strong coupling between the two methyl rotors and examining the tunnelling behaviour for hydrostatic pressures up to 4.5 kBar.

This work has been published in Molecular Physics [34].

3.4.1 NMR Stir-Scan Measurements

The Stir-Scan technique has been applied to measure the methyl tunnel splitting of Dimethyl Sulphide at 4.2 K temperature. Similarly to the Methyl Acetate results discussed above, the recovered magnetisation spectra have been normalised and inverted for presentation. Figure 3.33 shows a stir-scan spectrum obtained at 1.0 kBar pressure. The relaxation field $B_{\text{relax}}$ is equal to 13 mT.

![NMR Stir-Scan Spectrum of Dimethyl Sulphide at 1.0 kBar](image)

In analogy to the Methyl Acetate data presented above, we can identify the nuclear Zeeman transitions with $\Delta m = 1, 2$ giving rise to the peaks labelled $A$ and $B$, respectively. The peaks labelled $b-$ and $b+$ are tunnelling sidebands separated from their central peak $B$ by
\( h \omega_t(1) = 80 \text{ kHz} \), the smaller of the two tunnel splittings present in Dimethyl Sulphide. Due to the greater width of Larmor peak A, its tunnelling sidebands are not clearly observed. The other tunnel splitting, \( h \omega_t(2) = 750 \text{ kHz} \), gives rise to the peaks labelled 0 and Y, which are sidebands of the \( \Delta m = 0 \) and \( \Delta m = 1 \) transitions, respectively. Their respective transitions are normally not allowed but are observed here due to dipolar mixing occurring at low magnetic field. The two peaks labelled 0− and 0+ correspond to sidebands of the 0 sideband transition. Sideband of sideband transitions such as 0− and 0+ have not been reported before and their unprecedented observation suggests the presence of strong coupling between individual methyl rotors. This is discussed in more detail for the occurrence of sidebands of Y presented below. Again, the peak labelled H is due to a harmonic in the frequency generator signal and does not correspond to a tunnelling transition at 260 kHz.

Figure 3.34 shows a similar stir-scan spectrum recorded at a pressure of 0.7 kBar and a relaxation field of 10.6 mT.

![NMR Stir-Scan Spectrum of Dimethyl Sulphide at 0.7 kBar](image)

Figure 3.34: NMR Stir-Scan Spectrum of Dimethyl Sulphide at 0.7 kBar. The observation of sidebands of a tunnelling sideband corresponding to the peaks labelled y− and y+ is unprecedented and may be an indication of strong coupling occurring between methyl rotors.

The striking feature about this spectrum is the observation of the sidebands labelled y− and y+ which are separated from Y by the smaller tunnel splitting \( h \omega_t(1) \), whilst Y itself is a sideband of A with a separation of \( h \omega_t(2) \), the larger tunnel splitting. This is a second example of a sideband of a tunnelling sideband transition observed in a methyl tunnelling experiment.
Again, this observation may be of great significance since it indicates a possible strong coupling of methyl groups in Dimethyl Sulphide. This will be discussed in more detail further below. A few more examples of Dimethyl Sulphide stir-scan spectra obtained at various pressures are shown in figures 3.35–3.40 below. In total, 23 high-quality stir-scan spectra have been obtained from Dimethyl Sulphide.

The larger tunnel splitting $\hbar \omega_1(2) = 750$ kHz is independent of pressure. The pressure dependence of the smaller tunnel splitting is shown in figure 3.41. It decreases exponentially with applied hydrostatic pressure.

Application of the stir-scan technique in combination with applying hydrostatic pressure has provided an extremely powerful tool for measuring the small tunnel splittings associated with methyl group orientation in Dimethyl Sulphide whilst systematically changing the potential variation seen by the methyl groups. The unprecedented observation of sideband of sideband transitions indicates the possibility of strong coupling within pairs of methyl rotors in Dimethyl Sulphide, which is discussed in the following section.
Figure 3.36: Dimethyl Sulphide at 0.75 kBar. The smaller tunnel splitting is reduced to 90 kHz

Figure 3.37: NMR Stir-Scan Spectrum of Dimethyl Sulphide at 1.3 kBar with a smaller tunnel splitting of 70 kHz
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Figure 3.38: NMR Stir-Scan Spectrum of Dimethyl Sulphide at 2.2 kBar with $\omega_r(1)=55$ kHz

Figure 3.39: NMR Stir-Scan Spectrum of Dimethyl Sulphide at 2.7 kBar. The smaller tunnel splitting is about 40 kHz
Figure 3.40: NMR Stir-Scan Spectrum of Dimethyl Sulphide at 4.0 kBar. The smaller tunnel splitting is less than 35 kHz.

Figure 3.41: The pressure dependence of the smaller tunnel splitting $\hbar \omega_1(1)$ of Dimethyl Sulphide shows an exponential decrease with applied hydrostatic pressure. The other, larger tunnel splitting $\hbar \omega_1(2)$ is equal to 750 kHz for all pressures.
3.4.2 Theory: System of Coupled Methyl Rotors

In order to account for pair-wise coupling between methyl rotors we can extend the rotational Hamiltonian for a single methyl group (see page 9)

\[ \mathcal{H}_R = B \nabla^2 + V \]  

(3.13)

where \( B = -\left(\hbar^2/2I\right) \) with \( I = 5.31 \times 10^{-47} \) [kg m²] being the moment of inertia of the methyl group. The hindering potential term \( V \) for a single methyl rotor is

\[ V = \frac{V_0}{2} (1 - \cos 3 \phi) \]  

(3.14)

The extension to a pair of coupled rotors has been carried out previously by Aibout et al [35] to explain methyl coupling phenomena observed by neutron scattering and involves adapting the hindering potential \( V \) such that

\[ V = \frac{V_1}{2} (1 - \cos 3 \phi_1) + \frac{V_2}{2} (1 - \cos 3 \phi_2) + \frac{W}{2} (1 - \cos 3(\phi_1 - \phi_2)) \]  

(3.15)

where the subscripts 1 and 2 refer to the two methyl groups and \( W \) represents a coupling potential. Note that only two possible values for the phase difference between the hindering terms and the coupling term are accounted for here, namely \( \alpha = 0^\circ \) and \( \alpha = 180^\circ \). The latter is accommodated by allowing for negative values of \( W \). Naturally, there is an infinite number of configurations when allowing for any value of \( \alpha \) by assuming a hindering potential given by

\[ V = \frac{V_1}{2} (1 - \cos 3 \phi_1) + \frac{V_2}{2} (1 - \cos 3 \phi_2) + \frac{W}{2} (1 - \cos 3(\phi_1 - \phi_2 + \alpha)) \]  

(3.16)

However, for the analysis presented here it is sufficient to consider the more simple configurations of the two types of potential being in-phase or out-of-phase.

The possible extreme configurations for explaining the observed tunnelling spectra represent either a system of pairs of strongly coupled methyl rotors or very weak coupling between the methyl groups. The former corresponds to \( W \gg 0 \) and \( V_1 = V_2 = V \) whilst in the latter case \( W \approx 0 \) and \( V_1 \neq V_2 \).

3.4.3 Data Analysis: Strong and Weak Methyl Rotor Coupling

Pairs of Strongly Coupled Methyl Rotors

We shall firstly suppose that there is strong coupling between the methyl groups in Dimethyl Sulphide and hence \( W \gg 0 \) and \( V_1 = V_2 = V \).
Evaluation of the eigenvalues of $H_\pi$ using spatial basis functions $[1/(2\pi) \exp(i\phi_1) \exp(i\phi_2)]$ leads to four non-degenerate energy levels labelled $AA$, $AE^a$, $E^aE^b$ and $E^aE^a$ according to the rotational symmetry of the two methyl groups. For this particular analysis, the evaluation of the eigenvalues has been carried out for a range of $W$ and $V$ with $[-2000 \text{ K} < W < 2000 \text{ K}]$ and $[0 \text{ K} < V < 2000 \text{ K}]$. A Hamiltonian matrix size of 289x289 has been chosen in order to prevent loss of accuracy due to matrix size limitation.

At zero magnetic field, but accounting for spin, the $AA$ levels are 16-fold degenerate, the $AE^a$ levels are 32-fold degenerate and the $E^aE^b$ and $E^aE^a$ levels are each 8-fold degenerate, giving 64 levels in total. The four energy levels are shown schematically in figure 3.42. This figure also indicates the nomenclature for the four splittings as defined in [36].

Contour maps of constant tunnel splitting have been plotted in $(W,V)$ space for each of $\hbar\omega_0$, $\hbar\omega_1$, $\hbar\omega_2$ and $\hbar\Delta\omega$. Points have been sought in $(W,V)$ space at which all theoretical tunnel splittings match the observed splittings or simple sums or differences of them or at which the
theoretical splittings are outside the observable range taken as 20 to 1000 kHz. There is only one point for which these matching criteria are fulfilled with respect to the atmospheric pressure data. This is at \( W = 1857 \text{ K} \) and \( V = 420 \text{ K} \). The assignment of the splittings at this point is that the observed splitting \( \hbar \omega_1(1) = \hbar \omega_2 = 100 \text{ kHz} \) and \( \hbar \omega_1(2) = \hbar \Delta \omega = 750 \text{ kHz} \). \( \hbar \omega_0 \) is equal to 1.5 MHz and is outside the observable range and \( \hbar \omega_1 \) is equal to the sum of the two observed tunnel splittings \( \hbar \omega_1(1) \) and \( \hbar \omega_1(2) \) and is observable as the sideband of a sideband transition.

The application of hydrostatic pressure affects the observed smaller tunnel splitting \( \hbar \omega_1(1) \) whilst \( \hbar \omega_1(2) \) remains constant. A contour map of the region of interest in \((W,V)\) space is shown in figure 3.43.

![Contour map in (W,V) parameter space for splittings \( \omega_1, \omega_2 \) and \( \Delta \omega \). The contour labels are in kHz.](image)

Figure 3.43: Contour map in \((W,V)\) parameter space for splittings \( \omega_1, \omega_2 \) and \( \Delta \omega \). The contour labels are in kHz.

