PROTON MAGNETIC RESONANCE IN METHANE AND ITS DEUTERATED MODIFICATIONS

by

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We accept this thesis as conforming to the required standard

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FACULTY OF GRADUATE STUDIES

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DOCTOR OF PHILOSOPHY

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PROTON MAGNETIC RESONANCE IN METHANE AND ITS DEUTERATED MODIFICATIONS

ABSTRACT

Proton magnetic resonance has been studied in methane and its deuterated modifications. Measurements of relaxation time were carried out at a frequency of 30 Mc/sec. using pulse techniques. The spin-lattice relaxation time $T_1$ has been measured in liquid and solid samples of $\text{CH}_4$, $\text{CH}_3\text{D}$, $\text{CH}_2\text{D}_2$ and $\text{CHD}_3$ between $110^\circ\text{K}$ to $56^\circ\text{K}$. The simplest possible interpretation of our results in both the liquids and solids is that only one mechanism, that associated with the inter-molecular interactions, is probably predominant in causing relaxation. The spin-rotational and intra-molecular dipolar interactions do not seem to contribute appreciably to relaxation.

The effect of dissolved paramagnetic ions has also been studied in samples of $\text{CH}_4$ between $110^\circ\text{K} - 78^\circ\text{K}$ and we have developed a very simple and reliable technique for obtaining oxygen-free samples in order to study $T_1$ in pure samples because $T_1$ has been found by us to be very sensitive to small amounts of oxygen. The results verify the invers proportionality of $T_1$ to the oxygen concentration.

The spin-spin relaxation time $T_2$ has been measured in liquid and solid samples between $110^\circ\text{K}$ and $56^\circ\text{K}$. The results show that the line shape is predominantly due to inter-molecular interactions. Furthermore the resonance line has a gaussian shape at temperatures below $65^\circ\text{K}$ and changes to a Lorentzian shape at higher temperatures.
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Electronic Instrumentation F.K. Bowers
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ABSTRACT

The work reported here is a study of proton magnetic resonance in methane and its deuterated modifications. There is a strong isotope effect on the proton spin relaxation which makes it possible to distinguish, at least partially, between the various proposed spin interactions leading to nuclear spin relaxation.

The measurements of nuclear spin relaxation times were carried out at a frequency of 30 Mc/sec. using pulse techniques in samples of CH₄, CH₃D, CH₂D₂ and CHD₃.

The spin-lattice relaxation time $T₁$ has been measured in liquid and solid samples between 110 K to 56°K. Our results show that $T₁$ is temperature dependent and this temperature dependence is independent of the number of deuterons in the samples. We can make only plausible statements about the mechanisms that contribute to relaxation because our results have not been able to provide conclusive evidence about the relative contributions of different mechanisms. The simplest possible interpretation of our results in both the liquids and solids is that only one mechanism, that associated with the inter-molecular dipolar interactions, is probably predominant in causing relaxation. The spin-rotational interactions and intra-molecular interactions do not seem to contribute appreciably to the relaxation. Certainly they are not as important as predicted by conventional theory which predicts
that intra-molecular interactions should be more important than the inter-molecular interactions in the liquids (90°K - 110°K) and in the solids below about 80°K.

The effect of dissolved paramagnetic ions has also been studied and we have developed a very simple and reliable technique for obtaining oxygen-free samples in order to study T₁ in pure samples because T₁ has been found by us to be very sensitive to small amounts of oxygen in the sample. T₁ has also been measured in liquid and solid samples of CH₄ (110°K - 78°K) containing 1.08% and 2.54% oxygen. The results verify the inverse proportionality of T₁ to the concentration of oxygen.

The spin-spin relaxation time T₂ has been measured in liquid and solid samples between 110°K and 56°K. The results show that the line shape is predominantly due to inter-molecular interactions. Furthermore, the resonance line has a Gaussian shape at temperatures ≤ 65°K and changes to a Lorentzian shape at higher temperatures.

The activation energies from T₂ measurements are found to be 3.2 kcal/mole independent of the number of deuterons in the samples. These results agree with the values of activation energies obtained from T₁ measurements in the solids just below the melting point (80°K - 90°K). Since the line-width is due to inter-molecular interactions, it confirms that T₁ between 80°K and 90°K is predominantly due to inter-molecular interactions.

M. Bloom
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter/Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td></td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td></td>
<td>viii</td>
</tr>
<tr>
<td>CHAPTER I</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER II</td>
<td>EXPERIMENTAL APPARATUS AND MEASUREMENT OF RELAXATION TIMES</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2-1 Apparatus</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2-2 Measurement of Relaxation Times</td>
<td>25</td>
</tr>
<tr>
<td>CHAPTER III</td>
<td>THEORY OF SPIN-LATTICE RELAXATION</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3-1 Methane (CH₄)</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3-2 Theory</td>
<td>33</td>
</tr>
<tr>
<td>CHAPTER IV</td>
<td>SPIN-LATTICE RELAXATION MEASUREMENTS</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>4-1 Estimation of Accuracy</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>4-2 Results</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>4-3 In Liquids (90°K - 110°K)</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>4-4 In Solids (90°K - 56°K)</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>4-5 Effect of Paramagnetic Impurities on T₁</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>4-6 Estimation of O₂ Concentration in a Pure CH₄ Sample</td>
<td>67</td>
</tr>
<tr>
<td>Chapter</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>V</td>
<td>N.M.R. LINE-SHAPE STUDIES</td>
<td>69</td>
</tr>
<tr>
<td>5-1</td>
<td>Measurement of T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>74</td>
</tr>
<tr>
<td>5-2</td>
<td>Results and Discussion</td>
<td>74</td>
</tr>
<tr>
<td>VI</td>
<td>SUMMARY AND CONCLUSIONS</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>BIBLIOGRAPHY</td>
<td>89</td>
</tr>
</tbody>
</table>
### LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Proton energy levels in a magnetic field</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Block diagram of n.m.r. spectrometer</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>3 Pulse time base generator</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>30 Mc/sec. gated pulsed oscillator</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>The tuned circuit</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>Low temperature system</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>Bomb</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>Schematic diagram of the sample container</td>
<td>23</td>
</tr>
<tr>
<td>9</td>
<td>Oscilloscope display - two pulse n.m.r. experiment</td>
<td>27</td>
</tr>
<tr>
<td>10</td>
<td>$A(\infty) - A(t)$ versus time showing uncertainty in a $T_1$ measurement</td>
<td>47</td>
</tr>
<tr>
<td>11</td>
<td>$(1/T_1)$ versus 1000/$T^0$K in liquid and solid samples of $CH_4$, $CH_3D$, $CH_2D_2$ and $CHD_3$ between 56$^0$K and 110$^0$K</td>
<td>48</td>
</tr>
<tr>
<td>12</td>
<td>$(1/T_1)_n / (1/T_1)_o$ versus no. of deuterons in liquid samples</td>
<td>50</td>
</tr>
<tr>
<td>13</td>
<td>$(1/T_1)_n / (1/T_1)_o$ versus no. of deuterons in solid samples</td>
<td>55</td>
</tr>
<tr>
<td>14</td>
<td>$(1/T_1)_x$ versus 1000/$T^0$K for $CH_4$, $CH_3D$, $CH_2D_2$ and $CHD_3$ below 80$^0$K</td>
<td>58</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>15.</td>
<td>( (1/T_1)<em>{x(n)} / (1/T_1)</em>{x(o)} ) versus no. of deuterons</td>
<td>59</td>
</tr>
<tr>
<td>16.</td>
<td>( T_1 ) versus temperature for ( CH_4 ) samples containing known amounts of oxygen</td>
<td>65</td>
</tr>
<tr>
<td>17.</td>
<td>( 1/T_1 ) versus oxygen concentration in ( CH_4 ) at 108°K</td>
<td>66</td>
</tr>
<tr>
<td>18.</td>
<td>Corrected amplitude of the induction signal versus time and ((time)^2) for ( CH_4 ) at 78.15°K</td>
<td>75</td>
</tr>
<tr>
<td>19.</td>
<td>Corrected amplitude of the induction signal versus time and ((time)^2) for ( CH_4 ) at 61.4°K</td>
<td>76</td>
</tr>
<tr>
<td>20.</td>
<td>( T_2 ) versus 1000/T°K for solid ( CH_4, CH_3D, CH_2D_2 ) and ( CHD_3 ) between 56°K and 90°K</td>
<td>77</td>
</tr>
<tr>
<td>21.</td>
<td>Diagram illustrating the motion of the vector ( \vec{r} ) between two nuclear spins</td>
<td>79</td>
</tr>
<tr>
<td>22.</td>
<td>( (\Omega^2_p)_n / (\Omega^2_p)_o ) versus no. of deuterons in rigid lattice</td>
<td>82</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

The nuclear magnetic resonance technique makes possible the study of the interactions between a nuclear spin system and its magnetic environment. The mechanism of the exchange of energy between a system of nuclear spins immersed in a strong magnetic field, and the heat reservoir consisting of the other degrees of freedom (the lattice) of the substance containing the magnetic nuclei, is of considerable interest since it provides valuable information about physical processes which are going on in the system. The system of nuclear spins refers to an assembly of all the nuclei of the same type contained in a bulk sample. The sample may be in any of the three states of matter; gas, liquid or solid.

Our work is the study of proton magnetic resonance in samples of CH₄, CH₃D, CH₂D₂ and CHD₃ in the liquid and solid phases from 110°K to 56°K. There is a strong isotope effect on the proton spin relaxation. This effect enables us to distinguish, at least partially, between the various proposed spin interactions leading to nuclear spin relaxation.

We will, first of all, discuss briefly the n.m.r. technique essential for our discussion. Consider an assembly of identical atomic nuclei in thermal equilibrium in the presence of a steady magnetic field \( \vec{H}_0 \) in the z direction (\( H_0 = H_z \)). Since our work is limited to proton resonance, the nuclear spin \( I = \frac{1}{2} \). Each
nucleus has two possible energy levels a and b, corresponding to the proton spin pointing in the upward and downward directions respectively as shown in Fig. 1.

![Diagram of energy levels](image)

The difference in energy between the two levels is equal to $2\mu_I H_0$ where $\mu_I$ is the magnetic moment of the protons. The population of the lower level exceeds that of the upper level by the Boltzmann factor $\exp(2\mu_I H_0/kT)$ where $k$ is Boltzmann's constant and $T$ is the equilibrium temperature of the sample. This excess of population in the lower level corresponds to a net macroscopic magnetization $\vec{M}$ oriented parallel to $H_0$.

The system is then subjected to an rf magnetic field at the resonance condition $\omega = \omega_0 = \gamma H_0$, where $\gamma$ is the gyromagnetic ratio of the protons and $\omega_0$ is the Larmor frequency. Transitions are induced between the Zeeman levels which corresponds to the transfer of some of the excess population from the level a to b. This causes a change in the z component of macroscopic nuclear magnetization which, in general, acquires a non-equilibrium orientation. After the removal of the rf magnetic field, $\vec{M}$ precesses freely with components $M_x$, $M_y$ and $M_z$. The nuclear magnetization vector $\vec{M}$ then recovers towards its equilibrium value: $M_x = 0$, $M_y = 0$ and $M_z = M_0$. The recovery of the nuclear magnetization vector $\vec{M}$ towards equilibrium is affected by

(1) interactions of the spin system with the lattice, which
involve an exchange of energy from the spin system to the lattice; 

(2) interactions of the spins among themselves which do not involve any change in the total energy of the system.

Since the dominant part of the total spin energy is caused by the strong field $H_Q$ in the z direction, major changes of the total energy are due to a change of the z component of nuclear magnetization vector $\vec{M}$. If $M_z$ be the instantaneous value of the z component of $\vec{M}$, then in simple systems $M_z$ will tend to the equilibrium value $M_o$ at a rate determined by the degree of thermal motion according to the equation

$$\frac{dM_z}{dt} = -\frac{M_z - M_o}{T_1} \quad \text{(1.1)}$$

The solution of equation (1.1) is

$$M_z = M_o \times \left[1 - \exp\left(-\frac{t}{T_1}\right)\right] \quad \text{(1.2)}$$

taking the initial value of $M_z = 0$. $T_1$ is called the "spin-lattice" or "longitudinal" relaxation time.