Close inspection of the contour map shows that the path taken in \((W,V)\) space, when increasing pressure from atmospheric \((\hbar \omega_2 = 100 \text{ kHz} \text{ and } \hbar \Delta \omega = 750 \text{ kHz}) \) to 4.0 kBar \((\hbar \omega_2 = 35 \text{ kHz} \text{ and } \hbar \Delta \omega = 750 \text{ kHz}) \), follows the \( \hbar \Delta \omega = 750 \text{ kHz} \) contour line which is approximately parallel to the coupling potential axis. We can hence conclude that the dominant effect of applied hydrostatic pressure is on the coupling potential only and not on the hindering potential. It
has been shown by Clough et al [37], using partial deuteration methods, that the two coupled methyl rotors cannot be on the same molecule. Moreover, it is likely that the coupling potential which must be of intermolecular origin is more sensitive to applied pressure than the hindering potential which is likely to have intramolecular origin.

Figure 3.44 shows the energy level diagram for a pair of strongly coupled methyl groups with the Zeeman interaction simply added. In this case, \( W = 1864 \) K and \( V = 420 \) K which corresponds to a pressure of 0.7 kBar.

![Energy levels and NMR transitions for pairs of strongly coupled methyl rotors in Dimethyl Sulphide. The diagram is calculated with parameters chosen to give the splittings observed at 0.7 kBar](image)

The vertical dotted line indicates the relaxation field \( B_{\text{Relax}} = 10.7 \) mT, the field at which the sideband of sideband transitions \( y^- \) and \( y^+ \) were observed (seen in figure 3.34 above). Closer inspection of the diagram shows that those transitions correspond to level crossings of the energy levels - this may explain the fact that the sideband of sideband transitions are only observed over a very narrow range of relaxation fields. It is also possible to assume that the dipolar interaction causes mixing of the states which causes the levels to anti-cross [37]. It is in the
regions of the anti-crossing where the rotational states are mixed that the additional transitions can be observed.

Very Weakly Coupled Methyl Rotors

The observed tunnelling characteristics of Dimethyl Sulphide have also been analysed by assuming very weak coupling between the methyl rotors. In the weak coupling regime the coupling potential $W \approx 0$. Two distinct methyl groups face different hindering potentials $V_1$ and $V_2$, corresponding to two methyl tunnel splittings $\hbar \omega(1)$ and $\hbar \omega(2)$. Diagonalization of the Hamiltonian matrix leads to an energy level diagram as shown in figure 3.45.

![Energy levels for a pair of very weakly coupled methyl groups](image)

Figure 3.45: Energy levels for a pair of very weakly coupled methyl groups (not drawn to scale). The sideband of sideband transitions are shown as well. The energies $\Delta_1$ and $\Delta_2$ correspond to rotations of methyl rotor 1 and 2, respectively. $\nu_0$ and $\nu_1$ are the two tunnel splittings.

All observed tunnel splittings can be accounted for with this model including the sideband of sideband transitions which are indicated in the diagram. Once again the observation of those
transitions over only a narrow range of relaxation fields is attributed to appropriate dipolar mixing and anti-level crossing.

Since the observed stir-scan tunnelling spectra can be explained by both models of strongly and weakly coupled methyl rotors it is difficult to distinguish between the two. This discussion is continued further below. For the moment, the analysis of the temperature dependence of the NMR spin-lattice relaxation time $T_1$ will be considered as a possible aid in determining the degree of coupling between methyl rotors in Dimethyl Sulphide.

### 3.4.4 Spin-Lattice Relaxation $T_1$

The NMR spin-lattice relaxation time, and in particular its temperature dependence, may provide information about the tunnelling characteristics, as already demonstrated for Methyl Acetate and Dimethyl Urea above. The $T_1$-temperature dependence of Dimethyl Sulphide at atmospheric pressure has been examined before [33] and an unusually broad minimum observed. Figure 3.46 shows the experimentally obtained temperature dependence of $T_1$ for atmospheric pressure as measured in this work.

![Graph showing the temperature dependence of the NMR spin-lattice relaxation time $T_1$ for Dimethyl Sulphide at atmospheric pressure.](image)

Figure 3.46: The temperature dependence of the NMR spin-lattice relaxation time $T_1$ for Dimethyl Sulphide at atmospheric pressure shows an unusually broad minimum.

A possible explanation for the broadness of the atmospheric $T_1$ minimum is that it is actually
an inadequately resolved double-minimum. This is confirmed by the high pressure data, such as for 4.5 kBar shown in figure 3.47.

Figure 3.47: $T_1$-temperature dependence at 4.5 kBar. The applied pressure makes the two tunnel splittings more unequal and hence separates the minima such that the double minimum can be resolved. The solid line indicates the (poor) theoretical fit assuming two uncoupled methyl groups with tunnel splittings of 30 and 750 kHz observed at 4.5 kBar.

This represents another nice example as to how the application of hydrostatic pressure aids in interpreting methyl tunnelling data. Also shown in figure 3.47 is the theoretical temperature dependence of the NMR spin-lattice relaxation time, assuming a pair of uncoupled methyl groups facing three-fold hindering potentials such that their tunnel splittings are equal to 30 kHz and 750 kHz as we would expect for that pressure. Apparently the fit is very poor - we can conclude that the model of weakly coupled methyl rotors fails in interpreting Dimethyl Sulphide $T_1$ data. The introduction of six-fold contributions to the hindering potential terms of the two methyl rotors may yield a good fit of the $T_1$ data, as shown for Methyl Acetate and Dimethyl Urea above. The analysis of the $T_1$ temperature dependence of Dimethyl Sulphide allowing for six-fold terms in the hindering potential is given further below, at this stage the strong coupling model shall be considered. Figure 3.48 shows an attempt to fit the data by assuming pairs of strongly coupled methyl rotors. The spin-lattice relaxation time $T_1$ for a pair of strongly coupled methyl rotors is calculated in analogy with the $T_1$ calculation for a single methyl rotor, the main difference lying in the calculation of the theoretical reorientation rate $\tau_c^{-1}$. We recall (from chapter 2, page 21)
that the reorientation rate $\tau_c^{-1}$ is calculated by evaluating the expectation value of the modulus of the angular momentum $<\Omega>$ of the excited states and subtracting that of the ground state. Since A states have no angular momentum only the E states $E^a$ and $E^b$ are considered and their angular momenta have equal and opposite values. Therefore, $\tau_c^{-1}$ for a single methyl rotor is given by

$$\tau_c^{-1} = \frac{3}{4\pi I} \sum_p \left( <\Omega >_1 + 3p - <\Omega >_1 \right) \exp \left( \frac{-E_{1+3p}}{k_B \Theta} \right)$$

where

$$<\Omega >_p = \hbar \sum_m c_{pm}^2 m.$$  

For a pair of strongly coupled methyl rotors, there are eight different symmetry combinations which may have a total of three different values for the modulus of the angular momentum. Therefore, the symmetry species are grouped into three groups of equal modulus of the angular momentum: $(E^a E^a, E^b E^b)$, $(E^a E^b, E^b E^a)$ and $(E^a A, E^b A, AE^a, AE^b)$. In analogy with the expression for $\tau_c^{-1}$ for a single methyl rotor in equation 3.17 above, the molecular reorientation rate for a pair of strongly coupled methyl groups is therefore given by

$$\tau_c^{-1} = \frac{3}{4\pi I} \frac{A}{B}$$

where

$$A = \sum_p \sum_q \left[ 2 \left( <\Omega >_{(3p+1)(3q+1)} - <\Omega >_{(1)(1)} \right) \exp \left( \frac{-E_{(3p+1)(3q+1)}}{k_B \Theta} \right) + 
2 \left( <\Omega >_{(3p+1)(3q-1)} - <\Omega >_{(1)(-1)} \right) \exp \left( \frac{-E_{(3p+1)(3q-1)}}{k_B \Theta} \right) + 
4 \left( <\Omega >_{(3p)(3q+1)} - <\Omega >_{(0)(1)} \right) \exp \left( \frac{-E_{(3p)(3q+1)}}{k_B \Theta} \right) \right]$$

and

$$B = \sum_p \sum_q \left[ 2 \exp \left( \frac{-E_{(3p+1)(3q+1)}}{k_B \Theta} \right) + 2 \exp \left( \frac{-E_{(3p+1)(3q-1)}}{k_B \Theta} \right) + 
4 \exp \left( \frac{-E_{(3p)(3q+1)}}{k_B \Theta} \right) \right].$$
The NMR spin-lattice relaxation time $T_1$ is then calculated from the reorientation rate as before, yielding the theoretical $T_1$-temperature dependence.

At 4.5 kBar, the coupling and hindering potential of strongly coupled methyl rotors is equal to $W=1880$ K and $V=420$ K, respectively. The resulting theoretical temperature dependence of the spin-lattice relaxation time also does not fit the experimentally observed one. Other than that it will always only show one minimum and not two as observed. Hence the strong coupling model also proves to be inadequate in explaining the spin-lattice relaxation time curve observed for Dimethyl Sulphide.

The analysis of the experimental tunnelling data obtained for Dimethyl Sulphide does not provide any conclusive evidence regarding the degree of coupling between the methyl rotors. On the one hand, we should expect strong coupling between the methyl rotors since firstly, the observation of sideband of a tunnelling sideband transitions, which are normally forbidden, are only observed over a narrow relaxation field range around 10.6 mT. This field corresponds directly to the magnetic field where a large number of level crossings occur in the strong coupling model, see figure 3.44 above, which seems more than a coincidence. These may be level anti-
crossings arising from dipolar mixing of the states - this undoubtedly increases the transition probabilities in this field range. Secondly, and with regard to the weak coupling model, the sideband transitions are individually forbidden for each group so that the sideband of sideband transitions are, in a sense, "doubly forbidden". Given that the groups are weakly coupled, it is difficult to see how sufficiently strong intergroup dipolar mixing can occur so as to make the transitions allowed. Finally, the fact that according to the strong coupling model only the coupling potential is affected by pressure seems to be in agreement with the fact that pressure primarily affects inter-molecular interactions rather than intra-molecular potentials.

Nevertheless, it is not possible to explain the existence of two minima in the temperature dependence of the NMR spin-lattice relaxation time by assuming strong coupling between pairs of rotors since the coupled pair constitutes the only contribution to $T_1$ and will hence result in a single minimum. We shall hence introduce a six-fold contribution in the hindering potential for each methyl group and interpret the $T_1$ data in terms of uncoupled methyl rotors with three- and six-fold hindering potential contributions. The assumption made here that the methyl rotors are independent of each other leads to the coupling parameter $W$ being equal to 0 for this analysis. Although the $T_1$ data is fitted quite well with this approach, caution should be exercised in accepting this model since it does not allow for coupling between the methyl rotors which should exist due to the reasons stated above. The main problem here is the fact that it is not possible to obtain an independent measure of the three- and six-fold contributions to the hindering potential. Regarding the observed tunnelling spectra, we may assume that after introducing an additional parameter for the hindering potential (the six-fold contribution) it will still be possible to account for all observed tunnelling transitions. The detailed energy level analysis is therefore omitted here, both for the case of allowing for six-fold hindering potential contributions and for the case of assuming phase differences other than $0^\circ$ or $180^\circ$ of the individual hindering- and coupling-potential contributions.

The temperature dependences of the spin-lattice relaxation time $T_1$ for Dimethyl Sulphide at pressures 4.5, 2.0 and 0.0 kBar are shown below.

The combinations of three- and six-fold contributions in the hindering potential of each methyl rotor are found by matching the theoretical tunnel splitting with the experimentally observed one (known from stir-scan experiments) and finding the best fit for the corresponding $T_1$ minimum. Naturally there is an infinite number of $(V_3, V_6)$ pairs which will give the required splitting. A range of these parameters will result in a reasonable fit of the corresponding $T_1$ minimum, the width of the range being defined by the error bars in the $T_1$ data. In order to illustrate
CHAPTER 3. EXPERIMENTAL RESULTS OF METHYL SYSTEMS

Figure 3.49: $T_1$-temperature dependence at 4.5 kBar. A good fit is achieved by allowing for six-fold contributions in the hindering potentials of weakly coupled methyl groups.

Figure 3.50: $T_1$-temperature dependence of Dimethyl Sulphide at 2.0 kBar, allowing for six-fold contributions in the hindering potentials.
CHAPTER 3. EXPERIMENTAL RESULTS OF METHYL SYSTEMS

Figure 3.51: \( T_1 \)-temperature dependence at atmospheric pressure, allowing for six-fold contributions in the hindering potentials.

this, contour maps with the observed splittings drawn as constant energy contours in \((V_3, V_6)\) parameter space are shown in figures 3.52 to 3.54 below. The range of hindering potential combinations giving a reasonable fit of \( T_1 \) are indicated as well.

The hindering potential parameters for the three different pressures are summarized in the tables below. Since the individual rotors are assumed to be independent of each other, the coupling parameter \( W \) is equal to 0.

<table>
<thead>
<tr>
<th>P[kBar]</th>
<th>( V_3[K] )</th>
<th>( V_6[K] )</th>
<th>( h\omega_t(1)[kHz] )</th>
<th>( V_3[K] )</th>
<th>( V_6[K] )</th>
<th>( h\omega_t(2)[kHz] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1450 ± 95</td>
<td>350 ± 100</td>
<td>100</td>
<td>1170 ± 70</td>
<td>273 ± 74</td>
<td>750</td>
</tr>
<tr>
<td>2.0</td>
<td>1525 ± 75</td>
<td>370 ± 80</td>
<td>60</td>
<td>1092 ± 78</td>
<td>361 ± 89</td>
<td>750</td>
</tr>
<tr>
<td>4.5</td>
<td>1606 ± 74</td>
<td>425 ± 75</td>
<td>30</td>
<td>990 ± 80</td>
<td>479 ± 95</td>
<td>750</td>
</tr>
</tbody>
</table>

3.4.5 Determination of the Structure of Dimethyl Sulphide by Neutron Diffraction

The structure of Dimethyl Sulphide has been determined for the first time as part of this project. This work has been carried out on the High Resolution Powder Diffractometer (HRPD) [38] at the ISIS facility which is part of the Rutherford Appleton Laboratory in Chilton, Oxfordshire,
Figure 3.52: Contour map of the splittings observed in Dimethyl Sulphide at atmospheric pressure, drawn in \((V_3, V_6)\) space. The contour labels are in kHz. The shaded area indicates the range of values for \((V_3, V_6)\) which yield an acceptable \(T_1\) fit within errors, with the boundaries and optimal fit point indicated by crosses.

Figure 3.53: Contour map similar to figure 3.52, corresponding to the 2.0 kBar \(T_1\) fit
in collaboration with Dr RM Ibberson, who is the HRPD instrument scientist. This structure determination is the most complex carried out to date using powder diffraction in terms of the number of independent atoms.

Two time-of-flight neutron diffraction spectra have been obtained for (Dimethyl Sulphide)-d6 at 5 K temperature, one at atmospheric pressure and the other at 2.0 kBar. For the former, backscattering data was analysed whilst for the latter the analysis was confined to 90°-bank data due to the aluminium high pressure sample cell giving rise to numerous peaks especially in the backscattering spectra.

The analysis and structure refinement were carried out according to the Rietveld method [39], using a program suite adapted to neutron time-of-flight measurements. The unit cell is triclinic, with centrosymmetric space group $P1\*$. The neutron diffraction spectrum recorded at atmospheric pressure is shown in figure 3.55 (diamond symbols) with its fit resulting from the structure refinement (solid line).

The unit cell parameters deduced from the ambient- and 2.0 kBar pressure data are listed in the table below, where $V$ indicates the unit cell volume.

<table>
<thead>
<tr>
<th>$P$ [kBar]</th>
<th>$a$ [Å]</th>
<th>$b$ [Å]</th>
<th>$c$ [Å]</th>
<th>$\alpha$ [°]</th>
<th>$\beta$ [°]</th>
<th>$\gamma$ [°]</th>
<th>$V$ [Å³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.5456</td>
<td>6.3265</td>
<td>5.8172</td>
<td>113.10</td>
<td>93.57</td>
<td>104.00</td>
<td>179.31</td>
</tr>
<tr>
<td>2.0</td>
<td>5.5267</td>
<td>6.2566</td>
<td>5.7802</td>
<td>112.89</td>
<td>93.60</td>
<td>103.88</td>
<td>176.01</td>
</tr>
</tbody>
</table>

* and contains two molecules.
Figure 3.55: Neutron Diffraction time-of-flight spectrum of Dimethyl Sulphide at 5 K temperature and atmospheric pressure, recorded on HRPD (diamond symbols) and its fit resulting from the structure refinement (indicated by solid line). The line in the bottom part of the graph is the residual obtained by subtracting experimental and theoretical values and translating it 20 units down the y-axis for clarity.
The bulk compressibility $\kappa$ is given by

$$\kappa = \frac{1}{V} \times \frac{\partial V}{\partial P}$$

(3.22)

where $V$ denotes the unit cell volume and $P$ is the hydrostatic pressure. Substituting the values for Dimethyl Sulphide from the table above yields the bulk compressibility for Dimethyl Sulphide

$$\kappa = \frac{1}{179.31} \times \frac{(179.31-176.01)}{2.0} \text{[kBar}^{-1}] = 9.20 \times 10^{-3} \text{kBar}^{-1}.$$  

(3.23)

This value compares very well with the widely accepted typical value for the bulk compressibility $\kappa$ for molecular solids of 0.01 kBar$^{-1}$ [31]. Due to additional peaks arising from the high pressure cell, along with Helium diffraction peaks caused by the solidified Helium (used as pressure medium), the high pressure structure refinement is less accurate. Only the unit cell parameters could be deduced with high accuracy (errors range in last digit in the unit cell parameter table above). The fractional atomic coordinates for Dimethyl Sulphide at atmospheric pressure and 5 K are listed in the following table.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.373(6)</td>
<td>0.234(7)</td>
<td>0.107(0)</td>
</tr>
<tr>
<td>C1</td>
<td>0.240(3)</td>
<td>0.127(7)</td>
<td>-0.232(1)</td>
</tr>
<tr>
<td>C2</td>
<td>0.187(4)</td>
<td>0.438(1)</td>
<td>0.240(6)</td>
</tr>
<tr>
<td>D11</td>
<td>0.274(4)</td>
<td>0.279(5)</td>
<td>0.717(3)</td>
</tr>
<tr>
<td>D12</td>
<td>0.038(0)</td>
<td>0.043(5)</td>
<td>0.738(2)</td>
</tr>
<tr>
<td>D13</td>
<td>0.336(0)</td>
<td>0.000(8)</td>
<td>0.663(2)</td>
</tr>
<tr>
<td>D14</td>
<td>0.242(1)</td>
<td>0.513(5)</td>
<td>0.446(1)</td>
</tr>
<tr>
<td>D12</td>
<td>0.223(9)</td>
<td>0.576(2)</td>
<td>0.171(3)</td>
</tr>
<tr>
<td>D23</td>
<td>-0.011(8)</td>
<td>0.344(0)</td>
<td>0.184(9)</td>
</tr>
</tbody>
</table>

An impression of the structure of Dimethyl Sulphide at atmospheric pressure is illustrated graphically in figure 3.56.

One interesting result from the structure determination with respect to the molecular dynamics is that the nearest neighbours to each methyl group is always another methyl group, rather than a Sulphide atom. This confirms the high probability that the methyl rotors are interacting and possibly coupled, as suggested by the NMR data. A detailed analysis of the correlation of the inter-atomic distances and the observed tunnelling parameters is carried out for hydrogen bond dynamics, which are discussed in the following chapters.
Figure 3.56: Illustration of the structure of Dimethyl Sulphide at ambient pressure.
Chapter 4

Theory of Hydrogen Bond Dynamics

4.1 Introduction to the Dynamics of Hydrogen Bond Systems

4.1.1 Importance of Hydrogen Bond Systems

Hydrogen bond dynamics represent another very interesting type of molecular reorientation. However, the motion involved is more of a translational nature rather than the rotational dynamics described by methyl groups. There are two main aspects which emphasise the fundamental importance of hydrogen bond dynamics. Firstly, the hydrogen bond is a very important entity in chemical, biochemical and biological systems. In particular, understanding the transfer of the constituent protons from one location to another within the hydrogen bond may play a key role when considering the overall kinetics of these systems. The other aspect of the great importance of hydrogen bond dynamics is that a hydrogen bond provides a relatively simple system of a small particle being subjected to a potential energy surface which is of great interest generally to any condensed matter scientist. As for rotational methyl group dynamics discussed in the previous chapters, hydrogen bond dynamics may exhibit a transition from purely quantum mechanical tunnelling at low temperatures to classical hopping at elevated temperatures - a phenomenon which continues to stimulate great interest. Since at low temperatures the hydrogen bond dynamics are of purely quantum mechanical nature and the particles exhibit phonon activated tunnelling motion, a classical description of the dynamics is inadequate for this regime. At high temperatures, however, the dynamics are described by thermally assisted classical hopping. Great interest has evolved to describe the transition from one regime to the other and to find a model which spans both regimes.
4.1.2 Mechanism of Hydrogen Bond Dynamics of Carboxylic Acid Dimers