The interactions which do not change the total energy of the spin system affect only the transverse components $M_x$ and $M_y$, and the approach to equilibrium of these components may be represented by the following equations for a spin system which obeys the Bloch equations

$$\frac{dM_x}{dt} + \frac{M_x}{T_2} = 0 \quad \text{(1.3)}$$
$$\frac{dM_y}{dt} + \frac{M_y}{T_2} = 0$$
where $T_2$ is termed the "spin-spin" or "transverse" relaxation time. The solutions of equation (1.3) can be written as

$$M_x = M_x(0) \exp\left(-\frac{t}{T_2}\right)$$

$$M_y = M_y(0) \exp\left(-\frac{t}{T_2}\right)$$

Thus $M_x$ and $M_y$ will tend to attain zero values at a rate determined by $T_2$. Therefore, the study of recovery of $M_x$, $M_y$ and $M_z$ by n.m.r. technique provides a measure of $T_1$ and $T_2$ and hence provides a means of studying the mechanisms that enable the spin system to relax back into thermal equilibrium with the lattice.

We now consider the possible mechanisms which cause relaxation. We have seen that the spin system is disturbed from thermal equilibrium by the application of an external rf magnetic field. In order to relax there must be some interaction mechanism between the spins and the lattice by virtue of which energy can be continually transferred to the lattice from the spin system, leading to equilibrium conditions in a time of the order of $T_1$ after the application of the rf magnetic field. In most diamagnetic substances, the dipole-dipole interaction among the nuclear magnetic moments seems to be dominant. We neglect electric quadrupole interactions because they are important for spins $I \geq 1$ and our work is confined to the proton resonance ($I = \frac{1}{2}$). A simple picture is to consider each spin as "seeing" a fluctuating local magnetic field produced by a neighbour which induces transitions among its levels tending to restore the system to its equilibrium value. These fluctuations in the local magnetic fields are brought about by molecular motions. These motions may be rotational, translational or...
of some other form.

The three basic contributions to the local field due to molecular motions are

(i) intra-molecular dipolar interactions which involve interactions between nuclear spins on the same molecule;

(ii) inter-molecular dipolar interactions which involve interactions between nuclei on different molecules or between nuclear spins and paramagnetic ions;

(iii) spin-rotational interactions between the nuclear spin and rotational angular momentum of the molecule.

There has been some evidence that spin-rotational interactions are predominant in systems such as liquid CHF$_3$\(^{(2)}\) and Johnson and Waugh\(^{(3)}\) have suggested that these interactions may also be important for liquid CH$_4$. Our study of $T_1$ has not been able to provide conclusive evidence about the relative contributions of (i), (ii) and (iii) to the relaxation rate $1/T_1$. We have only been able to give the upper and lower limits for each of them and therefore, we can make only plausible statements about the mechanisms that contribute to relaxation.

The simplest possible interpretation of our results in both the liquids and solids is that only one mechanism, that associated with the inter-molecular dipolar interactions, is probably predominant in causing relaxation. The spin-rotational interactions and intra-molecular interactions do not seem to contribute appreciably to the relaxation. Certainly, they are not as important as predicted by conventional theory which predicts that intra-molecular interactions should be
more important than inter-molecular interactions in the liquids (90°K - 110°K), and in the solids below about 80°K.

We will now consider briefly the effect of dissolved paramagnetic ions on $T_1$. The magnetic moment of the paramagnetic ion is about $10^3$ times larger than the nuclear magnetic moment. This results in larger fluctuating local fields and considerably shorter $T_1$, which however depends upon the concentration of paramagnetic ions in the sample. Previous measurements of $T_1$ in CH$_4$ gave values much shorter than these obtained here and were due to dissolved oxygen which is paramagnetic. A crucial step in our experiments was the establishment of a simple and reliable technique for obtaining oxygen-free samples. As a by-product of measurements, we have been able to verify the dependence of $T_1$ on the concentration of oxygen and also to estimate an upper limit for the oxygen concentration in our pure sample of CH$_4$.

The measurement of $T_2$ can provide valuable information in the study of the n.m.r. line shape since $T_2$ is a measure of the spread in Larmor frequencies due to the local magnetic fields produced by the neighbouring nuclear magnets. A magnetic resonance line of a spin system in an inhomogeneous magnetic field has a certain width owing to the spread of Larmor frequencies which is due to the differences among the resonance frequencies of the individual spins, rather than the interaction among them. We will, however, consider the case when the line-width is due to the existence of coupling between neighbouring spins. The interaction between two nuclear spins
depends upon the magnitude and orientation of their magnetic moments and also on the length and orientation of the vector describing their relative positions. The effect of this interaction depends strongly on whether the vector is fixed in space or changes because of motion of the nuclei.

At very low temperatures where very little translational motion of the molecules is taking place, the nuclei may be considered as fixed (rigid lattice). At each instant the microscopic distribution of local fields throughout the sample is of a stationary character. This rigid lattice line shape is often closely approximated by a Gaussian shape and the nuclear magnetic resonance absorption as a function of frequency is usually independent of temperature.

When rapid molecular motion sets in, the local field produced at any resonant nucleus by its neighbouring dipoles is now time-varying. If the variation is sufficiently rapid, the time average of the local field over all permitted orientations of the dipole pair during a time $T_2$ can, in general, be expected to be less than for a rigid system. This results in a narrowing of the resonance line and also the observable line shape changes to a Lorentzian form.

The second moment of the resonance line is unaffected by the narrowing "motion". The calculation of second moment from rigid lattice line shape enables us to study the temperature dependence of $\tau_c$ (the correlation time for changes in local fields due to translational motions) in the region where the line shape is Lorentzian, using the theory of motional
"narrowing". The contribution to second moments comes from intra-molecular dipolar interactions and inter-molecular dipolar interactions. One can, therefore, study the mechanism that may be contributing to the observable line shape. We find that intra-molecular interactions do not contribute to the observable second moments because our experimental values agree with the values of second moments predicted from inter-molecular interactions. We can, therefore, say that the line shape is predominantly due to inter-molecular interactions. We also observe that the resonance line has Gaussian shape at temperatures <65°K and changes to a Lorentzian shape at higher temperatures. Thus, we find that the n.m.r. technique enables us to study the line shape and to gain some insight into the different mechanisms that contribute to it.

In Chap. II, we describe the experimental equipment involved in this work and the techniques of the measurements of the relaxation times $T_1$ and $T_2$. In Chap. III, the theory of spin-lattice relaxation is presented in greater detail. In Chap. IV, the experimental results of $T_1$ are presented and interpreted on the basis of the theory outlined in Chap. III. We also discuss the effect on $T_1$ of the dissolved paramagnetic ions and present our measurements of $T_1$ in the presence of known amounts of oxygen in CH₄. In Chap. V, we discuss the theory of n.m.r. line shape and present our experimental results of $T_2$ along with their interpretation. In Chap. VI, we review the main results and make some suggestions for further work, although work along the suggested lines is already in progress.
CHAPTER II

EXPERIMENTAL APPARATUS AND MEASUREMENT OF RELAXATION TIMES

2-1 APPARATUS

A block diagram of the equipment used in this work is shown in Fig. 2. In addition to this, the equipment not shown in the diagram, consisted of:

(a) A low temperature system capable of maintaining the samples at any temperature between 56°K and room temperature.

(b) A vacuum system required for the purification of various samples used in this work.

The equipment was specially constructed for this work and a general description of each item will now be given.

1. MAGNET

The magnet made available for the preliminary work was the 7000 gauss permanent magnet already described by Watermann (5). The frequency of the spectrometer had to be matched to the magnetic field, leading to a choice of a frequency of approximately 30 Mc/sec. Most of the later work was done with a Varian Model V-4007-1 six inch Rotatable Laboratory Electromagnet with 2-inch air gap.

2. TIME BASE GENERATOR

The circuit diagram of this timer is shown in Fig. 3, and is of standard design. This unit gives out pulses to
FIG. 2  BLOCK DIAGRAM OF N.M.R. SPECTROMETER.
FIG. 3 3 PULSE TIME-BASE GENERATOR
trigger the gate which drives the rf power unit. It also
triggers the oscilloscope. The sequence of pulses could be
repeated automatically at any interval up to 4 seconds or at
longer intervals with the help of a manual switch.

3. **RADIO FREQUENCY CIRCUITRY**

The circuit diagram of the 30 Mc/sec. pulsed oscillator is
shown in Fig. 4. This oscillator has already been described by
Bloom, Hahn and Herzog (6). The oscillator gives rise to a
peak to peak 30 Mc/sec. rf voltage of about 200 volts across
the sample coil while gating time was variable between 10 and
150 μsec. During most of the work pulse lengths used were
about 40 μsec. However, some work was done with pulse lengths
of about 15 μsec. since T₂ becomes of the order of 20 μsec.
at the lowest temperatures studied.

4. **AMPLIFIER**

The rf amplifier is built commercially by Linear Equipment
Laboratory. It has a maximum gain of approximately 10⁶ and a
band width of approximately 2 Mc/sec. The final stage of the
amplifier has a IN34 diode detector.

The signal to noise ratio was of the order of 20:1 for
methane and was further improved by a factor of 2 by using a
simple R–C filter at the input of the oscilloscope. This
improvement was particularly useful in the solid samples when
the relaxation time became longer than 50 sec.

The signals observed on the Tektronix 545 oscilloscope
FIG. 4 30 MC/SEC. GATED PULSED OSCILLATOR.
were of the order of $\frac{1}{2}$ volt amplitude.

5. **THE TUNED CIRCUIT**

The tuned circuit consists of a sample coil $L$ of 11 turns and inner diameter of 6 mm. The sample coil shown in Fig. 5 was connected to the tuning capacitor $C$ by a $\frac{1}{2}$ wave line RG58U, approximately 3 meters in length. The tuned circuit was isolated from the oscillator and amplifier by means of capacitors $C_1(10 \text{ pF})$ and $C_2(22 \text{ pF})$.

6. **LOW TEMPERATURE SYSTEM**

The low temperature system described here was used for making measurements between $56^\circ\text{K}$ and $110^\circ\text{K}$. The magnet had a two inch air gap and this imposed some restrictions in designing such a system. A "blow cryostat" system was finally decided upon which will be described now.

A schematic diagram of the low temperature system is shown in Fig. 6. The copper bomb is surrounded by two dewars A and B. Dewar A is evacuated by a mercury diffusion pump while dewar B is filled with liquid nitrogen. Dewar C is the storage dewar which is filled with liquid nitrogen. Dewars A and B are made vacuum tight with brass caps $C_1$ and $C_2$; the vacuum tight seal is provided with "O" rings. Liquid nitrogen is pushed into the copper bomb via $F$, the jacket around $F$ being evacuated by a mercury diffusion pump. The flow of liquid nitrogen is controlled by valves (11) and (12), which provide coarse and fine flow controls respectively.
FIG. 5  TUNED CIRCUIT.
FIG. 6  LOW TEMPERATURE SYSTEM.
The flow rate is monitored by an oil manometer, $M_1$, attached to an orifice place flowmeter $G$ inserted in the return line, by means of which the gas after cooling the copper bomb either escapes into the air via valve (10) or to the recovery tank via valves (13) and (14). The mercury manometer $M_2$ provides pressure measurements either on the flow system or in any other part of the system.

The copper bomb shown in Fig. 7 is jacketed by a concentric brass cylinder. The four brass strips shown in section A - B of Fig. 7 force the liquid nitrogen entering from the top to travel all around the outside of the copper bomb, before it can enter the inside of the bomb from the bottom. The lower $\frac{1}{3}$ portion of the bomb is filled with copper wool to provide a good thermal contact. The sample coil is held inside the bomb by teflon spacer so that a sample tube can be inserted into it from the top, each sample tube having a ground glass seal attached to it. One end of the sample coil is soldered to the bomb and grounded. The other end of the coil is first brought out of bomb through a German silver tubing (3 mm. diameter) through a teflon spacer and then through a kovar glass seal soft soldered to the end of Germen silver tubing.

It was found in practice that a constant flow of nitrogen gas could not be maintained through the bomb because of pressure instability generated by liquid nitrogen boiling in the dewar C. Numerous unsuccessful attempts were made but ultimately this technique was dropped. However, it was found that if the bomb was cooled to liquid nitrogen temperature, the warm up rate of
the bomb could be controlled by controlling the pressure inside the dewar A and the space between its walls.

For temperatures in the range of $80^\circ K - 110^\circ K$, dewar B was filled with liquid oxygen because liquid oxygen in B was found to give better temperature stability than liquid nitrogen in this temperature range. Dewar A, the space between the walls of dewar A and the jacket around F were evacuated by mercury diffusion pump. The bomb was cooled to liquid nitrogen temperature in about 10-15 minutes by pushing liquid nitrogen over from dewar C as described earlier and then valve (13) was closed while valves (10) and (11) were opened to allow the rest of liquid nitrogen in the dewar C to boil off into the air. The pressure inside the dewar A and its walls was maintained at $10^{-4} - 10^{-5}$ mm. The bomb was then allowed to warm up and measurements of relaxation times were made during the warm up. The temperature stability during the warm up was as follows:

- $80^\circ K - 95^\circ K$ rise of $0.1^\circ K$ to $0.15^\circ K$ in about 10 minutes.
- $95^\circ K - 110^\circ K$ rise of $0.15^\circ K$ to $0.25^\circ K$ in about 5 minutes.

However, the relaxation measurements could be completed in about 5 minutes.

For temperatures in the range $56^\circ K - 80^\circ K$, dewar A was filled with liquid nitrogen. The space between its walls had been pumped hard to a pressure of approximately $10^{-6}$ mm., baked and then sealed off permanently. Dewar C was taken off and the opening H was closed by a rubber stopper. Tube F leading to the bomb was connected to valve (7) by a rubber tubing and helium gas at one atmosphere pressure was introduced into
the bomb via valves (8) and (7), which were then closed. Liquid nitrogen in the dewar A was then pumped off by a rotary pump via valves (1) and (5) and its pressure was observed via valves (6) and (9). The rate of pumping was controlled by valve (1) and by introducing a variable leak via valve (2) in order to obtain a desired temperature. The bomb temperatures were always constant for a considerable length of time (20 - 30 minutes) to within ± 0.05°K.

7. **PURIFICATION TECHNIQUE**

The basic problem in our work was to find the most effective way of removing oxygen from the samples of CH$_4$ and its deuterated compounds. It was found by us that T$_1$ in CH$_4$ was very sensitive to small amounts of oxygen in the sample, because the oxygen molecule is paramagnetic. The effect of paramagnetic impurities on T$_1$ in diamagnetic liquids has long been known$^7$. Our preliminary measurements with samples of CH$_4$ supplied commercially by Fisher Scientific Instruments, gave us T$_1$ values of the order of 10 msec. These values agreed with the values reported earlier$^4$. The vapour pressure readings for such samples, however, disagreed with those published$^8$ for pure CH$_4$. It was suspected that this disagreement could be due to the presence of impurities, oxygen and nitrogen being the chief impurities. It was considered necessary to eliminate such impurities in order to study T$_1$ in the pure liquid$^9$.

An attempt was first made to use the fact that the normal boiling point of oxygen (90°K) is lower than that of CH$_4$ (112°K).
The liquid was maintained at a temperature (106^0K) such that most of the oxygen might boil off. The vapours were then pumped off. This process was repeated a number of times. Each time we pumped off the vapours we obtained a longer relaxation time. Although T_1 values as long as 10 seconds were obtained, this technique for purification was finally dropped for three reasons.

1. This method was very wasteful of methane.
2. T_1 values so obtained were not reproducible. It was suspected that this change in T_1 values with time could be due to the small amounts of oxygen adsorbed in the walls of the glass system.
3. It was also found that methane attacked the vacuum grease on the stop cocks if it was left in the glass system for a couple of days.

It was, therefore, considered necessary to bake the system thoroughly and then to store the purified sample in a sealed glass bulb.

The second technique employed was to circulate methane over heated copper. This method was not satisfactory because the gas decomposed during the process.

The technique found to be most suitable for our purposes involved the use of a getter, misch metal, which consists of rare earths derived from monazite and alloyed with iron. This metal was selected because it was found by Ehrke and Slack(10) in their study of the gettering power of various metals like aluminum, magnesium, barium and misch metal that misch metal is the most effective for removal of oxygen. As described in
the following paragraph, our procedure\textsuperscript{(11)} is a slightly simplified version of that described by Ehrke and Slack\textsuperscript{(10)}.

A \(\frac{1}{2}\) litre flask drawn into a long tube on one side is used as shown in Fig. 8. The end of the tube fits into an NMR probe to make \(T_1\) measurements on the condensed liquid. A tungsten coil of five or six turns of 0.01 inch diameter wire with two or three small pieces of misch metal in the coil is sealed into the flask. The flask is then connected to a diffusion pump through a trap and evacuated to a pressure of the order of \(10^{-6}\) mm. The flask is baked by flaming several times during pumping to get rid of oxygen adsorbed on the walls. The tungsten coil is also degassed during pumping. When the flask has been thoroughly baked and pumped, it is filled with argon to a pressure of 1-2 mm. The getter is then flashed by passing current through the tungsten coil using a variac to control the current, until a characteristic diffused layer of the deposit is produced. The presence of argon is necessary to produce a diffused deposit, the gettering power of which is much higher than the bright shiny type\textsuperscript{(10)}. The argon is then pumped off, leaving an uncontaminated gettering layer of high activity. Methane at one atmosphere pressure is introduced into the flask which is then sealed off from the system.

When this procedure was followed, \(T_1\) was always found to increase to 16 seconds at 108\(^{\circ}\)K, this value being reproduced whether the measurements were done on different samples or the same sample at different times during a period of several days. Since the original measurements, \(T_1\) has been found to be
FIG. 8  SCHEMATIC DIAGRAM OF THE SAMPLE CONTAINER.
reproducible over a period of several years (12).

It would seem that the technique described here would be well suited to remove oxygen from other hydrocarbons and deuterated samples of CH$_4$ have been also prepared using this technique.

8. **TEMPERATURE MEASUREMENTS**

All temperature measurements were made using a platinum resistance thermometer (Hartman-Braun).

The thermometer was mounted in a copper tube soldered deep into the main body of the copper bomb. The thermometer was immersed into copper tube which contained some glycerine to ensure good thermal contact at low temperatures. A Rubicon Mueller bridge was used for accurate measurement of the temperature.

The thermometer was calibrated against the platinum resistance thermometer (No. 60-597) which was very accurately calibrated by National Bureau of Standards. The calibration was done at three temperatures by immersing the two thermometers together in liquid nitrogen, liquid oxygen and an ice-water mixture. The resistances of the two thermometers were read on the Mueller bridge. The temperatures were found from the thermometer calibrated by NBS. These temperature values were then plotted against the measured value of resistance of the thermometer used in this work. A line drawn through these points turned out to be parallel to the line plotted for the calibrated thermometer. The line was then extended to lower temperatures; the lowest temperature used in these experiments being 56°K.
2-2 MEASUREMENT OF RELAXATION TIMES

All measurements reported in this work were carried out using the pulse method developed by Hahn\(^{(13)}\) at a frequency of 30 Mc/sec. Since this method has already been discussed in detail by various authors, only a brief account will be given in this chapter.

We consider an ensemble of nuclear spins placed in a strong steady dc magnetic field \(\vec{H}_0\) oriented in the z direction. When thermal equilibrium is attained, the nuclear ensemble gets distributed among the different spin states according to the Boltzmann law of distribution. As a result there will be a net magnetic moment vector \(\vec{M} = \vec{M}_0\) oriented parallel to \(\vec{H}_0\). The spin ensemble is then subjected to a linearly polarized radio frequency field of amplitude \(2H_1\) normal to \(\vec{H}_0\), where \(|H_1| < |H_0|\) and has the frequency \(\omega_0 = \gamma H_0\), \(\gamma\) being the gyromagnetic ratio for protons. The total external field vector has the components

\[
H_x = 2H_1 \cos \omega_0 t, \quad H_y = 0, \quad H_z = H_0 \quad ---- (2.1)
\]

In practice, this radio frequency field is applied in the form of intense, short pulses which excite a coil surrounding the sample containing nuclei and having its axis in the x direction. This oscillating field in the x direction is equivalent to two circularly polarized radio frequency fields

\[
H_x = H_1 \cos \omega_0 t, \quad H_y = + H_1 \sin \omega_0 t \quad ---- (a)
\]

\[
H_x = H_1 \cos \omega_0 t, \quad H_y = - H_1 \sin \omega_0 t \quad ---- (b)
\]
rotating around the z direction.

It is convenient to transform to a coordinate system rotating at the Larmor frequency around z axis. The gyromagnetic ratio of the protons being positive, field (a) will be synchronous with the gyromagnetic precession of the protons about the fixed field $\mathbf{H}_0$ while field (b) being far from synchronous with the gyromagnetic precession of the protons, will have very little effect and may be neglected\(^\text{(14)}\). As a result of the field (a) applied for a time $t_w$, the macroscopic magnetization $\mathbf{M}_0$ will be deflected by an angle $\theta = \gamma H_1 t_w$ from its equilibrium direction along $\mathbf{H}_0$. $\mathbf{M}$ will then precess about $\mathbf{H}_0$ at the Larmor frequency which in the rotating coordinate system may be represented by the vector $\mathbf{M}$ being tipped from the z axis.

Due to the precessional motion of the vector $\mathbf{M}$ after the pulse, an alternating voltage is set up by magnetic induction in the same coil as is used to produce the rf magnetic field, and the magnitude of this voltage will be maximum when $\theta = \frac{\pi}{2}$ i.e. when the nuclear magnetization is completely in the transverse (x-y) plane. This induced voltage is then amplified, detected and applied to the y axis of the oscilloscope, the sweep of which has been triggered just before application of the pulse. This induced voltage decays because of (1) different rates of precession throughout the sample caused by the static "local" fields or by an inhomogeneous magnetic field (2) spin-lattice relaxation (3) processes which cause random fluctuation of precessional frequency and phase arising from spin-spin coupling and, particularly in the case of liquids,
molecular self-diffusion in an external inhomogeneous field. Since the amplitude of the induction voltage immediately following the pulse is proportional to the magnetization of the nuclear spins at the time the pulse is applied, the measurement of the maximum amplitudes of the induction signals following each of a pair of identical pulses as a separation of the two pulses is used to measure $T_1$.

If, in the absence of an rf field, $M_z(t)$, the component of magnetization of the nuclear spin system in the direction of $H_0$, returns from $M_z(T)$ to its equilibrium value $M_0$ according to the equation

$$M_z(t) = M_0 - \left[ M_0 - M_z(\tau_1) \right] \exp \left[ - \left( \frac{t - \tau_1}{T_1} \right) \right] \quad (2.3)$$

and if $M(0) = M_0$ i.e. the spin system is in thermal equilibrium before the first pulse is applied, one gets the following relationship between the values of the detected rf signals $A(0)$ immediately following the first pulse, and after the pulse $A(\tau)$ at a time $\tau$ later

$$A(0) - A(\tau) = \text{constant} \exp \left( - \frac{\tau}{T_1} \right) \quad (2.4)$$

Fig. 9

Fig. 9 is a drawing of oscilloscope display showing amplitude
of the detected rf signal as a function of time for the two-pulse nuclear magnetic resonance experiment. Following the pulses at 0 and \( T \) indicated by shaded regions are induction signals of maximum amplitude \( A(0) \) and \( A(\gamma) \) respectively. At \( 2\gamma \) a spontaneous pulse appears which has been called "spin echo" by Hahn (13). It has maximum amplitude at \( 2\gamma \).

**TECHNIQUE A**

Thus, a simple method of measuring \( T_1 \) is to apply two \( \frac{\pi}{2} \) pulses separated by a known time \( \gamma \). The pulse sequence of two \( \frac{\pi}{2} \) pulses is repeated at a repetition rate which allows the system to recover to equilibrium before each sequence. The first pulse disturbs the system from equilibrium and the second pulse is a measure of the regrowth of the z component of magnetization. \( A(\gamma) \) is obtained by varying the separation between pulses. The slope of the plot of \( \log [A(0) - A(\gamma)] \) versus \( \gamma \) is a measure of \( T_1 \). This method was used for samples of \( \text{CH}_4 \) containing known amounts of oxygen, where \( T_1 \) happens to be fairly short (of the order of msec.).

**TECHNIQUE B**

Since the relaxation times were fairly long in the pure samples of methane used in this work, the method described above was slightly modified. A train of pulses each of which rotated the magnetization vector through an angle of \( \frac{\pi}{2} \) approximately was applied in a time short compared with \( T_1 \). The condition \( \bar{M} \equiv 0 \) was established by applying a train of many pulses
within a time short compared with $T_1$. At a time $t$ later a similar train was applied and the height $A(t)$ of the induction signal immediately after the first pulse was measured as a function of time $t$. $T_1$ was deduced from the relation

$$A(\infty) - A(t) = \text{constant} \exp \left(- \frac{t}{T_1}\right)$$

which one gets from equation (2.4) by substituting $\infty$ for 0. $A(\infty)$ is the value of $A(t)$ for $t \gg T_1$. Usually we waited a time $t \geq 5 T_1$ to $10 T_1$ to obtain $A(\infty)$. The virtue of this method is that it is not necessary to wait for a time long compared with $T_1$ between successive measurements, since each train gives $\bar{M} \equiv 0$ regardless of the previous history.