In this project, the study of hydrogen bond dynamics has been focused on the dynamics of double hydrogen bonds resulting from the formation of molecular dimers of carboxylic acids. This type of hydrogen bond dynamics can be envisaged as an exchange between two possible tautomers by rearrangement of the constituent hydrogen atoms, as shown in figure 4.1. The transfer of both hydrogen atoms and the change in electron configuration is commonly considered as being strongly correlated and may therefore be described as a one-dimensional problem. Along this single coordinate $x$, there is a variation of the potential energy seen by the protons and the two tautomer configurations correspond to two energy minima. Due to asymmetries in the surrounding structure those minima are commonly not of equal depth, resulting in an energy difference $A$ between the lowest lying energy states of each potential well. Figure 4.2 illustrates the potential energy variation and schematically shows the four lowest-lying energy levels.

\[
\begin{align*}
(1) & \quad C=O \quad \cdots \quad H \quad \cdots \quad O=\quad C \\
\text{O} & \quad \cdots \quad \text{H} \quad \cdots \quad \text{O} \\
(2) & \quad C=O \quad \cdots \quad \text{H} \quad \cdots \quad \text{O} \\
\text{O} & \quad \cdots \quad \text{H} \quad \cdots \quad \text{O} \\
\end{align*}
\]

Figure 4.1: Hydrogen bond dynamics involve the interchange between two tautomeric forms (1) and (2).

As indicated in figure 4.2, transformations between the two tautomeric forms (1) and (2) are associated with tunnelling through (or, at high temperatures: hopping over) the barrier between the two wells. Also, one may attribute rate constants $k_{12}$ and $k_{21}$ to forward and reverse tautomer transformations, respectively.
Figure 4.2: One-dimensional asymmetric double well used to describe the potential energy variation. $E_1$ and $E_2$ denote the two lowest lying energy levels, their difference is defined as the asymmetry $A$. $k_{12}$ and $k_{21}$ are the rate constants for forward and reverse transitions, respectively.
4.2 Modelling the Dynamics

4.2.1 Reorientation Rate $\tau_c^{-1}$

As stated earlier, one important feature of hydrogen bond dynamics is the transition from phonon assisted quantum tunnelling through the potential barrier at low temperatures to thermally assisted classical hopping over the barrier at high temperatures. Skinner and Trommsdorff [40] have derived expressions for the tunnelling rate as a function of temperature and their results are summarised here. For full details on their derivations the reader is referred to their paper since only the expressions for the tunnelling rate resulting from those derivations are of primary importance to the NMR data analysis presented further below.

At low temperature, the tautomer exchange is characterised by phonon-assisted quantum mechanical tunnelling with rate constants (the superscript L indicates the low temperature regime):

$$
\begin{align*}
  k_{21}^L &= k_0[n(\omega_{21}) + 1] \\
  k_{12}^L &= k_0[n(\omega_{21})]
\end{align*}
$$

where

$$
n(\omega) = \frac{1}{\exp\left(\frac{\hbar \omega_{21}}{k_B T}\right) - 1}.
$$

Here, a Debye density of states has been assumed and the energy $\hbar \omega_{21} = (E_2 - E_1)$ is equal to $A$, the asymmetry. $k_0$ is a constant related to the effective tunnelling matrix element, the coupling between the hydrogen bond system and the phonon bath and the Debye cut-off frequency. It is considered independent of temperature $T$ and its value will be determined as part of the data fitting procedure. The functional form of $k_0$ is stated here for completeness, as derived in [40].

$$
k_0 = \frac{3\pi}{2} p^2 \left(\frac{J}{\hbar \omega_D}\right)^2 \omega_{21}
$$

Here, $p$ is a dimensionless phonon coupling parameter, $J$ is the tunnelling matrix element and $\omega_D$ is the Debye cut-off frequency. The forward and reverse rate constants $k_{12}$ and $k_{21}$ have to satisfy the detailed balance condition

$$
\frac{k_{12}}{k_{21}} = \exp\left(-\frac{\hbar \omega_{21}}{k_B T}\right) = \exp\left(-\frac{A}{k_B T}\right)
$$
At high temperature, thermally activated classical hopping across the barrier dominates the dynamics and the rate constants follow an Arrhenius law \([41]\) such that

\[
k^H_{12} = \tau_0^{-1} \exp \left( \frac{-V}{k_BT} \right) \quad (4.6)
\]

\[
k^H_{21} = \tau_0^{-1} \exp \left( \frac{-(V - A)}{k_BT} \right) \quad (4.7)
\]

where \(\tau_0^{-1}\) is the pre-exponential factor in the Arrhenius rate law, the superscript \(H\) indicates the high temperature regime and \(V, A\) are the activation energy (to an excited state) and the asymmetry \((E_2 - E_1)\), respectively. \(V\) is normally considered equal to the potential barrier height, but since tunnelling will occur rapidly between excited energy states the effective value of \(V\) may be taken as the difference between the average energy of the first excited states \(E_3\) and \(E_4\) and the average energy of the lowest lying states \(E_1\) and \(E_2\). This energy difference, and therefore also \(V\), may be referred to as the activation energy.

This defines the rate constants in the low- and high-temperature regimes. In the intermediate temperature range the values of the rate constants are determined by simple interpolation:

\[
k_{21} = k^L_{21} + k^H_{21} \quad (4.8)
\]

\[
k_{12} = k^L_{12} + k^H_{12} \quad (4.9)
\]

The inverse of the correlation time \(\tau_c\) of the dynamics, \(\tau_c^{-1}\), is known as the reorientation rate and

\[
\tau_c^{-1} = k_{12} + k_{21} \quad (4.10)
\]

The correlation time \(\tau_c\) can be used to calculate a theoretical value of the NMR spin-lattice relaxation time \(T_1\) for a given temperature. This is discussed in the following section.

### 4.2.2 NMR Spin-Lattice Relaxation Time \(T_1\)

Look and Lowe \([42]\) originally derived a formula for proton transfer between inequivalent sites for interpreting NMR spin-lattice relaxation time measurements

\[
T_1 = \frac{(1 + a)^2}{aCB(\tau_c)} \quad (4.11)
\]
where
\[
a = \exp \left( \frac{A}{k_B T} \right) \tag{4.12}
\]
and
\[
B(\tau_c) = \frac{\tau_c}{(1 + \omega_0^2 \tau_c^2)} + \frac{4\tau_c}{(1 + 4\omega_0^2 \tau_c^2)} \tag{4.13}
\]

Here, \( C \) is a constant related to the lattice sum of dipole-dipole matrix elements and \( \omega_0 = 2\pi \nu_0 \) where \( \nu_0 \) is the proton NMR frequency.

Therefore, each value of the correlation time of the dynamics \( \tau_c \) can be used to obtain a theoretical value for the spin-lattice relaxation time \( T_1 \) for a given temperature. Hence we can model the NMR spin-lattice relaxation time \( T_1 \) as function of temperature for a given hydrogen bond system. Figure 4.3 shows the modelled \( T_1 \) against inverse temperature as an example, where values for a typical double hydrogen bond system of carboxylic acid dimers have been chosen.

Similar to methyl systems, the spin-lattice relaxation time typically shows a minimum in its temperature dependence. The parameters chosen for this example are given in the table below.

<table>
<thead>
<tr>
<th>Asymmetry ((E_2 - E_1))</th>
<th>( A )</th>
<th>100 ([K])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy ( V )</td>
<td>( 800 ) ([K])</td>
<td></td>
</tr>
<tr>
<td>Lattice Constant ( C )</td>
<td>( 3 \times 10^8 ) ([s^{-2}])</td>
<td></td>
</tr>
<tr>
<td>Tunnelling Constant ( k_0 )</td>
<td>( 2 \times 10^9 ) ([s^{-1}])</td>
<td></td>
</tr>
<tr>
<td>Arrhenius Rate Factor ( \tau_0 )</td>
<td>( 10^{-12} ) ([s])</td>
<td></td>
</tr>
<tr>
<td>Proton NMR frequency ( \omega_0 )</td>
<td>( 2\pi \times 24 ) ([MHz])</td>
<td></td>
</tr>
</tbody>
</table>

In order to analyse experimentally obtained \( T_1 \) data the modelled \( T_1 \) - temperature dependence is fitted to the observed data by adjusting all model parameters. For a given proton NMR frequency there are five fitting parameters. Although this may seem like an equation with too many variables, it is usually possible to determine all parameters with sufficiently high accuracy.