**TECHNIQUE C**

Spin-spin relaxation time $T_2$ in solid samples for temperatures near the melting point was measured from the amplitude $A(2\tau)$ of the "echo" at $t = 2\tau$ as a function of $2\tau$(see Fig. 9). It has been shown that if the Bloch equations hold\(^{(1)}\) and if one satisfies the condition $t_w < \tau < T_1$, $T_2$\(^{(13)}\), the height of the "echo" obeys the relation

$$A(2\tau) = \text{constant} \exp \left(- \frac{2\tau}{T_2}\right)$$

where $t_w$ is the width of the pulse and $\tau$ is the interval between two pulses. Equation (2.6) has to be modified if diffusion effects are to be taken into account. However, diffusion in solids is too slow to affect the "echo" directly and equation (2.6) can be used as it stands. From the plot
of the ln $A(2\gamma)$ as a function of $2\gamma$, one gets a straight line graph with slope $1/T_2$.

**TECHNIQUE D**

At lower temperatures, it becomes extremely difficult to observe the "echo" and, therefore, $T_2$ cannot be measured by the method just described above. This is because the local field due to lattice neighbours ($\Delta H \sim 1/\gamma T_2$) is superimposed on the externally applied field ($\Delta H \sim 1/\gamma T_2^*$) at the position of the precessing nuclei and this local field is spread over a width much greater than the width due to the magnet (i.e. $T_2 < T_2^*$). Extremely intense rf power is required to excite all of the spins over a broad spectrum of Larmor frequencies in a pulse time $t_w$ and the condition $T_2^* \ll \gamma < T_2$ has to be satisfied in order to prevent damping down of the echo. Because of our limitation in satisfying these conditions, $T_2$ was measured from the decay of the induction signal following the pulse (the tail). This was done by taking photographs of the induction signal in the solid and liquid phases of the sample. The two signals were first normalized after applying appropriate corrections due to non-linearity of the amplifier. Then the amplitude $A(t)$ of the induction signal in solid for values of $t$ was divided by the corresponding amplitudes of the induction signal in liquid phase. This correction was necessary because the inhomogeneity in the externally applied field brings about an attenuation of observed induction signals in solids in addition to the decay due to $T_2$ whereas in liquid
state, the decay of the induction signal is governed by the spread caused by the external field inhomogeneity over the sample; any contributions to the local field at the nucleus by neighbours in the lattice averages out completely. In making this correction in this way, it is assumed that the influence of the local fields in the solids is independent of the inhomogeneity of the applied field. It can be shown that the induction signal has the form

\[ A(t) = \text{constant} \exp \left( - \frac{t}{T_2} \right) \]

if the line shape is Lorentzian. If the line shape is Gaussian, the form of the induction signal is

\[ A(t) = \text{constant} \exp \left( - \frac{t^2}{2T_2^2} \right) \]

(to be discussed in Chap. V). Plot of the logarithm of \( A(t) \) for different values of \( t \) or \( t^2 \) gave a straight line depending upon the line shape being Lorentzian or Gaussian. In either case \( T_2 \) was derived from the slope of the line.
CHAPTER III

THEORY OF SPIN-LATTICE RELAXATION

In this chapter the theory of nuclear spin-lattice relaxation will be discussed in order to explain our results in methane and its deuterated modifications.

It is necessary to discuss the properties of methane before proceeding to the theory itself.

3-1 METHANE (CH$_4$)

Normal Boiling Point  --------- 111.67°K
Normal Melting Point  --------- 90.66°K

The methane molecule is a highly symmetrical molecule. It is composed of one carbon atom and four atoms of hydrogen arranged in a tetrahedral array about the carbon atom.

There are three types of modifications of the molecule: meta (I = 2), ortho (I = 1) and para (I = 0) with statistical weights 5:9:2. Since the rotational states associated with each of these modifications are not identical$^{(15)}$, we might expect, in general, to observe a relaxation process described by two time constants arising from the ortho and meta molecules respectively. Hubbard$^{(16)}$ has also shown in his analysis of the spin-lattice relaxation process in methane, that one would expect two time constants for a molecule with four identical spin $\frac{1}{2}$ nuclei even if the quantum mechanical considerations (Fermi-Dirac statistics of the spin $\frac{1}{2}$ nuclei)
leading to the existence of ortho, para and meta modifications were neglected.

In the work reported here the relaxation of $M_z$ towards equilibrium was always describable in terms of a single exponential, and no evidence for more than one time constant was found within experimental error. In this connection it should be said that in Hubbard's analysis, the two exponential decays have relative amplitudes of 50:1 and time constants which differ by only about 25%. The differences of this order are too difficult to resolve experimentally because of signal to noise considerations. The dominant relaxation term in Hubbard's analysis gives a result which differs from the results quoted below by only a few percent for the special case of CH$_4$ to which Hubbard's analysis applies.

3-2 THEORY

$T_1$ may be expressed in terms of Fourier transforms of the correlation functions of those interactions which enable energy to be exchanged between the nuclear spin system and the other degrees of freedom (lattice) of the material in which the spins are located. For a system of non-identical nuclei a and b of spins $I$ and $S$ and gyromagnetic ratios $\gamma_I$ and $\gamma_S$ respectively, Abragam\(^{(17)}\) (page 295, eqs. 87 and 88) has given the following equations to describe the approach to equilibrium of the $z$ components of the average angular momenta per spin $\langle I_z \rangle$ and $\langle S_z \rangle$ respectively: (Note that the $z$ component of magnetization is proportional to $\langle I_z \rangle$ and
\[ \frac{d\langle I_z \rangle}{d\tau} = -\left[ \frac{1}{T_{ii}^{II}} + \frac{1}{T_{ii}^I} \right] \langle I_z \rangle - \frac{1}{T_{iIS}} \left[ \langle S_z \rangle - S_0 \right] \]  

\[ \frac{d\langle S_z \rangle}{d\tau} = -\frac{1}{T_{iIS}} \left[ \langle I_z \rangle - I_0 \right] - \left[ \frac{1}{T_{ISS}^I} + \frac{1}{T_{iS}^S} \right] \left[ \langle S_z \rangle - S_0 \right] \]

with

\[ \frac{1}{T_{iI}^I} = \frac{3}{2} \gamma I \hbar^2 I(I + 1) \left[ J_{II}^{(1)}(\omega_I) + J_{II}^{(2)}(\omega_I) \right] + \frac{1}{T_{iS}^S} \]

\[ \frac{1}{T_{iS}^I} = \frac{3}{2} \gamma S \hbar^2 S(S + 1) \left[ J_{SS}^{(1)}(\omega_S) + J_{SS}^{(2)}(\omega_S) \right] + \frac{1}{T_{iI}^I} + \frac{1}{T_{iS}^S} \]

\[ \frac{1}{T_{iI}^{II}} = \gamma^2 I \hbar^2 S(S + 1) \left[ \frac{1}{12} \int_{IS}^{(0)}(\omega_I - \omega_S) + \frac{3}{2} \int_{IS}^{(1)}(\omega_I) + \frac{3}{4} \int_{IS}^{(2)}(\omega_I + \omega_S) \right] \]

\[ \frac{1}{T_{iS}^{II}} = \gamma^2 S \hbar^2 I(I + 1) \left[ -\frac{1}{12} \int_{IS}^{(0)}(\omega_I - \omega_S) + \frac{3}{4} \int_{IS}^{(1)}(\omega_I + \omega_S) \right] \]

and similar expressions for \( \frac{1}{T_{iSS}} \) and \( \frac{1}{T_{iSI}} \) by interchanging the indices I and S. \( I_0 \) and \( S_0 \) are the equilibrium values of the z components of the angular momenta per spin. We have added two terms \( \frac{1}{T_{iI}^I} \) and \( \frac{1}{T_{iS}^S} \) to include contributions to relaxation due to interactions between spins I and S on the same molecule respectively. Also, one must include contributions to relaxation which do not involve interactions between a and b type nuclei. Therefore, we have added two terms \( \frac{1}{T_{iS}^S} \), \( \frac{1}{T_{iSI}^S} \) and \( \frac{1}{T_{iI}^I} \) which include contributions to relaxation due to spin-rotational and quadrupole interactions respectively. All these terms have been added because Abragam's original expressions assume only one
nucleus of type a interacting with one nucleus of type b, whereas in the deuterated methanes we may have more than one spin of each type per molecule. The spectral densities are given by:

\[ J^{(m)}(\omega) = \int_{-\infty}^{\infty} G^{(m)}(\tau) \, e^{i\omega \tau} \, d\tau \quad m = 0, 1 \text{ and } 2 \]

where

\[ G^{(m)}(\tau) = \langle F^{(m)}(0) \, F^{(m)*}(\tau) \rangle \]

\[ F^{(m)} = \alpha^{(m)} \frac{\gamma_{2m}(\theta_{ab}, \phi_{ab})}{\zeta_{ab}^3} \]

\[ \alpha^{(0)} = \left( \frac{48\pi}{15} \right)^{1/2} \]

\[ \alpha^{(1)} = \left( \frac{8\pi}{15} \right)^{1/2} \]

\[ \alpha^{(2)} = \left( \frac{32\pi}{15} \right)^{1/2} \]

The external magnetic field \( \vec{H}_0 \) is oriented along z axis and the vector \( \vec{r}_{ab} \) joining the nuclei a and b has polar and azimuthal angles \( \theta_{ab} \) and \( \phi_{ab} \) respectively.

Equations (3.1 a) and (3.1 b) can be greatly simplified for our purposes, if an experimental result of G. de Wit(18) is used. de Wit has measured the deuteron spin relaxation in CD₄ and CHD₃. He finds that the relaxation of \( \langle S_z \rangle \) is exponential with a time constant \( T_1 = 10 \) seconds for each molecule roughly independent of temperature between 55⁰K and 105⁰K. This means that the deuteron spin relaxation is independent of the number of protons. If the relaxation were
due to dipole-dipole interactions, the deuteron $T_1$ for CHD$_3$ would be shorter than for CD$_4$ since

$$\gamma^2_{I} I(I + 1) \approx 20 \gamma^2_{S} S(S + 1).$$

The deuteron spin-lattice relaxation is due to the quadrupolar interaction between the deuteron quadrupole moment and the electric field gradient of the molecule. This interaction is present for the deuteron but not for the proton since $S = 1$ and $I = \frac{1}{2}$.

This result means that in equation 3.1(b), the term $\frac{I}{T_1}$ is dominant and equation 3.1(b) is well approximated by

$$\frac{d <S_z>} {dt} = - \left(\frac{I}{T_1}\right) ( <S_z> - S_0) \quad \text{(3.2)}$$

In the experiments reported here $< I_z >$ is disturbed from its equilibrium value $I_0$ by a pulse. Initially $<S_z> = S_0$. Therefore, according to equation (3.2) it remains at this value for all times and the second term in equation 3.1(a) can be dropped. Equation 3.1(a) can now be rewritten for our purposes as follows:

$$\frac{d <I_z>}{dt} = \left[ \frac{1}{T_{II}} + \frac{1}{T_{I}} \right] \left[ <I_z> - I_0 \right]$$

which has an exponential solution [e.g. equation (2.3), Chap. II] with
For non-metallic liquids the important mechanism is that arising from the thermal motion of the atoms or molecules which constitute the lattice. The atoms or molecules are regarded as vehicles conveying the nuclei from point to point. Thus each nuclear magnetic moment takes part in the random translational and rotational Brownian motion of the molecules. In consequence, the local magnetic field at any point contributed by the neighbouring nuclear magnetic moments and by any electronic magnetic moments which may also be present, is a rapidly fluctuating function of time. The component at the resonant frequency $\omega_0$ of the Fourier spectrum of this fluctuating field, then, is capable of inducing transitions between the nuclear magnetic energy levels and causing relaxation.

The interactions which contribute to $T_1$ are divided into three groups:

(a) dipole–dipole interactions between nuclei on the same molecules whose contribution to $1/T_1$ is usually denoted by $(1/T_1)_{rot}$ and this contribution is included in the first two terms of equation (3.3).
(b) dipole-dipole interactions between nuclei on different molecules or between nuclear spins and paramagnetic ions, whose contribution to \( \frac{1}{T_1} \) is denoted by \( (1/T_1)_{\text{transl}} \) and this contribution is included in the first two terms of equation (3.3).

(c) spin-rotational interaction between the nuclear spin and rotational angular momentum of the molecule, whose contribution to \( \frac{1}{T_1} \) is denoted by \( (1/T_1)_{\text{spin-rot}} \) and this contribution is given by the third term in equation (3.3).

We have then

\[
\frac{1}{T_1} = \left( \frac{1}{T_1} \right)_{\text{rot}} + \left( \frac{1}{T_1} \right)_{\text{transl}} + \left( \frac{1}{T_1} \right)_{\text{spin-rot}} \quad --- \quad (3.4)
\]

The reasons for using the above notation is clearly that fluctuations in (a) are brought about by effects which cause the molecule to reorient or rotate, while fluctuations in (b) are mainly brought about by translational motion of the molecules relative to each other. Fluctuations in (c) are also brought about by molecular reorientations.

(a) **ROTATIONAL CONTRIBUTION** \( \left( \frac{1}{T_1} \right)_{\text{rot}} \)

In the Debye model \( (BPP(7)) \) the molecule is regarded as a rigid sphere undergoing random reorientations. The orientation of the vector joining the two nuclear spins then varies randomly. If the diffusion equation describes the motion and the correlation functions are taken to be of the following form as is commonly done (7)
where \( \tau_r \) is the correlation time of the order of the average time for appreciable reorientations, then using the fact that the inter-nuclear separation \( r \) is fixed in a rigid sphere, equation (3.5) gives

\[
\begin{align*}
J_{II}^{(o)} &= \frac{8}{5} \times \frac{\tau_r}{1 + \omega_o^2 \tau_r^2} \times \kappa^{-6} \\
J_{II}^{(1)} &= \frac{4}{15} \times \frac{\tau_r}{1 + \omega_o^2 \tau_r^2} \times \kappa^{-6} \\
J_{II}^{(2)} &= \frac{16}{15} \times \frac{\tau_r}{1 + \omega_o^2 \tau_r^2} \times \kappa^{-6}
\end{align*}
\]

and similar expression for \( J_{IS} \). In the special case of the rotation being described by solutions to the rotational diffusion equation, \( \tau_r \) is given by relation

\[
\tau_r = \frac{4 \kappa \eta_v \alpha^3}{3kT}
\]

where \( \eta_v \) is the coefficient of viscosity and \( \alpha \) is the radius of sphere. Therefore, if one has \( N_a \) nuclei of type \( a \) per molecule, \( N_b \) nuclei of type \( b \) per molecule and if one satisfies the short correlation time approximation \((\omega_o^2 \tau_r^2) << 1\) the expression for \( (1/T_1)_{rot} \), using equation (3.3), becomes

\[
(1/T_1)_{rot} = \frac{3}{2} \gamma I^4 \hbar^2 \tau_r^{-6} \left[ \frac{4(N_a - 1)I(I + 1)}{3} + \frac{8 \gamma^2 N_b S(S + 1)}{9 \gamma_a^2} \right]
\]
We define a quantity

\[ F_a = \frac{3}{2} \gamma^4 I h^2 \gamma r^{-6} \] which has the dimensions sec\(^{-1}\).

In our work, since nuclei a are protons for which \( I = \frac{1}{2} \) and nuclei b are deuterons for which \( S = 1 \), we get

\[
\left( \frac{1}{T_1} \right)_{\text{rot}} = \left[ (N_a - 1) + \frac{16}{9} R x N_b \right] x F_a
\]

where \( R = \frac{\gamma_S^2}{\gamma_I^2} \)

\( \gamma_S \) for deuteron = \( 4.1 \times 10^3 \) gauss\(^{-1}\) sec\(^{-1}\)

\( \gamma_I \) for proton = \( 2.7 \times 10^4 \) gauss\(^{-1}\) sec\(^{-1}\)

This gives

\[
\left( \frac{1}{T_1} \right)_{\text{rot}} = \left[ (N_a - 1) + 4.1 \times 10^{-2} N_b \right] x F_a \quad --- (3.6)
\]

(b) \underline{TRANSLATIONAL CONTRIBUTION} \( \left( \frac{1}{T_1} \right)_{\text{transl}} \).

We assume that the motion is described by the solutions of the diffusion equation. If we consider an interacting nucleus at a distance \( r \) from the nucleus under study, then we may regard the correlation time \( \tau_d \) for this nucleus as the time in which this nucleus moves a distance \( r \) in any direction relative to the other nucleus. The relative motion is by diffusion and may be described by means of the diffusion coefficient \( D \) of the liquid, which has the approximate value \( kT/6\pi\eta a \) for spherical molecules of radius \( a \) and
coefficient of viscosity $\eta$.

If short correlation time limits are again satisfied and the radial distribution function is approximated by a flat distribution from a distance of closest approach $d = 2a$ to $\infty$, then the expressions for spectral densities are

\begin{align*}
J^{(0)}_{II} &= \frac{32\pi}{75} \frac{N_a N}{dD} \\
J^{(1)}_{II} &= \frac{16\pi}{225} \frac{N_a N}{dD} \\
J^{(2)}_{II} &= \frac{64\pi}{225} \frac{N_a N}{dD}
\end{align*}

and similar expressions for $J_{IS}$ by substituting $N_b$ for $N_a$. $N$ is the number of molecules per cm$^3$, so that $N_a N$ is the number of nuclei per cm$^3$.

The expression for $1/T_1$, using equation (3.3), becomes

\[ \left( \frac{1}{T_1} \right)_{\text{transl}} = \frac{8\pi}{15} \gamma_1^4 h^2 I(I + 1) \frac{N_a N}{dD} + \frac{16\pi}{45} \gamma_1^2 \gamma_2^2 h^2 S(S + 1) \frac{N_b N}{dD} \]

We define again a quantity

\[ F_b = \frac{2 \times \gamma_1^4 h^2 N}{5} \frac{dD}{dD} \text{ which has the dimensions sec}^{-1}. \]

Substituting the values for $I$, $S$, $\gamma_1$, and $\gamma_2$, we get

\[ \left( \frac{1}{T_1} \right)_{\text{transl}} = (N_a + 4.1 \times 10^{-2} N_b) F_b \quad ----- (3.7) \]
(c) **SPIN-ROTATIONAL CONTRIBUTION** \( \left( \frac{1}{T_1} \right) \)

This interaction, in general, is of the form \( A \bar{I} \bar{J} \) between the nuclear spin \( \bar{I} \) and the rotational angular momentum of the molecule \( \bar{J} \), \( A \) being a constant. Spin-lattice relaxation occurs because molecular collisions cause \( m_J \) and \( J \) to change thereby producing fluctuations in the rotational magnetic field at the nuclei.

There has been some evidence that this mechanism is probably predominant for fluorine nuclei in systems such as liquid \( \text{CHF}_3 \). Recently Johnson and Waugh (3) have suggested that it is also important for liquid \( \text{CH}_4 \). In making this suggestion, they have surmised that the relaxation rate due to this mechanism is proportional to \( \langle J(J + 1) \rangle \). If \( P_J \) is the equilibrium transition probability, then

\[
\langle J(J + 1) \rangle = \sum_{J=0}^{\infty} J(J + 1) P_J
\]

where

\[
P_J = \frac{(2J + 1) \exp \left[ -\frac{J(J + 1) \hbar^2}{2I_0 kT} \right]}{\sum_{J}(2J + 1) \exp \left[ -\frac{J(J + 1) \hbar^2}{2I_0 kT} \right]}
\]

\( I_0 \) is the moment of inertia of the molecules.

For high \( J \), we can write

\[
\langle J(J + 1) \rangle = \oint J(J + 1)(2J + 1) e^{-\frac{J(J+1)\hbar^2}{2I_0 kT}} dJ
\]

\[\propto T I_0 \quad \text{---- (3.8)}\]

where \( T \) is the absolute temperature.
If we accept this assumption, then the complete expression for $1/T_1$ from equations (3.6), (3.7) and (3.8), is

$$\frac{1}{T_1} = \left[(N_a - 1) + 4.1 \times 10^{-2} N_b \right] F_a + \left[N_a + 4.1 \times 10^{-2} N_b \right] F_b + (4 + N_b) F_c$$

where $F_c$ is the contribution to $1/T_1$ due to spin-rotational interaction in $\text{CH}_4 (N_b = 0)$.

If we put

$$N_b = n$$
$$N_a = 4 - n$$

where $n$ is the number of deuterons in our case, then $1/T_1$ in the molecule $\text{CH}_4 - D_n$ has the following dependence on $n$ at constant temperature.

$$\left(\frac{1}{T_1}\right)_n = \left[(3 - n) + 4.1 \times 10^{-2} n \right] F_a + \left[(4 - n) + 4.1 \times 10^{-2} n \right] F_b + (4 + n) F_c \quad \text{(3.9)}$$

Equation (3.9) can be written in the form

$$\left(\frac{1}{T_1}\right)_n = \left[(i - \frac{n}{3}) + \frac{4.1 \times 10^{-2} n}{3} \right] R_a + \left[(i - \frac{n}{4}) + \frac{4.1 \times 10^{-2} n}{4} \right] R_b + (1 + n) R_c \quad \text{(3.10)}$$

where $R_a$, $R_b$ and $R_c$ are the contributions to $1/T_1$ for $n = 0$ due to the mechanisms a, b and c respectively.

In writing equation (3.10), we neglect the changes in the correlation functions appearing in $R_a$, $R_b$, $R_c$ due to changes in $n$. In the conventional theories of $T_1$ (17), $R_a$ and $R_b$ would depend on the diffusion coefficient $D$, and both are proportional to $1/D$. If $D$ were proportional to
(molecular mass)^{-\frac{1}{2}}$, then for our system $R_a$ and $R_b$ would be
multiplied by $(1 + \frac{n}{16})^{\frac{1}{2}}$, having at most an influence of
9\% for CHD$_3$. The expression for $1/T_1$ is then

$$
\left(\frac{1}{T_1}\right)_n = (1 + \frac{n}{16})^{\frac{1}{2}} \left[ \left\{ \left(1 - \frac{n}{3}\right) + \frac{4.1\times10^{-2}}{3} n \right\} R_a \\
+ \left\{ \left(1 - \frac{n}{4}\right) + \frac{4.1\times10^{-2}}{4} n \right\} R_b \right] \\
+ \left(1 + \frac{n}{4}\right) R_c
$$

(3.11)
CHAPTER IV

SPIN-LATTICE RELAXATION MEASUREMENTS

A series of measurements of the spin-lattice relaxation time $T_1$ in $CH_4$, $CH_3D$, $CH_2D_2$ and $CHD_3$ were performed in liquid and solid samples covering a range of temperature from $110^0K$ to about $56^0K$. In addition to this, some measurements of $T_1$ were made by adding known amounts of oxygen in samples of $CH_4$ in the temperature range $78^0K - 110^0K$. Measurements of $T_1$ in pure samples were carried out at 30 Mc/sec. using the technique (B) for long relaxation described in Chap. II. The samples were prepared very carefully using the purification technique described in Chap. II. These measurements will now be presented and the results will be interpreted in terms of the theory outlined in Chap. III.

If $(1/T_1)_n$ is fitted to a linear function of $n$ at each temperature as implied by equation (3.10), one obtains only two parameters from the equations

$$\left(\frac{1}{T_1}\right)_o = R_a + R_b + R_c \quad ---- \quad (4.1)$$

and

$$\frac{b}{\sigma n}(\frac{1}{T_1})_n = -0.32 R_a - 0.24 R_b + 0.25 R_c \quad ---- \quad (4.2)$$

Since it is not possible to obtain a unique solution of these equations, one cannot evaluate the exact order of magnitude of $R_a$, $R_b$ and $R_c$. However, the fact that $R_a$, $R_b$ and $R_c$ must all
be positive, enables us to establish the upper and lower bounds for $R_a$, $R_b$ and $R_c$.

Before presenting our experimental results, we will mention the estimation of accuracy of our results.

4-1 ESTIMATION OF ACCURACY

If we take into account an uncertainty of ± .2 of a division on the oscilloscope screen in our measurement of $T_1$, a typical plot of $T_1$ at high temperatures (Fig. 10) shows a maximum variation of about ± 10%, although at low temperatures this figure was improved to ≤ ± 5%.

4-2 RESULTS

The results are shown in Fig. 11 where $1/T_1$ is plotted versus $1000/T_0^K$ for liquid and solid $CH_4$, $CH_3D$, $CH_2D_2$ and $CHD_3$ between $56^0K$ and $110^0K$.

These results show that $T_1$ is strongly dependent on temperature both in liquid and solid samples and undergoes an abrupt change at the melting point, which is due to the change in phase. Furthermore, this temperature dependence is independent of the number of deuterons both in the liquid and solid samples of $CH_4$.