The lattice constant \( C \) can be calculated from the crystal geometry but since it represents a prefactor of \( T_1 \), a change in its value results in a vertical shift of the entire \( T_1 \) curve. Therefore, it is usually easy to determine \( C \) by fitting the absolute values of the experimentally obtained \( T_1 \) curve. The remaining four parameters may be attributed to the two regimes of high and low temperature. As shown below, \( k_0 \) and \( A \) are dominant in the low temperature regime whilst \( \tau_0 \) and \( V \) influence the high temperature dynamics. Looking at the expressions for the rate constants at low temperature (equations 4.1 and 4.2 above) and high temperature (equations 4.6 and 4.7 above), we recognise \( k_0 \) and \( \tau_0^{-1} \) as prefactors for the rate constants in the two domains,
CHAPTER 4. THEORY OF HYDROGEN BOND DYNAMICS

Figure 4.3: Example theoretical temperature dependence of the NMR spin-lattice relaxation time $T_1$ for a typical hydrogen bond system. The chosen parameters are given in the table respectively. The asymmetry $A$ which is normally much smaller than the activation energy $V$ plays an important role in the low temperature domain of quantum mechanical tunnelling whilst the classical hopping dynamics at high temperature depend on the activation energy $V$. This turns out to be of great advantage when fitting experimental $T_1$ data since it effectively reduces the number of parameters fitted at a time. A closer look at the $T_1$ expression in equation 4.11 above illustrates this pairwise association of the remaining four fitting parameters with the two extreme temperature regimes. This is accomplished by the following rearrangement of the $T_1$ expression, originally suggested by O'Reilly [43]. An initial approximation which is valid for the entire observed temperature range is required which is based on the fact that the smallest value of the reorientation rate $\tau_c^{-1}$ occurs at temperature $T = 0$ K where $\tau_c^{-1} = k_0$. For an NMR frequency of 24 MHz, the expected value of $k_0$ is at least a factor of 10 greater than $\omega_0$. Therefore,

$$\tau_c^{-1} \gg \omega_0 \quad (4.14)$$

for all temperatures. Hence,

$$\omega_0 \tau_c \ll 1. \quad (4.15)$$
Hence, we can approximate $B(\tau_c)$ given in equation 4.13 above to

$$B(\tau_c) \approx 5\tau_c. \quad (4.16)$$

Therefore, equation 4.11 becomes

$$T_1 \approx \frac{(1 + a)^2}{5aC} \times \frac{1}{5\tau_c}. \quad (4.17)$$

We can expand the expression for $\tau_c$ and rearrange equation 4.17 to identify the low- and high-temperature contributions in $T_1$. We firstly recall that

$$\frac{1}{\tau_c} = (k_{21}^L + k_{12}^L + k_{21}^H + k_{12}^H), \quad (4.18)$$

where (from equations 4.1, 4.2, 4.6 and 4.7 above)

$$k_{21}^L = k_0 \left[ \frac{1}{e^{k_BT} - 1} + 1 \right], \quad (4.19)$$

$$k_{12}^L = k_0 \left[ \frac{1}{e^{k_BT} - 1} \right], \quad (4.20)$$

$$k_{21}^H = \tau_0^{-1} e^{-\frac{V}{k_BT}}, \quad (4.21)$$

and

$$k_{12}^H = \tau_0^{-1} e^{-\frac{(V-A)}{k_BT}}. \quad (4.22)$$

Hence, equation 4.17 becomes

$$T_1 = \frac{(1 + a)^2}{5aC} \left[ k_0 \left[ \left( \frac{1}{e^{k_BT} - 1} + 1 \right) + \left( \frac{1}{e^{k_BT} - 1} \right) \right] \right.
+ \left. \tau_0^{-1} \left[ e^{-\frac{V}{k_BT}} + e^{-\frac{(V-A)}{k_BT}} \right] \right]. \quad (4.23)$$

Introducing

$$V_{av} = V - (A/2) \quad (4.24)$$

and making the substitutions

$$e^{-\frac{V}{k_BT}} + e^{-\frac{(V-A)}{k_BT}} = 2 e^{\frac{V_{av}}{2k_BT}} \cosh \left( \frac{A}{2k_BT} \right), \quad (4.25)$$
\[
\frac{e^{\frac{A}{k_B T}} + 1}{e^{\frac{A}{k_B T}} - 1} = \coth \left( \frac{A}{2k_B T} \right), \quad (4.26)
\]

and

\[
\frac{(1 + a)^2}{a} = 4 \cosh^2 \left( \frac{A}{2k_B T} \right) \quad (4.27)
\]

yields

\[
T_1 = \frac{4 \cosh^2 \left( \frac{A}{2k_B T} \right)}{5C} \left[ k_0 \left[ \coth \left( \frac{A}{k_B T} \right) \right] + 2\tau_0^{-1} e^{\frac{V_{av}}{k_B T}} \cosh \left( \frac{A}{k_B T} \right) \right]. \quad (4.28)
\]

We finally get (from equation 4.28)

\[
T_1 = \frac{4 \cosh^3 \left( \frac{A}{2k_B T} \right)}{5C} \left[ \frac{k_0}{\sinh \left( \frac{A}{2k_B T} \right)} \right]_{\text{Low Temp.}} + 2\tau_0^{-1} e^{\frac{V_{av}}{k_B T}} \left[ \right]_{\text{High Temp.}} \quad (4.29)
\]

Equation 4.29 above shows the low- and high-temperature contributions of \( T_1 \) quite clearly. Parameters \( k_0 \) and \( A \) determine the low temperature fit, whilst in the high temperature regime \( \tau_0^{-1} \) and \( V_{av} = V - (A/2) \) are the dominant fitting parameters. Figure 4.4 shows the individual contributions of the two terms, having chosen the same set of parameters as above (page 81); their linear addition results in the \( T_1 \) curve which is identical to the one shown in figure 4.3.

This clear distinction of the low- and high-temperature terms aids in fitting the experimentally obtained \( T_1 \)-temperature dependence since it allows the separate determination of pairs of fitting parameters by considering the high- and low-temperature regimes individually.

This method has been successfully employed in this project for fitting the \( T_1 \) data obtained with Terephthalic Acid as a sample. This is described in the following chapter.
Figure 4.4: Theoretical $T_1$-temperature dependence illustrating the low- and high-temperature contributions identified in equation 4.29. The resulting $T_1$ curve is identical to figure 4.3 with identical fitting parameters.
Chapter 5

Hydrogen Bond Dynamics:
Experimental Results

5.1 Terephthalic Acid

Terephthalic acid crystallises in two forms I and II, identified in the X-ray structure determination by Bailey and Brown [44]. There has been evidence to suggest that type I is more stable at low temperature. The molecular structure is schematically shown in figure 5.1.

![Molecular structure of Terephthalic Acid](image)

Figure 5.1: Molecular structure of Terephthalic Acid

Previous NMR measurements of the temperature dependence of the $^1$H spin-lattice relaxation time at atmospheric pressure have been reported by Meier et al [45] (NMR frequencies of 100 MHz and 25 MHz) and Horsewill and Aibout [46] (NMR frequency of 21 MHz).

5.1.1 NMR Spin-Lattice Relaxation Time Measurements

The temperature dependence of the $^1$H NMR spin-lattice relaxation time of Terephthalic Acid in powder form has been measured for various hydrostatic pressures up to 4.5 kBar. The theory for hydrogen bond dynamics discussed in chapter 4 has been employed to analyse the data. Figures 5.2 to 5.6 show the experimentally obtained $T_1$ curves with their respective theoretical fits indicated by solid lines.
Figure 5.2: Temperature dependence of the NMR spin-lattice relaxation time $T_1$ for Terephthalic Acid at atmospheric pressure. The solid line represents the theoretical fit with fitting parameters given in the text.

Figure 5.3: $T_1$-temperature dependence for Terephthalic Acid at 1.5 kBar
Figure 5.4: $T_1$-temperature dependence for Terephthalic Acid at 2.5 kBar

Figure 5.5: $T_1$-temperature dependence for Terephthalic Acid at 3.5 kBar. Extrapolation of the fitting parameters determined for lower pressure data yields the theoretical fit indicated by the solid line.
Figure 5.6: The $T_1$-temperature dependence for Terephthalic Acid at 4.5 kBar shows a discontinuity at around 0.012 K$^{-1}$. This is discussed in the text.

We can observe that, with increasing pressure, the $T_1$ minima become more shallow, the absolute values of $T_1$ at the minima increase, and the low temperature gradients decrease. We also notice that the $T_1$-temperature dependence obtained at 4.5 kBar, and to a lesser extend also at 3.5 kBar, shows a discontinuity at a temperature of around 85 K. The origin of this discontinuity remains unclear, one possible reason may be a minor structural phase transition which occurs at that temperature for pressures above $\approx 3.5$ kBar, due to the ratio of type I to type II structural forms reaching a "critical" value for that temperature at those pressures.

The theoretical fitting is done by modelling the dynamics for the low- and high-temperature regimes and then deducing the theoretical $T_1$-temperature dependence from the molecular re-orientation rate as described in the previous chapter. Additionally, the continuous variation of all fitting parameters with pressure is a criterion, especially for the data recorded at elevated pressures where larger error bars are associated with the fitting parameters. The lattice constant $C$ (which represents a prefactor of $T_1$) has been fixed for all datasets and is equal to $3.0 \times 10^8$ s$^{-2}$. This assumption of $C$ being independent of hydrostatic pressure over the range of pressures applied has also been made in [47]. Since $C$ is closely related to the dipolar interaction between nuclei which in turn has an inverse cube dependence on the inter-nuclear
distance, the change in $C$ due to pressure has a minimal effect on $T_1$ when considering a typical value of the compressibility of a molecular crystal of 0.01 kBar$^{-1}$ [31].

As described above, the asymmetry $A$ and the tunnelling constant $k_0$ determine the low temperature fit whilst the activation energy $V$ and the Arrhenius rate factor $\tau_0$ are dominant in the high temperature region. The fitting parameters for the various hydrostatic pressures are shown in the table below.

<table>
<thead>
<tr>
<th>$P$ [kBar]</th>
<th>$A$ [K]</th>
<th>$V$ [K]</th>
<th>$\tau_0$ [s]</th>
<th>$k_0$ [Hz]</th>
<th>$C$ [s$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>153</td>
<td>665</td>
<td>$6.5 \times 10^{-12}$</td>
<td>$1.38 \times 10^9$</td>
<td>$3.0 \times 10^8$</td>
</tr>
<tr>
<td>1.5</td>
<td>137</td>
<td>775</td>
<td>$2.3 \times 10^{-12}$</td>
<td>$3.20 \times 10^9$</td>
<td>$3.0 \times 10^8$</td>
</tr>
<tr>
<td>2.5</td>
<td>127</td>
<td>870</td>
<td>$1.2 \times 10^{-12}$</td>
<td>$4.50 \times 10^9$</td>
<td>$3.0 \times 10^8$</td>
</tr>
<tr>
<td>3.5</td>
<td>116</td>
<td>980</td>
<td>$0.8 \times 10^{-12}$</td>
<td>$5.75 \times 10^9$</td>
<td>$3.0 \times 10^8$</td>
</tr>
</tbody>
</table>

The pressure dependence of the fitting parameters is shown graphically in figure 5.7.
The error bars for the various fitting parameters at atmospheric pressure are estimated by assessing the goodness of fit for a range of values for each parameter. The relative errors are listed in the table below.