4-3 IN LIQUIDS ($90^0K$ - $110^0K$)

Since the plot of $\ln (1/T_1)_n$ versus reciprocal of temperature has been found experimentally to be a straight line whose slope is independent of the number of deuterons within experimental error, we can therefore, express $(1/T_1)_n$ in
FIG. 10  PLOT OF $[A(\infty) - A(t)]$ VERSUS TIME SHOWING UNCERTAINTY IN A $T_1$ MEASUREMENT.
FIG. 11  Plot of $\frac{1}{T_1}$ versus $\frac{1000}{T}$ in liquid and solid CH$_4$, CH$_3$D, CH$_2$D$_2$, and CHD$_3$ between 56°K and 110°K

M.P. = 90.2° K

CH$_4$  x x x x
CH$_3$D  ----
CH$_2$D$_2$  --------
CHD$_3$  o o o o o
terms of the following relation:

\[
\frac{(1/T_1)_n}{(1/T_1)_o} = 1 + \frac{b}{a} n = 1 + \frac{\partial (1/T_1)_n}{\partial n} n \quad \text{(4.4)}
\]

In order to establish limits on \(R_a\), \(R_b\) and \(R_c\), we plot \((1/T_1)_n/ (1/T_1)_o\) versus \(n\) (Fig. 12). Since the ratio is independent of temperature, the slope of the plot gives a reasonable fit of the experimental data over the entire temperature range for

\[
\frac{\partial}{\partial n} (1/T_1)_n = - (0.21 \pm 0.02) (1/T_1)_o \quad \text{(4.5)}
\]

This limit of ±10% has been established on the basis of the uncertainty in our measurements of \(T_1\).

\(R_a\), \(R_b\) ≥ 0 give the following approximate limits for \(R_c\).

\[
(0.06 \pm .04) \left(\frac{1}{T_1}\right)_o \leq R_c \leq (0.19 \pm .04) \left(\frac{1}{T_1}\right)_o
\]

Now limits on \(R_a\) and \(R_b\) are obtained as follows:

For \(R_a = 0\), \(R_c = (0.06 \pm .04) \left(\frac{1}{T_1}\right)_o\), \(R_b = (0.94 \pm .04) \left(\frac{1}{T_1}\right)_o\)

For \(R_b = 0\), \(R_c = (0.19 \pm .04) \left(\frac{1}{T_1}\right)_o\), \(R_a = (0.81 \pm .04) \left(\frac{1}{T_1}\right)_o\)

If we take into account the change in correlation functions
FIG. 12 PLOT OF $\frac{\frac{1}{T_n}}{\frac{1}{T_{n0}}}$ VERSUS NO OF DEUTERONS IN LIQUID SAMPLES.

SLOPE = (0.21 ± 0.02)
appearing in $R_a$, $R_b$ and $R_c$ due to change in $n$, then the correction factor $\left[ 1 + \frac{n}{16} \right]^{\frac{3}{2}} = 1 + 0.03 n + \ldots$ explained in equation (3.11) for $R_a$ and $R_b$ is applied, and equation (4.2) is changed to

$$\frac{\partial}{\partial n} \left( \frac{1}{T_1} n \right) = -0.29 R_a - 0.21 R_b + 0.25 R_c \quad \text{(4.6)}$$

Then the limits for $R_c$ are

$$0 \leq R_c \leq (0.15 \pm 0.04) \left( \frac{1}{T_1} \right)_o$$

thereby causing a change of 4 - 6%.

On the basis of the above analysis if we take the upper limit on $R_c$ we may say that Johnson and Waugh (3) may be correct in predicting that $R_c$ may be contributing to the relaxation mechanism but the upper experimental limit on $R_c$ is at least a factor of 2 lower than their predicted value which represents a theoretical upper limit assuming no quenching of rotational angular momentum. This means that the maximum possible contribution to relaxation from the spin-rotational interactions is $(19 \pm 4)\%$ in which case the contribution from the intra-molecular interactions is $(81 \pm 4)\%$ and the intermolecular interactions do not contribute at all ($R_b = 0$).

H. S. Gutowsky, I. J. Lawrenson and K. Shimomura (2) have shown that spin-rotational interactions are strongly temperature dependent, giving an increasing contribution to the relaxation rate with increasing temperature.

G. de Wit (18) has measured deuteron spin relaxation in
CD$_4$ and CHD$_3$. He found that the deuteron $T_1$ in these samples is independent of temperature within 10% between 55°K - 105°K. The correlation functions associated with the quadrupolar interactions, which produce the deuteron spin relaxation, are identical to the correlation functions associated with the intra-molecular interactions\(^{(18)}\). Since the observed relaxation probability in our methane proton spin relaxation studies decreases with increasing temperature, it seems highly improbable that the limits obtained with $R_b = 0$ are close to the correct values. It is more likely that the limit $R_a = 0$ is closer to being correct, in which case the principal contribution (94 ± 4)% to relaxation would come from inter-molecular interactions and the contribution from spin-rotational interactions is (6 ± 4)%. Taking the lowest limit of 2% we can say that spin-rotational interactions do not seem to contribute appreciably to $T_1$ in our case and may well be zero. In addition, it should be noted that our $T_1$ measurements give the same activation energy for different $n$ i.e. we do not observe different temperature dependence for different $n$ within experimental error. Since the relative contributions to the relaxation rate from different mechanisms change with $n$, this also indicates that only one mechanism is probably predominant. Thus we may say that inter-molecular interactions are predominant in causing the relaxation. However, further experiments will have to be done to settle this point conclusively.

If we use the conventional theory of relaxation\(^{(17)}\) as applied to liquid CH$_4$, we can calculate $(1/T_1)_{\text{rot}}$ using
equation (3.6). Taking

\[ \gamma_I = 2.7 \times 10^4 \text{ Gauss}^{-1} \text{ sec}^{-1} \]
\[ \hbar = 10^{-27} \text{ ergs-sec} \]
\[ k = 1.38 \times 10^{-16} \text{ ergs/deg.} \]
\[ a = 2.0 \times 10^{-8} \text{ cm} \]
\[ r = 1.78 \times 10^{-8} \text{ cm} \]
\[ \eta_{\text{at 91°K}} = 0.2005 \times 10^{-2} \text{ poise} \]
\[ \eta_{\text{at 110°K}} = 0.1214 \times 10^{-2} \text{ poise} \]

we find that \((1/T_1)_{\text{rot}}\) varies from 0.37 to 0.18 sec\(^{-1}\) between 91°K to 110°K respectively.

\((1/T_1)_{\text{transl}}\) can be calculated from equation (3.7).

Taking

\[ d = 4.0 \times 10^{-8} \text{ cm} \]
\[ D \text{ at 91°K} = 1.66 \times 10^{-5} \text{ cm}^2/\text{sec} \]
\[ D \text{ at 110°K} = 3.316 \times 10^{-5} \text{ cm}^2/\text{sec} \]
\[ N \text{ at 91°K} = 1.7 \times 10^{22} \]
\[ N \text{ at 110°K} = 1.59 \times 10^{22} \]

we find that \((1/T_1)_{\text{transl}}\) varies from 0.1 to 0.05 sec\(^{-1}\) between 91°K to 110°K respectively. The values of D are calculated from measured viscosity values using the Stokes-Einstein relationship \(D = kT/6\pi \eta a\).

This leads to the ratio of \((1/T_1)_{\text{rot}}\) to \((1/T_1)_{\text{transl}}\) as 4:1 approximately, which indicates that intra-molecular interactions should be dominant. This is contrary to what we expect from our experimental results. This discrepancy
has also been found by B. H. Muller and J. D. Noble in their $T_1$ measurements of liquid ethane. They find that although the conventional theory of relaxation applied to liquid ethane predicts that the ratio of $(1/T_1)^{\text{rot}}$ to $(1/T_1)^{\text{transl}}$ is 4:1, the experimental results show that spin-rotational interactions may well be zero and the principal contribution comes from inter-molecular interactions. They further suggest that this depression of the intra-molecular contribution relative to the inter-molecular contribution is due in part to the averaging-out effect of either internal motion or rotation of the molecule itself. This may well be the true in our case.

4-4 IN SOLIDS ($90^\circ \text{K} - 56^\circ \text{K}$)

The experimental results show that from $90^\circ \text{K}$ to approximately $80^\circ \text{K}$, the plot of $\ln (1/T_1)$ versus $1000/T$ is a straight line and the slope is independent of $n$. In this region in order to establish limits on $R_a$, $R_b$ and $R_c$, we can use again equation (4.4). We plot again $(1/T_1)_n / (1/T_1)_o$ versus no. of deuterons in Fig. 13. Since this ratio is again independent of $n$, the slope of this plot gives a reasonable fit of the experimental data given in Fig. 11 for

$$\frac{\partial}{\partial n} \left( \frac{1}{T_1} \right)_n = -(0.24 + 0.02) \left( \frac{1}{T_1} \right)_o$$

----- (4.7)

Using equations (4.1) and (4.2), the following approximate limits are obtained for $R_c$
FIG. 13 PLOT OF $(\frac{1}{n})_n/\frac{1}{n}_0$ VERSUS NO OF DEUTERONS IN SOLID SAMPLES.
\[ 0 \leq R_c \leq (0.14 \pm 0.04) \left( \frac{1}{T_{10}} \right) \]

There is much evidence that \( R_c \) is considerably quenched in the liquids due to the quenching of rotational angular momentum. It should, therefore, be absent in the solids as indicated by these results.

In this temperature region, there is additional evidence available which enables us to choose \( R_c = 0 \). The activation energies are found to be 3.2 k cal/mole independent of \( n \), from the plot of \( \ln (1/T_1)_n \) versus 1000/T (Fig. 11). This confirms that mechanism (b) is predominant in this region since the activation energies are the same as obtained from \( T_2 \) measurements (to be discussed in Chapter V) and the contributions to \( T_2 \) can be said with considerable certainty to be solely intermolecular dipolar interactions.

At temperatures below 80°K, the plot of \( \ln (1/T_1) \) versus 1000/T departs from a straight line relationship. It appears that a new relaxation mechanism is dominant at these lower temperatures (81°K - 56°K). If we assume that the contribution of \( (1/T_1) \) from translational diffusion \( (1/T_1)_{\text{diff}} \) and the contribution to \( (1/T_1) \) from this new mechanism \( (1/T_1)_x \) add to give \( (1/T_1)_{\text{expt}} \), then we can write

\[
\left( \frac{1}{T_1} \right)_{\text{expt}} = \left( \frac{1}{T_1} \right)_{\text{diff}} + \left( \frac{1}{T_1} \right)_{x}
\]

or

\[
\left( \frac{1}{T_1} \right)_{x} = \left( \frac{1}{T_1} \right)_{\text{expt}} - \left( \frac{1}{T_1} \right)_{\text{diff}} \quad \text{----- (4.8)}
\]
If we extend the straight line portion just below the melting point (Fig. 11), we obtain \( \frac{1}{T_1} \text{diff} \). Subtracting this contribution from \( \frac{1}{T_1} \text{expt} \), we obtain \( \frac{1}{T_1} \text{X} \). In Fig. 14, we then plot \( \ln \left( \frac{1}{T_1} \text{X} \right) \) versus \( 1000/T \). This plot shows that within experimental errors, the slopes are independent of \( n \), although there seems to be some deviation at the higher temperature end. But this deviation can be attributed to subtracting two larger quantities from each other in equation (4.8). We now plot the ratio \( \frac{\frac{1}{T_1} \text{X}(n)}{\frac{1}{T_1} \text{X}(0)} \) versus no. of deuterons in Fig. 15. Within experimental error, the slope of this plot is the same as obtained from second moments using line-width data (to be discussed in Chapter V).

If this new mechanism is predominant at lower temperatures (\( \leq 80^\circ\text{K} \)), it seems that this mechanism is associated with dipolar inter-molecular interactions modulated by the reorientation of the molecules. Using the rigid-lattice line-width data (Chap. V), we can calculate the correlation times for molecular reorientation required to give these results. In order to calculate these correlation times, we must calculate terms of the form \( F(t)F(t + T) \) for interactions between pairs of nuclei on different molecules. If \( T_c \) is the correlation time for reorientation of a single molecule and if we assume that the correlation functions are well approximated by assuming uncorrelated motions of the members of a pair, then

\[
F(t)F(t + T) = |F(0)|^2 \exp\left(-\frac{2t}{T_c}\right) \quad (4.9)
\]
FIG. 14  PLOT OF \( \frac{1}{T} \) VS. \( \frac{1000}{T^o K} \) FOR \( CH_4, CH_3D, CH_2D_2 \) AND \( CHD_3 \) BELOW 80° K.

ACTIVATION ENERGY \( E_a = 0.2 \text{ Kcal/Mole} \)
FIG. 15  PLOT OF \( \frac{1}{T_i} x(n) \) \( \times (n) \) VERSUS NO. OF DEUTERONS
We must, therefore, calculate an average of the form 
\[ \left| \frac{\gamma_{2m}(\theta, \phi)}{k^3} \right|^2 \]
The average must be calculated for all possible rotations of the individual molecules and in the case of a crystalline powder or a liquid, over all possible orientations of the carbon-carbon vector. The averaging may be done in any order. If the last average is done first, keeping \( r \) fixed, we see that

\[ \left| \frac{\gamma_{2m}(\theta, \phi)}{k^3} \right|^2 = \frac{1}{4\pi} < \frac{1}{r_6} > \quad \text{---- (4.10)} \]

Abragam\(^{(17)}\) (page 289 - 291) gives the following expression for \( T_1 \) for a system of identical spins

\[ \frac{1}{T_1} = \frac{3}{2} \gamma^4 I \hbar^2 I(I + 1) \sum_k \left[ J_{ik}^{(0)}(\omega_o) + J_{ik}^{(2)}(\omega_o) \right] \]

Using equations (4.9) and (4.10) and assuming \( \omega_o^2 T_c^2 \ll 1 \), \( J_{ik}^{(1)}(\omega_o) \) and \( J_{ik}^{(2)}(2\omega_o) \) are given by

\[ J_{ik}^{(1)}(\omega_o) = \gamma_c \frac{1}{4\pi} < \frac{1}{r_6} > \times \frac{8\pi}{15} = \frac{2\gamma_c}{15} < \frac{1}{r_6} > \]

\[ J_{ik}^{(2)}(2\omega_o) = \gamma_c \frac{1}{4\pi} < \frac{1}{r_6} > \times \frac{32\pi}{15} = \frac{8\gamma_c}{15} < \frac{1}{r_6} > \]

This gives

\[ \frac{1}{T_1} = \frac{3}{2} \gamma^4 I \hbar^2 I(I + 1) \gamma_c \sum_k < \frac{1}{r_6} > \quad \text{---- (4.11)} \]

For the rigid-lattice, Abragam\(^{(17)}\) (page 112, equation 39)
gives the following expression for second moment ($M_2$)

$$M_2 = \frac{3}{5} \gamma^4 I_2 \sum_k \frac{1}{r_{1k}}$$

--- (4.12)

Combining equations (4.11) and (4.12)

$$\tau_c = \frac{3}{5} \times \frac{1}{T_1} \times \frac{1}{M_2}$$

--- (4.13)

We will show in Chap. V that intra-molecular interactions do not contribute to the observable second moments. Second moments calculated from intra-molecular interactions have much larger values than those determined from experimental results, while second moments calculated from inter-molecular interactions agree with the experimental values. Using our experimental value of the second moment $M_2 = 4.8 \times 10^9$ sec$^{-2}$ (see Chap. V) for a sample of CH$_4$ and taking $T_1 = 50$ sec., we get

$$\tau_c = 10^{-12} \text{ sec.}$$

Thus, if the new mechanism is causing relaxation at these low temperatures ($< 80^0K$) and the motion can be described by a single reorientation time $\tau_c$, one would expect $1/T_1$ values to rise as the temperature is lowered and $\tau_c$ to rise until a maximum is reached for $\omega_0^2 \tau_c^2 \sim 1$. Then the values of $1/T_1$ should fall as the temperature is still lowered where $\omega_0^2 \tau_c^2 >> 1$.

From our experimental results of $1/T_1$ (Fig. 11), we do observe that $1/T_1$ values start rising at our lowest
temperature (56°K). The activation energies obtained from a plot of \( \ln \left( \frac{1}{T_1} \right)_x \) versus 1000/T (Fig. 14) are 0.2 kcal/mole independent of \( n \). As mentioned earlier we also observe that the plot of the ratio \( \frac{(1/T_1)_x(n)}{(1/T_1)_x(o)} \) versus \( n \) (Fig. 15) gives the same slope as obtained from the second moments using line-width data (Chap. V) within experimental error and the second moments are due to intermolecular interactions. Since the correlation times for molecular reorientation (10^{-12} sec.) are quite reasonable, we may probably be justified in suggesting that the new mechanism which contributes to relaxation in this region is due to dipolar inter-molecular interactions modulated by the reorientation of the molecules. However, our results seem to be in conflict with the conventional theory which predicts that for such reorientational motions \( R_a \) should be several times larger than \( R_b \). Therefore, further work will have to be done to clarify this. It should be emphasized that in drawing the conclusion that \( R_a = 0 \), the assumption has been made that the spin-rotational interaction is not effective in the solids \( (R_c = 0) \). It is well established that \( R_c = 0 \) between 80°K and 90°K, but below 80°K it is only a guess based on the fact that \( \frac{(1/T_1)_x(n)}{(1/T_1)_x(o)} \) is independent of temperature.

4-5 EFFECT OF PARAMAGNETIC IMPURITIES ON \( T_1 \)

The addition of paramagnetic impurities to substances can influence markedly the proton relaxation time. The magnetic moment of a paramagnetic ion is of the order of one Bohr
magneton and this is some $10^3$ times larger than a nuclear magnetic moment. Therefore, larger $\gamma$-values of the electronic moments will result in a larger interaction of the nuclear moments with the electronic moments. The fluctuating local magnetic field will, therefore, be correspondingly larger and the relaxation time $T_1$ shorter. The relaxation produced by the ions is inter-molecular.

Assuming that the diffusion equation describes the relative motions of the nuclei and paramagnetic ions correctly and the correlation time $\tau$ is small compared with the Larmor period $1/\omega$ of the paramagnetic ion, Abragam (17) (page 304, equation 118) has given the following formula for $T_1$

$$\frac{1}{T_1} = \frac{16}{15} \kappa^2 N_{\text{ion}} \gamma_p^2 \gamma_S^2 \hbar^2 S(S + 1) \frac{\eta}{kT} \quad \text{--- (4.14)}$$

where $\eta$ is the coefficient of viscosity and $\gamma_p$ is the gyromagnetic ratio of protons. $S$ is a dimensionless number defined by

$$\gamma_S^2 \hbar^2 S(S + 1) = \langle \mu^2 \rangle$$

$\langle \mu^2 \rangle$ being the mean square of the magnetic moment of the ion and is denoted by $\mu_{\text{eff}}^2$. $N$ is the number of ions per cm$^3$.

This leads to

$$\frac{1}{T_1} = \frac{16}{15} \kappa x \gamma_p^2 \times \mu_{\text{eff}}^2 \times \frac{\eta}{kT} \times N_{\text{ion}} \quad \text{--- (4.15)}$$

Of course, we should add to this expression, the contri-
bution of the protons in the solution, which in pure CH$_4$ are solely responsible for the relaxation time. But as $\gamma^2_{\text{ion}}$ is about $10^6$ times larger than $\gamma^2_p$, the influence of paramagnetic ions is predominating even in a concentration of $10^{-3}$ N.

According to the above expression, the relaxation time should be inversely proportional to the concentration of the paramagnetic ions.

We have studied the effect of dissolved paramagnetic ions in CH$_4$. Roughly known amounts of oxygen were added to a pure sample of CH$_4$. These samples were then analysed by a mass spectrometer at the Department of Chemistry, University of Washington, Seattle, Washington, U. S. A. The oxygen concentrations were 1.08% and 2.54% respectively. $T_1$ was measured in these samples from $110^0$K - $78^0$K with the technique (A) described in Chapter II. The results of these measurements are shown in Fig. 16. We find that above the melting point ($90^0$K - $110^0$K), $T_1$ has the same temperature dependence as observed in our purest sample of CH$_4$. Fig. 17 shows a plot of $1/T_1$ as a function of oxygen concentration at $108^0$K. The dotted line shows the values calculated from equation (4.15), taking

\[
\gamma_p = 2.68 \times 10^4 \text{ gauss}^{-1} \text{ sec}^{-1}
\]
\[
\mu_{\text{eff}} = 1.4 \times 10^{-20} \text{ erg-gauss}^{-1}
\]
\[
\eta = 1.262 \times 10^{-3} \text{ poise}
\]
\[
N_{\text{ion}} (1.08\% O_2) = 1.5 \times 10^{20} / \text{ cm}^3
\]
\[
N_{\text{ion}} (2.54\% O_2) = 4.0 \times 10^{20} / \text{ cm}^3
\]
\[
k = 1.38 \times 10^{-16} \text{ ergs (}^0\text{K})^{-1}
\]
FIG. 16 PLOTS OF $T_1$ vs TEMPERATURE FOR CH₄ SAMPLE CONTAINING DIFFERENT AMOUNTS OF OXYGEN.
\( \frac{1}{T_1} \text{ (SEC)} \) AT \( 108^\circ \text{K.} \)

FIG. 17  PLOT OF \( \frac{1}{I} \) VS OXYGEN CONCENTRATION.
Our experimental values agree reasonably well with the calculated values and our results also verify the inverse proportionality of $T_1$ and oxygen concentration. This shows that $T_1$ in the liquid can be well represented by equation (4.15).

In the solid samples ($90^\circ$K - $78^\circ$K), $T_1$ is fairly short and independent of temperature. Bloembergen\(^\text{20}\) has shown that if the concentration of paramagnetic ion is greater than 1%, the spin diffusion process is unnecessary; within a few lattice spacings of every nuclear dipole there is an ion with which energy can be exchanged directly. Moreover, the magnetic interaction of the ions, now relatively close to each other, may endow their energy levels with a breadth greater than $\hbar \omega_0$, the magnitude of the quanta which the nuclear dipoles wish to exchange. The system of ionic spins can now absorb these small quanta directly merely by rearrangement of the spins, a process which is independent of lattice vibrations; the spin-lattice relaxation is then short and independent of temperature. This is what we have found experimentally.

Nitrogen, which is not paramagnetic, was also added in a CH\(_4\) sample, the concentration of nitrogen being about 3%. As anticipated it was found to have no measurable effect on $T_1$.

4-6 ESTIMATION OF $O_2$ CONCENTRATION IN A PURE CH\(_4\) SAMPLE

Because of oxygen background in the mass spectrometer it is impossible to analyse the oxygen concentration with it in a region where $T_1$ measurements indicate that the oxygen concentration is less than about 0.1%. Therefore, our $T_1$
measurements represent a more sensitive means of detecting oxygen than a mass spectrometer unless special steps are taken to cut down the oxygen background in the mass spectrometer.

We can calculate the percentage of oxygen concentration in our pure sample of CH$_4$ using the relation:

$$\frac{1}{T_1} = \left(\frac{1}{T_{1n}}\right) + \left(\frac{1}{T_{1o}}\right)$$

where $1/T_{1n}$ represents the natural relaxation time of pure CH$_4$ and $1/T_{1o}$ is the contribution due to oxygen.

The measured $T_1 = 16.5$ sec. at 108$^0$K whereas $T_{1o} = 40$ msec. and 16.7 msec. with oxygen concentration of 1.08% and 2.54% respectively. If $T_{1o}$ were about 16.5 sec. at 108$^0$K, this would correspond to oxygen concentration $f = 2.6 \times 10^{-3}$ %. Since $1/T_1 \geq 1/T_{1o}$, we can say that $f \leq 2.6 \times 10^{-3}$ % in our pure sample of CH$_4$. Our measurements of $T_1$ were reproducible from day to day and in different samples. Since we would have been able to detect a change of less than 10% in $T_1$, we are probably justified in saying that our purification procedure described in Chap. II resulted in $f \leq 2.6 \times 10^{-4}$ %.
CHAPTER V

N.M.R. LINE-SHAPE STUDIES

The purpose of this chapter is to discuss measurements of the nuclear magnetic resonance line shape in methane where the measurements have been made using pulse techniques.

Line-width may be characterized in several ways: by a width in magnetic field or frequency, or, alternatively, by a time conventionally called $T_2$, which is known as the spin-spin relaxation time and is the inverse of the width in frequency ($T_2 = \frac{1}{\Delta \omega}$). Classically the time $T_2$ represents the time for a group of spins initially precessing about $H_0$ in phase to dephase as a result of their slightly different precession frequencies. The reason for the differences in the precession frequency of individual spins is due to the fact that each spin is acted upon by the local magnetic field of its environment. The local field may be considered to give rise to a spread of Larmor frequencies given by $\Delta \omega$ where $\Delta \omega$ may have value ranging from zero to a certain value determining the width of the Larmor frequency distribution. The dephasing time $T_2$ depends on the spread of precessional frequencies and on the rate at which these change due to molecular motions.

The various types of motions such as molecular rotation or translation etc., which give rise to relaxation processes, influence also the width of the resonance lines. With a few exceptions these motions result in a narrowing of the resonance
lines and this is given the name of "motional narrowing". The physical explanation of the motional narrowing is that if the spins are in rapid relative motion, the local field "seen" by a given spin will fluctuate rapidly in time. Only its average value taken over a time of the order of Larmor period in the local magnetic field is observable. If this time is long compared with the duration of a fluctuation, this average value of the local field will be much smaller than the instantaneous value of the local field. This gives rise to line-width much smaller than the width obtained from the steady local field for a rigid system. The narrower line corresponds to a longer dephasing time \( T_2 \). In contrast, when there is no motion, a given spin experiences a constant local field. It either precesses at a fixed rate faster than the average, or slower. The dephasing of a group of spins arises from the accumulation of positive or negative phase. Since the local fields "seen" by a given spin are much greater than the mean local field "seen" by that spin when there is motion, the line is broadened.