<table>
<thead>
<tr>
<th>$\Delta A$ [K]</th>
<th>$\Delta V$ [K]</th>
<th>$\Delta \tau_0$ [s]</th>
<th>$\Delta k_0$ [Hz]</th>
<th>$\Delta C$ [s$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm 6$</td>
<td>$\pm 25$</td>
<td>$\pm 0.7 \times 10^{-12}$</td>
<td>$\pm 0.8 \times 10^8$</td>
<td>$\pm 0.1 \times 10^8$</td>
</tr>
<tr>
<td>$\pm 4%$</td>
<td>$\pm 4%$</td>
<td>$\pm 11%$</td>
<td>$\pm 6%$</td>
<td>$\pm 3%$</td>
</tr>
</tbody>
</table>

For the measurements taken at 3.5 kBar these errors are larger due to the discontinuity observed more clearly at 4.5 kBar, giving rise to considerable difficulty in obtaining a good fit. Figure 5.8 illustrates the effect of varying a single fitting parameter within its given error range (percentages in table above) for the four fitting parameters $A$, $V$, $\tau_0$ and $k_0$, taking the 1.5 kBar data as an example.

One important observation is that the applied pressure gradually equalises the depth of the two potential minima, causing the asymmetry $A$ to decrease linearly with increasing hydrostatic pressure.

### 5.1.2 Deduction of the Molecular Reorientation Rate $\tau^{-1}$ from $T_1$ measurements

An alternative way to illustrate the temperature dependence of the molecular dynamics of a double hydrogen bond system is to present the variation of the molecular reorientation rate $\tau^{-1}$ with temperature. We recall (from chapter 4, page 79) that the NMR spin-lattice relaxation time is given by

$$T_1 = \frac{(1 + a)^2}{aCB(\tau_c)}$$

(5.1)

where

$$B(\tau_c) = \frac{\tau_c}{(1 + \omega_0^2 \tau_c^2)} + \frac{4\tau_c}{(1 + 4\omega_0^2 \tau_c^2)}$$

(5.2)

and $a$ is related to the asymmetry $A$ by $a = \exp (A/k_BT)$. $\omega_0$ is the NMR frequency which is fixed and $C$ is the lattice constant which can be calculated from the crystal geometry and is also independent of temperature. Inspection of equation 5.1 above identifies $(1/C)$ as a prefactor.
Figure 5.8: Variation of the different fitting parameters within their error ranges, illustrated for the $T_1$ data obtained for Terephthalic Acid at 1.5 kBar
of all $T_1$ values, and equation (4.29) indicates that $C$ is not strictly an independent variable. Therefore, the only other parameter needed to deduce $\tau_c$ from a value of $T_1$ measured at a given temperature $T$ is the asymmetry $A$. As shown in the previous section, the parameter $A$ determines the low temperature gradient of the $T_1$ temperature dependence and can be found as part of the fitting procedure by inspection of the low temperature $T_1$ data. Therefore, once the temperature-independent parameters $\omega_0$, $C$ and $A$ have been determined, the molecular reorientation rate $\tau_c^{-1}$ can be expressed as a function of $T_1$ and $T$, the temperature. This allows a "conversion" of experimental $T_1$ values measured at a temperature $T$ to the molecular reorientation rate $\tau_c^{-1}$, as shown in figure 5.9 for the atmospheric Terephthalic Acid data presented in the previous section, taking the same values of $C = 3.0 \times 10^5 \text{s}^{-2}$ and $A = 153 \text{K}$ as obtained during the initial $T_1$ fitting procedure.

![Graph](image_url)

Figure 5.9: Temperature dependence of the molecular reorientation rate $\tau_c^{-1}$ obtained by "converting" the experimental $T_1$ values obtained for Terephthalic Acid at atmospheric pressure.

The theoretical reorientation rate $\tau_c^{-1}$ according to Skinner and Trommsdorff [40] is equal to the sum of the low- and high-temperature rate constants for both forward and reverse motion,
as discussed in chapter 4, namely

$$\tau_c^{-1} = k_{12}^L + k_{21}^L + k_{12}^H + k_{21}^H$$  \tag{5.3}$$

Defining the low- and high-temperature contributions to the reorientation rate as $k_L = k_{12}^L + k_{21}^L$ and $k_H = k_{12}^H + k_{21}^H$, yields

$$\tau_c^{-1} = k_L + k_H.$$  \tag{5.4}$$

Figure 5.10 illustrates the low- and high-temperature contributions and the molecular reorientation rate $\tau_c^{-1}$ obtained by linear addition of the two, together with the values of the reorientation rate obtained by converting the experimental $T_1$ values as in figure 5.9.

Figure 5.10: The molecular reorientation rates for Terephthalic Acid at atmospheric pressure deduced from the $T_1$ measurements (symbols) and the theoretical reorientation rate $\tau_c^{-1}$ obtained by linear addition of the low- and high-temperature rate constants according to Skinner and Trommsdorff, all plotted as lines.

Figures 5.11 and 5.12 show the temperature dependence of the two reorientation rates for the data obtained at 1.5 and 2.5 kBar, respectively. The corresponding values of the asymmetry $A$ are 137 K and 127 K, as determined during the initial $T_1$ fitting procedure.
Figure 5.11: The molecular reorientation rates for Terephthalic Acid at 1.5 kBar

Figure 5.12: The molecular reorientation rates for Terephthalic Acid at 2.5 kBar
5.1.3 Structure Determination of Terephthalic Acid by Neutron Diffraction

The structure of (Terephthalic Acid)-d4 has been determined at 5 K temperature and hydrostatic pressures of 0.0, 2.0 and 4.1 kBar. This work has been carried out on HRPD [38], the High Resolution Powder Diffractometer which is part of the ISIS pulsed neutron facility at the Rutherford Appleton Laboratory (RAL). Similarly to the structure determination of Dimethyl Sulphide, this work has been carried out as part of this project in collaboration with Dr RM Ibberson at RAL.

In total three high-quality time-of-flight neutron diffraction spectra have been recorded for (Terephthalic Acid)-d4 in powder form, with a data collection time of 19 hours each. The high pressure spectra were recorded in the 90°-bank, due to the vanadium-alloy pressure cell giving rise to many diffraction peaks predominantly present in the backscattering spectra, additionally to peaks due to the solidified Helium present in the cell.

An initial analysis of the recorded spectra and a detailed structure refinement following the Rietveld method [39] were carried out using a program suite developed at RAL for neutron time-of-flight measurements. The unit cell of deuterated Terephthalic Acid is triclinic and centrosymmetric with space group P1. The ambient pressure structure has been determined previously at various temperatures by Fisher et al [48]. So far, only the unit cell parameters could be deduced with accuracy. Work is ongoing to refine the individual atomic positions more exactly by imposing constraints in bond lengths and -angles on the system. The unit cell parameters are listed in the table below, along with a comparison to the low temperature (2K) structure previously determined by Fisher et al [48], also using neutron powder diffraction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fisher et al [48]</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ambient 2K</td>
<td>Ambient 2.0 kBar</td>
</tr>
<tr>
<td>a [Å]</td>
<td>7.6966</td>
<td>7.6765</td>
</tr>
<tr>
<td>c [Å]</td>
<td>3.6628</td>
<td>3.6494</td>
</tr>
<tr>
<td>α [°]</td>
<td>92.98</td>
<td>92.93</td>
</tr>
<tr>
<td>β [°]</td>
<td>107.88</td>
<td>107.68</td>
</tr>
<tr>
<td>γ [°]</td>
<td>94.60</td>
<td>94.59</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>168.97</td>
<td>168.15</td>
</tr>
</tbody>
</table>

The slight discrepancies in the structural parameters obtained for ambient pressure and those previously published by Fisher et al are due to a slightly different temperature and the fact that HRPD provides a superior resolution, in fact the highest neutron powder diffraction resolution in the world.
Close inspection of the dependence of the unit cell volume $V$ on pressure shows that the relative volume change between 2.0 and 4.1 kBar pressure is much smaller than between ambient and 2.0 kBar, although the change in pressure is similar. This could be due a minor structural phase transition occurring above 2.0 kBar. Considering the change of volume of the unit cell between 0.0 and 2.0 kBar, we can deduce the bulk compressibility $\kappa$ of Terephthalic Acid for that pressure range according to

$$\kappa = \frac{1}{V} \times \frac{\partial V}{\partial P},$$

(5.5)

which yields $\kappa = 9.16 \times 10^{-3}$ kBar$^{-1}$ for pressures below 2 kBar. This compares extremely well to the value of $\kappa$ of $9.20 \times 10^{-3}$ kBar$^{-1}$ obtained for Dimethyl Sulfide (see chapter 3, page 73), and the commonly accepted value of $\kappa$ for molecular solids of 0.01 kBar$^{-1}$ [31].

A more detailed analysis of the pressure dependence of the Oxygen-Oxygen bond distances (which correspond to the hydrogen bond lengths) for Terephthalic Acid is still to follow once the necessary accuracy in the refined atomic positions is obtained. However, this analysis has been carried out successfully for Benzoic Acid as part of this project. Benzoic Acid is closely related to Terephthalic Acid and provides another very interesting system for the study of hydrogen bond dynamics of carboxylic acid dimers. Benzoic Acid will be examined in the following section.

### 5.2 Benzoic Acid: Correlation between Molecular Dynamics and Structure

#### 5.2.1 Introduction

The hydrogen bond dynamics of Benzoic Acid dimers have been studied extensively by NMR [49], neutron scattering [50] and infrared spectroscopy [51]. These centrosymmetric dimers are connected by a pair of hydrogen bonds in analogy with many other carboxylic acids. Figure 5.13 schematically shows the molecular structure of a Benzoic Acid dimer.

A high-pressure NMR study of the molecular dynamics in Benzoic Acid has been carried out earlier at Surrey [47]. Within the pressure range up to 3.3 kBar the barrier asymmetry $\Lambda$ deduced from NMR spin-lattice relaxation time $T_1$ measurements has been found to decrease with increasing hydrostatic pressure. Measurements have also been carried out above 4 kBar, where a very different $T_1$-temperature dependence has been observed, leading to an unexpectedly high value for the asymmetry $\Lambda$. In fact the extrapolation of the pressure dependence
Figure 5.13: Molecular structure of a Benzoic Acid dimer
of $A$ for pressures up to 3.3 kBar to higher pressures indicates that the asymmetry is zero at 4 kBar. This may result in a structural phase change at that pressure, resulting in the observed dramatic change of the $T_1$-temperature dependence and the high value of $A$ deduced from it. These observations have constituted the main motivation to examine the structural pressure dependence of Benzoic Acid dimers described in the following section.

### 5.2.2 Measurements of the Structure of Benzoic Acid Dimers

Neutron powder diffraction measurements of Benzoic Acid dimers have been carried out as part of this work at the ISIS facility at the Rutherford Appleton Laboratory in Chilton, Oxfordshire. This work has been done in collaboration with Dr AJ Horsewill, Dr DF Brougham and Mr A Ikrarn from Nottingham University and Dr RM Ibberson who is the instrument scientist of the High Resolution Powder Diffractometer (HRPD) [38] at ISIS, on which the structure experiment has been carried out. This work has been published [52].

The structure of Benzoic Acid at ambient pressure has been determined previously by Feld et al [53] by X-ray and neutron diffraction. Their most accurate data were recorded using X-ray diffraction at room temperature and thus represented the motionally averaged atomic positions of the two tautomeric configurations A and B. It has previously been demonstrated that at low temperature the A tautomer is predominantly populated [54]. In the structure determination presented here, the hydrogen bond compression with pressure was of primary interest. Therefore a more accurate determination of the atomic positions for the A tautomer was required and consequently the temperature lowered to 5 K.

The acquired diffraction data were analysed using a program suite adapted for neutron time of flight measurements and based on the Rietveld method [39]. The 5K structure of Feld et al [53] provided a starting point for the full structural refinement of the ambient pressure data. The sample exhibited strong intrinsic line broadening in addition to a high degree of peak overlap mainly due to the comparatively long $c$ lattice parameter. This limited the information that could be extracted from the powder profile and necessitated the use of weak bond length and angle constraints to assist convergence during the refinement. Respective phenyl C-C and C-D bond lengths were therefore restrained to be equivalent to within $\pm0.01$ Å and the C-C-C and C-C-D bond angles were restrained to be equal to within $\pm2^\circ$. The diffraction spectrum and its fit obtained at ambient pressure and 5K is shown in figure 5.14.

Some bond distances resulting from the detailed refinement of the acquired spectrum are shown in the table below and compared to the motionally averaged values found by Feld et al in [53].
Figure 5.14: HRPD neutron diffraction spectrum of Benzoic Acid obtained at ambient pressure and 5K temperature. The lower line represents the difference between the data and the theoretical values (residual), multiplied by a factor of 2.
The bond lengths are given in Angstroms.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(d^{\text{BA}}) at 5K (Neutron Diffraction)</th>
<th>(h^{\text{BA}}) at 295K (X-ray Diffraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(this work)</td>
<td>Feld et al [53]</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.467(7)</td>
<td>1.4843(15)</td>
</tr>
<tr>
<td>C(1)-O(1)</td>
<td>1.227(7)</td>
<td>1.2575(15)</td>
</tr>
<tr>
<td>C(1)-O(2)</td>
<td>1.304(7)</td>
<td>1.2675(15)</td>
</tr>
<tr>
<td>O(1)-O(2)</td>
<td>2.231(7)</td>
<td>2.2240(15)</td>
</tr>
<tr>
<td>O(1)-O(2)'</td>
<td>2.657(8)</td>
<td>2.6273(13)</td>
</tr>
<tr>
<td>O(2)-H(2)</td>
<td>1.037(11)</td>
<td></td>
</tr>
<tr>
<td>H(2)-H(2)'</td>
<td>2.263(14)</td>
<td></td>
</tr>
</tbody>
</table>

Although it was initially intended to cover a pressure range beyond 4 kBar to investigate the structural phase transition occurring at that pressure, the initial experiments were carried out up to 3.2 kBar, due to limitations imposed by the high pressure cell used. The structure of Benzoic Acid was determined at 5 K for hydrostatic pressures of 0.0, 0.72, 2.0 and 3.2 kBar. The unit cell is monoclinic over this pressure range with a \(P2_1/c\) space group. The corresponding unit cell has dimensions specified by the parameters \(a\), \(b\) and \(c\) where the angle between the \(a\) and \(c\) axes is given by \(\beta\) and the other angles between \(a\) and \(b\) and \(b\) and \(c\) are 90°. The unit cell parameters as function of pressure are shown in the table below. The high precision 0.0 kBar values in the top line were recorded in a vanadium can, the others were obtained in an aluminium pressure cell.

<table>
<thead>
<tr>
<th>(P) [kBar]</th>
<th>(a) [Å]</th>
<th>(b) [Å]</th>
<th>(c) [Å]</th>
<th>(\beta) [°]</th>
<th>Volume [Å(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.37934(3)</td>
<td>5.01378(2)</td>
<td>21.75674(11)</td>
<td>98.5264(4)</td>
<td>580.312</td>
</tr>
<tr>
<td>0.0</td>
<td>5.3798(4)</td>
<td>5.0145(1)</td>
<td>21.7590(3)</td>
<td>98.529(1)</td>
<td>580.513</td>
</tr>
<tr>
<td>0.72</td>
<td>5.3631(5)</td>
<td>5.0081(1)</td>
<td>21.7230(5)</td>
<td>98.673(2)</td>
<td>576.788</td>
</tr>
<tr>
<td>2.0</td>
<td>5.3311(8)</td>
<td>4.9948(1)</td>
<td>21.6616(8)</td>
<td>98.856(2)</td>
<td>569.926</td>
</tr>
<tr>
<td>3.2</td>
<td>5.3152(5)</td>
<td>4.9870(1)</td>
<td>21.6304(6)</td>
<td>98.977(2)</td>
<td>566.327</td>
</tr>
</tbody>
</table>

One feature in the pressure dependence of the unit cell parameters is that above 2 kBar there is a structural phase change present which is observed in all unit cell parameters \(a\), \(b\), \(c\), and \(\beta\). Figure 5.15 shows the pressure dependence of the unit cell volume. Due to the structural phase change only the cell volumes determined for pressures up to 2 kBar were fitted and show a linear decrease with applied hydrostatic pressure. \textit{Since pressure-induced structural phase transitions normally cause a decrease in unit cell volume, it is more likely that the measured pressure of 3.2 kBar is inaccurate. This inaccuracy may have been caused by the Helium in the sample probe stick solidifying before the main sample pressure could settle. This typically yields a higher pressure reading than actually present in the sample.}
CHAPTER 5. HYDROGEN BOND DYNAMICS: EXPERIMENTAL RESULTS

Figure 5.15: The unit cell volume of Benzoic Acid as function of pressure. A phase transition above 2 kBar results in a discontinuity in the cell volume.

For the high pressure cell measurements, only the unit cell parameters could be determined with sufficiently high accuracy. The presence of Bragg peaks from the aluminium pressure cell and solid helium reduced the information content in the diffraction spectra. However, despite the lack of information about the exact atomic coordinates at elevated pressures, a scaling procedure based on the accurate coordinates determined at atmospheric pressure (using the vanadium can) and the change of unit cell volume with pressure could be applied to determine the corresponding oxygen-oxygen distances $r(O\cdot O)$. It was assumed that pressures up to 3 kBar have no effect on the structure and bond distances of the monomer, the effect of pressure is to compress the inter-monomer distances only [52]. By letting the hydrogen bonds take up all the compression, the oxygen-oxygen distances $r(O\cdot O)$ could be calculated as function of pressure - this is shown in figure 5.16, revealing a linear relationship for pressures below the structural phase transition value.

5.2.3 The Correlation between the Hydrogen Bond Dynamics and the Hydrogen Bond Length $r(O\cdot O)$

An investigation of the pressure dependence of the hydrogen bond dynamics in Benzoic Acid has been published by Horsewill et al in [47]. Their analysis of the obtained temperature

\* along the O-O bond axis,
dependences of the NMR spin-lattice relaxation time is very similar to the one presented for Terephthalic Acid in section 5.1.1 above.

We recall that one of the fitting parameters, \( k_0 \), is related to the tunnelling matrix element whilst \( A \) represents the asymmetry between the two lowest lying energy levels in the two potential wells. We may introduce a parameter \( k_A \) given by

\[
k_A = k_0 h / A
\]  \hspace{1cm} (5.6)

This dimensionless parameter \( k_A \) determines the rate of incoherent tunnelling, and in the case of Benzoic Acid, increases exponentially with applied pressure [47]. Using the pressure dependence of \( k_A \) along with the calculated oxygen-oxygen distances presented in figure 5.16, we may determine the relationship between \( k_A \) and \( r(O \cdot O) \). This is shown on a log-linear plot in figure 5.17. Also included in the figure are values determined for Terephthalic Acid (TA) [48], [46] and Tetrafluoroterephthalic Acid (TFTA) [55].

Compression of the hydrogen bond by applied pressure, resulting in a linear decrease of \( r(O \cdot O) \), causes the incoherent tunnelling rate \( k_A \) to increase exponentially.

Figure 5.16: The oxygen-oxygen distance, \( r(O \cdot O) \), in Benzoic Acid decreases linearly with pressure until the phase transition occurs between 2 and 3.2 kBar.
Figure 5.17: The tunnelling rate parameter $k_A$ as function of oxygen-oxygen distance $r(O\cdot O)$. The filled symbols correspond to measurements where $r(O\cdot O)$ has been determined at low temperature (≤ 5 K), and the open symbols represent those determined at room temperature. Terephthalic Acid (TA) and Tetrafluoroterephthalic Acid (TFTA) values are shown as squares and triangles, respectively, and taken from references shown in the text. The solid and dotted lines represent the best fit for the 5 K and RT data, respectively, and are discussed in the text.
The solid line in figure 5.17 represents a fit to the function

\[ k_A = C \exp[-\rho r(O \cdot O)] \]  

(5.7)

where \( \rho = 806 \text{Å}^{-1} \) and \( C = 8.5 \times 10^{87} \). This behaviour can be attributed to the exponential increase in the tunnelling matrix element which is governed by the overlap of the eigenfunctions from the two potential wells. Thus as the hydrogen bond is compressed the tunnelling matrix element increases since the potential wells are brought into closer proximity. The tails of the eigenfunctions are of exponential shape and therefore their overlap integral increases exponentially with decreasing distance \( r(O \cdot O) \). The experimental value of the exponent, \( \rho \), will be of interest to theoretical studies of the hydrogen bond.

Also in figure 5.17, the values of the incoherent tunnelling rate \( k_A \) for Benzoic Acid derivatives TA and TFTA are shown against their respective oxygen-oxygen distances \( r(O \cdot O) \) (open data points). Note that the structural data for these compounds were recorded at room temperature. The two sets of data in figure 5.17 clearly have very similar gradients, although the two curves are offset by approximately 0.03 Å. The temperature at which \( r(O \cdot O) \) was recorded is the only difference between the two sets. The solid black square in the figure represents another TA data point based on \( r(O \cdot O) \) determined at 2 K [48] and is in excellent agreement with the Benzoic Acid data recorded at 5 K and temperature is confirmed as the origin of the offset.

At higher temperatures, despite an increase in \( r(O \cdot O) \) due to thermal expansion, the effects of dynamical averaging of the oxygen positions evidently give rise to an underestimate of the \( r(O \cdot O) \) distance in diffraction studies.

This study represents a nice example for the application of hydrostatic pressure providing a powerful tool to investigate the relationship between molecular structure and dynamics, particularly in the tunnelling regime. The strong correlation between the incoherent tunnelling rate \( k_A \) and the hydrogen bond length \( r(O \cdot O) \) suggests that there may be a universal law linking structure and dynamics for this class of materials.

### 5.3 Hydrogen Bond Dynamics in DNA Base Pairs

#### 5.3.1 Introduction

The combination of NMR and hydrostatic pressure undoubtedly forms a unique tool to sense the fine details of molecular dynamics whilst being able to systematically alter the molecular
CHAPTER 5. HYDROGEN BOND DYNAMICS: EXPERIMENTAL RESULTS

potentials. In the case of hydrogen bond dynamics, the application of pressure compresses the intermolecular hydrogen bond and the hereby induced change in asymmetry and activation energy governing the tautomer exchange can be derived from the NMR data. There is a multitude of exciting hydrogen bond systems to study which attract great interest, particularly in the fields of chemistry and biochemistry.

An example hydrogen bond system which is currently of greatest interest in biochemistry is the one formed by the interlinking of DNA bases to build base pairs. DNA bases are the building blocks of genetic information which is "stored" in the DNA double helix.

There are four different types of bases, Adenine (A), Thymine (T), Guanine (G) and Cytosine (C). Two possible pairs can be formed (by key-lock principle), namely A-T and G-C pairs. The bases are held together by hydrogen bonds, of which there are two for A-T pairs and three for G-C pairs.

Great interest is stimulated by the fact that the key to point mutations in genetic information lies in instabilities in the inter-base hydrogen bonds. These point mutations usually constitute a change or loss of genetic information which in turn may cause some malfunction of the cell, in particular cancer. The relevance to cancer research becomes more visible by the fact that every cancer is caused by a change in genetic information by at least one point mutation in the DNA. For a point mutation to occur, the hydrogen bonds within a base pair have to be broken, ie have to be instable for a short amount of time.

5.3.2 Adenine-Thymine Base Pairs: Proton Transfer along Hydrogen Bonds

Some attention has been given to the double hydrogen bond in A-T base pairs during this project. As shown in figure 5.18, two tautomeric forms AT and A*T* exist which correspond to the two different hydrogen bond configurations in analogy with other hydrogen bond systems studied.

As shown by Florian et al [56], the double proton transfer into the rare tautomeric structure A*T* leads to a notable shortening of distances between the heavy atoms forming the hydrogen bonds. Two important consequences arise. Firstly, the structural change in base pair geometry resulting from the shortening of the hydrogen bonds will lead to a structural instability of that base pair within the DNA double helix. Secondly, any shortening of the hydrogen bond lengths induced by applied hydrostatic pressure will favour the formation probability and stability of
In analogy with other hydrogen bond systems, Adenine-Thymine base pairs may form the rare tautomer $A^*T^*$ by double proton transfer along the hydrogen bonds.
It is however acknowledged that an energy difference of this order of magnitude is outside the range where hydrogen bond dynamics can normally be examined using NMR spin-lattice relaxation time measurement techniques, it was nevertheless thought worthwhile to investigate this system, both because of the uncertainty in the calculated energy differences, and also because of the possibility that hydrostatic pressure might bring transitions into an observable frequency range.
the rare tautomeric form $A^*T^*$. Chen and Prohofsky [57] demonstrated the fact that hydro-
static pressure primarily shortens the hydrogen bond lengths of the inter-base hydrogen bonds.
Scheiner [58] pointed out the observation that the proton transfer is assisted by hydrogen bond
compression.
This fact that hydrostatic pressure may enhance the tautomer exchange probabilities sufficiently
such that the associated parameters (like the asymmetry $A$ and the activation energy $V$) can be
determined at high pressure formed the main motivation for examining the dynamics of A-T
base pairs as part of this project. Ultimately, these parameters could be deduced for various
elevated pressures and extrapolated to atmospheric pressure (which naturally is of greater rel-
evance when considering DNA mutations of living organisms).
There is no published evidence of previous attempts to deduce the parameters associated with
base pair proton transfers experimentally. There have, however, been several ab-initio calcula-
tions of the energy difference between the two tautomeric forms. Kong et al [59] found the
energy difference between AT and $A^*T^*$ tautomers to be 51.5 kcal/mol (2.6x10^4 K). Scheiner
and Kern [60] evaluated an energy difference of 82.8 kcal/mol (4.1x10^4 K) whilst Hrouda et al
[61] found that energy to be considerably lower at 9.5 kcal/mol (4.8x10^3 K). They then correc-
ted this value to 20.1 kcal/mol (1.0x10^4 K) in [56]. This demonstrates that these calculations
are not very accurate since small changes in the initial parameters and introduced approxima-
tions lead to significantly different results. Hence a determination of the energy difference from
experimental data would be of significant importance.

5.3.3 NMR Spin-Lattice Relaxation Time Measurements

One important fact to realise is that when measuring the NMR spin-lattice relaxation time
of a bulk sample the resulting value of $T_1$ may consist of contributions from several different
relaxation mechanisms. Since thymine contains a methyl group, significant contribution to $T_1$
originating from that methyl group may be expected. There is another base, Uracil, which is
identical to Thymine, except that it does not have that methyl group. Uracil replaces Thymine
in RNA, playing a dominant role in DNA-protein translation. Also, we do not have to expect
any changes to the structural configuration of the double hydrogen bond by substituting Thym-
ine by Uracil since the methyl group is located at the opposite side of the molecular ring. Hence
the NMR measurements were carried out with Adenine-Uracil (A-U) base pairs.
Both Adenine and Uracil are commercially available as white powders. In order to produce
Adenine-Uracil pairs, advantage was taken of the fact that both are insoluble in water but will dissolve in alkali. A 1-normal NaOH solution was prepared, dissolving equal amounts of Adenine and Uracil in it. This solution was then neutralised by adding HCl which in turn caused the A-U pairs (along with pure Adenine and Uracil) to precipitate in the resulting mixture of water and NaCl. The NaCl was dissolved by adding large quantities of distilled water and retaining the base mixture by repetitive filtering. This base mixture was then desiccated to produce Adenine-Uracil pairs in white powder form. Since Adenine and Uracil may each form hydrogen bonds to equal types, this resulting sample should contain 50% A-U pairs, and 25% of each A-A and U-U pairs. Each type should give an individual contribution to the spin-lattice relaxation.

Figure 5.19 shows the saturation recovery for the A-U sample at atmospheric pressure. The magnetisation $M$ is measured for exponentially increasing recovery times $\tau$ following a saturating train of $90^\circ$ pulses. Both a single and double exponential fit are attempted and it can be seen that the curve can not be fitted by a single exponential. We can deduce that there are at least two components in the overall spin-lattice relaxation.

![Figure 5.19: Saturation recovery for Adenine-Uracil base pairs at atmospheric pressure and 88 K temperature. The solid lines show fits of single- and double-exponential nature. The failure of the single exponential fit indicates the presence of at least two distinct contributions to the spin-lattice relaxation time $T_1$](image)
The NMR spin-lattice relaxation time $T_1$ of Adenine-Uracil base pairs has been recorded as function of temperature for atmospheric pressure and 3.0 kBar. For each temperature, the magnetisation recovery has been recorded as described above and fitted to a double-exponential function of the form

$$M = M_0^{(a)} x [1 - \exp (-\tau/T_1^{(a)})] + M_0^{(b)} x [1 - \exp (-\tau/T_1^{(b)})] + C$$  \hspace{1cm} (5.8)

where $M_0^{(a)}$ and $M_0^{(b)}$ represent the prefactors of the relaxation contributions with relaxation times $T_1^{(a)}$ and $T_1^{(b)}$, respectively. The fits suggested the presence of a long $T_1$ component ($\approx 30$ seconds) and a short $T_1$ component ($\approx 2$ seconds). As pointed out above, the existence of further components is possible but determination of these would require a much higher level of data quality. Figures 5.20 and 5.21 show the two $T_1$ components plotted against inverse temperature at pressures of 0.0 and 3.0 kBar, respectively.

![Graph showing spin-lattice relaxation time $T_1$ vs. inverse temperature]  

Figure 5.20: Adenine-Uracil base pairs at atmospheric pressure - temperature dependence of the two spin-lattice relaxation times $T_1^{(a)}$ (triangles) and $T_1^{(b)}$ (squares).

Large error bars have to be placed on these $T_1$ values due to the double exponential nature of the overall spin-lattice relaxation. Also the fact that the spin-lattice relaxation times are quite long contributes to the difficulty of obtaining more accurate measurements. Apparently a higher signal to noise ratio (S/N) is needed in order to determine and separate the two components.
more accurately. Other than that, the temperature dependence of the $T_1$ contributions shows no significant variation with temperature, the usual minimum is not observed here for temperatures below room temperature.

The observation of a clear minimum in any of the two $T_1$ components would require a tautomer-exchange rate of the same order as the NMR proton Larmor frequency ($10^8$ s$^{-1}$). The application of even higher hydrostatic pressures may yield the necessary enhancement of the tautomer-exchange probabilities and result in the observation of a $T_1$ minimum.

The NMR spin-lattice relaxation time measurements obtained could not help to determine the energy difference between the two tautomeric forms of the Adenine-Uracil base pair. However, should a better signal to noise ratio and higher hydrostatic pressures be attainable in the future, the temperature dependence of the NMR spin-lattice relaxation time contributions may provide sufficient information to learn more about the energetics involved in the tautomer exchange of base pairs. This would ultimately provide an important step forward in understanding spontaneous point mutations in DNA.

Figure 5.21: Adenine-Uracil base pairs at 3.0 kBar - temperature dependence of the two spin-lattice relaxation times $T_1^{(a)}$ (triangles) and $T_1^{(b)}$ (squares).
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