When diamagnetic solids are cooled to sufficiently low temperatures so that very little translational motion of the molecules is taking place, the nuclear magnetic resonance absorption as a function of frequency \( I(\omega) \) is usually independent of temperature. This rigid lattice line shape, that is, in a sample where the lengths and orientations of the vectors describing the relative positions of the spins do not change in time, is often closely approximated by a Gaussian function

\[
    I(\omega) \sim \exp \left[ - \frac{(\omega - \omega_o)^2}{2 \omega_p^2} \right]
\]
where $\omega_o = \gamma H_o$ is the Larmor frequency of the nuclear spins in the external field $H_o$, and $\omega_p^2$ is the second moment of the line for rigid lattice [Abragam (17), page 107 equation 24]

The amplitude of the free induction signal after a $90^\circ$ rf pulse observed in a pulse experiment (13) is proportional to the "relaxation function" $G(t)$ [Abragam (17) page 114] which is the Fourier transform of $I(\omega)$ i.e.

$$G(t) \sim \int_0^\infty I(\omega) \cos \omega t \, d\omega$$

which gives

$$G(t) \sim \exp \left[ - \frac{\omega_p^2 t^2}{2} \right]$$

for a Gaussian line shape.

With the onset of rapid molecular motion the observable line shape or relaxation function changes to a Lorentzian form,

$$G(t) \sim \exp \left[ - \omega_p^2 \gamma_c t \right]$$

[Abragam (17) page 433, eq. 22]

where $\gamma_c$ is the correlation time for changes in local fields due to translational motion with $\omega_p^2 \gamma_c^2 \ll 1$.

If one assumes that at each instant the microscopic distribution of local fields through the sample is the same as for the rigid lattice, but that the local field at each point fluctuates at a rate described by a correlation function

$$G_\omega(\tau) = \omega_p^2 g_\omega(\tau),$$

we can predict the relaxation function for all times to be [Abragam (17) page 432 eq. 19]

$$G(t) \sim \exp \left[ - \omega_p^2 \int_0^t (t - \tau) g_\omega(\tau) d\tau \right]$$

where $g_\omega(\tau)$ is the reduced correlation function of $\omega(t)$ such that $g_\omega(0) = 1$.  


Because of self-diffusion which exists in many solids except at very low temperatures, the effect on the resonance line can be described by assuming the reduced correlation function $g_{\omega}(\tau)$ for the frequency $\omega(t)$ of the random local field that fluctuates on account of the diffusion, to be of the form

$$g_{\omega}(\tau) = \exp \left[ -\frac{\tau}{\tau_c} \right]$$

This leads to the following expression for the relaxation function $G(t)$:

$$G(t) \sim \exp \left[ -\omega_p^2 \tau_c^2 \left\{ \exp \left( -\frac{t}{\tau_c} \right) - 1 + \frac{t}{\tau_c} \right\} \right] \quad (5.1)$$

The general form of $G(t)$ in equation (5.1) has not been extensively used in evaluating experimental results. Normally, in order to obtain $\tau_c$ as a function of temperature in a system where diffusion takes place, one works in a region where $\tau_c$ is so short that $G(t)$ is only studied for $t \gg \tau_c$ so that the Lorentzian form is obtained. When the motion has slowed down to the point that the "rigid lattice" line shape is obtained, it is usually assumed that no further information on $\tau_c$ can be obtained.

Abragam (17) (page 455) has pointed out that from the general form for $G(t)$ in equation (5.1), it is possible to obtain, the detailed shape of the resonance curve, to correlate the observed line-width parameter with the correlation time $\tau_c$ and obtain the variation of $\tau_c$ with temperature. Thus it enables us to interpret our experimental results. In
fact, we have found in studying the proton resonance in CH$_4$, CH$_3$D, CH$_2$D$_2$ and CHD$_3$ that the use of the pulse technique enables the direct study of equation (5.1) over a range of $\tau_c$ not usually accessible to absorption methods.

When $\tau_c$ in such systems becomes of the order of $10^{-5}$ seconds or longer, the absorption signal gives the temperature-independent, rigid lattice line shape. For $t/\tau_c \ll 1$, equation (5.1) reduces to

$$G(t) \sim \exp \left[ -\omega_p^2 \frac{t^2}{2} \right] \sim \exp \left[ -\frac{t^2}{2(T_2)^2} \right]$$

where $(T_2)^2_{\text{rigid lattice}} = \frac{1}{\omega_p^2}$  \hspace{1cm} ---- (5.2)

$G(t)$ is Gaussian and the measurement of $T_2$ enables to calculate the (temperature-independent) second moment. However, the proton induction signals in such systems are so large that we can also study $G(t)$ for $t/\tau_c \gg 1$. Equation (5.1) reduces to

$$G(t) \sim \exp \left[ -\omega_p^2 \tau_c t \right] \sim \exp \left[ -\frac{t}{T_2} \right]$$

where $T_2 = \frac{1}{\omega_p^2 \tau_c}$  \hspace{1cm} ---- (5.3)

Actual measurements of $T_2$ enables us to obtain $\tau_c$ as a function of temperature. Here, the line shape is indeed found to be Lorentzian.

The corresponding observation in absorption experiments
is that \( I(\omega) \) is Lorentzian for \( (\omega - \omega_0)^2 \gamma_c^2 \ll 1 \) which agrees with our results. However, the observation of a Lorentzian pip near the center of an absorption line is difficult since one must subtract the large Gaussian contribution to \( I(\omega) \). In the pulse experiment, the Gaussian portion is allowed to die away, leaving the Lorentzian tail to be studied separately.

5.1 MEASUREMENT OF \( T_2 \)

\( T_2 \) in the various samples of methane was measured by the technique C or D described in Chap. II. In the region where the "echo" was observable, \( T_2 \) was measured from the "echo" amplitude while in the region where echo was unobservable, \( T_2 \) was measured from the induction signal (tail).

In Fig. 18, we have compared plots of \( \ln A(t) \) versus \( t \) and \( t^2 \) for a sample of \( CH_4 \) at 78.15°K. We find that (a) gives a straight line only, which confirms that the line shape is indeed Lorentzian.

In Fig. 19, we again plot \( \ln A(t) \) versus \( t \) and \( t^2 \), for a sample of \( CH_4 \) at 61.4°K. A straight line graph is obtained only in (b). Here the line shape is Gaussian.

5.2 RESULTS AND DISCUSSION

The experimental results are shown in Fig. 20 where \( T_2 \) is plotted versus \( 1000/T^0K \). The crosses show \( T_2 \) evaluated from free precession signals observed at \( t/\gamma_c \ll 1 \) fitting the curve \( G(t) \sim \exp \left[ -\frac{t^2}{2T_2^2} \right] \). The circles are obtained
Fig. 18 PLOTS OF THE CORRECTED AMPLITUDE OF THE INDUCTION SIGNAL A(t) VERSUS (TIME) AND (TIME)^2 FOR CH₄ AT 78.15°K
FIG. 19  PLOTS OF THE CORRECTED AMPLITUDE OF THE INDUCTION SIGNAL A(t) VERSUS TIME AND (TIME)² FOR CH₄ AT 61.4°K.
FIG. 20 PLOT OF $T_2$ VERSUS FOR SOLID CH$_4$, CH$_3$D, CH$_2$D$_2$ AND CHD$_3$ BETWEEN 56° K AND 90° K.

ACTIVATION ENERGY $E_a = 3.2$ K CAL/MOLE

$T_2$ IN "RIGID-LATTICE" FITTING EXP. \( \left( -\frac{1}{2T_2^2} \right) \)

$T_2$ MEASURED FROM INDUCTION TAIL EXP. \( \left( -\frac{1}{T_2} \right) \)

$T_2$ MEASURED WITH "ECHO" FITTING EXP \( \left( -\frac{1}{T_2} \right) \)
from spin echo experiments at higher temperatures where $\tau_c$ is short. The squares are obtained from free precession signals for $t/\tau_c \gg 1$, fitting $G(t) \sim \exp \left(-\frac{t}{T_2}\right)$. The results show that for the molecule $\text{CH}_{4-n}\text{D}_n$, the correlation times accurately follow the activation energy curve over the entire temperature range

$$\left(\tau_c\right)_n = \left(\tau_0\right)_n \exp\left[\frac{E_a}{RT}\right] \quad (5.4)$$

where $E_a$ is the activation energy corresponding approximately to the height of the potential barrier between two equivalent molecular positions. As the temperature increases, $\tau_c$ decreases and the resonance likewise narrows.

From the plot of $\ln T_2$ versus $1000/T$ (Fig. 20), the activation energies $E_a$ are found to be 3.2 kcal/mole independent of $n$, in disagreement with previous measurements of 1.5 kcal/mole for $\text{CH}_4$ \cite{21}. However, our value is in agreement with the value obtained from $T_1$ measurements. Professor Waugh's estimates are based on the line-width data of Thomas, Alpert and Torrey \cite{4}. The lack of agreement between our activation energies and those obtained from the line-width data is probably due to the change in line shape as the temperature is changed.

A knowledge of second moments provides useful information on the line shape and the interactions that contribute to the line shape. The second moments can be calculated from equation (5.2) using $T_2$ measurements for the rigid lattice line-width data. The experimental values of $T_2$ for the
samples of CH$_4$, CH$_3$D, CH$_2$D$_2$ and CHD$_3$ from Fig. 20, are 14.5, 16.0, 18.0 and 27.0 $\mu$sec. respectively. The values of the second moments are 4.8, 3.95, 3.1 and 1.4 in units of $10^9$ sec$^{-2}$ for $n = 0, 1, 2$ and 3 respectively corresponding to the ratios 1 : 0.82 : 0.64 : 0.29.

The contributions to second moments come from intramolecular dipolar interactions and inter-molecular dipolar interactions. For a system of two unlike spins I and S, Abragam (17) (page 122) gives the following expression for the second moments for the case of dipolar broadening.

\[
(\omega^2_p) = (\omega^2_p)_\text{II} + (\omega^2_p)_\text{IS} \quad ---- (5.5)
\]

where

\[
(\omega^2_p)_\text{II} = \frac{3}{4} \gamma^4 I h^2 I(I + 1) \sum_{n_1} \frac{(1 - 3 \cos^2 \theta)^2}{r^6}
\]

and

\[
(\omega^2_p)_\text{IS} = \frac{1}{3} \gamma^2 I \gamma^2 S h^2 S(S + 1) \sum_{n_1} \frac{(1 - 3 \cos^2 \theta)^2}{r^6}
\]

$\theta$ is the angle of vector $\overrightarrow{r}$ with the applied magnetic field $H_0$ as shown in the Fig. 21, and the sum $\sum_{n_i}$ is to be taken over all the sites of the spins S surrounding a spin I.
The contributions to second moments from inter-molecular interactions and intra-molecular interactions can be evaluated separately by using equation (5.5).

Let us first evaluate the contribution to the second moments from inter-molecular interactions. In our case spins I refer to protons and spins S to deuterons. For a polycrystalline material, there is an isotropic distribution of the axes of reorientation and it is permissible to average \((1 - 3 \cos^2 \theta)^2\) over all directions. Replacing it by its mean value of \(4/5\) and taking

\[
\gamma_I = 2.67 \times 10^4 \text{ gauss}^{-1} \text{ sec}^{-1} \\
\gamma_S = 4.1 \times 10^3 \text{ gauss}^{-1} \text{ sec}^{-1}
\]

Equation (5.5) can be written as

\[
(\omega_p^2)_{nn} = 228.7 \times 10^{-39} \sum (4-n) \frac{1}{r^6} + 6.39 \times 10^{-39} \sum n \frac{1}{r^6} \quad --- \ (5.6)
\]

In order to calculate \(\sum 1/r^6\), let us assume a uniform distribution of protons or deuterons over a sphere of radius \(a = 1.09 \text{ A}\) given by C-H distance in CH\(_4\). This model assumes that the centres of mass of the molecules are fixed (no diffusion), and that the molecules reorient very rapidly. If \(\vec{r}\) represents the distance between a proton and a deuteron situated at A and B, \(\theta_1\) and \(\theta_2\) are the polar angles on the two spheres as shown and \(\phi_1\) and \(\phi_2\) are the corresponding azimuthal angles, then

\[
\frac{1}{r^2} = x^2 + y^2 + z^2
\]
where

\[ x = a \left( \sin \theta_1 \cos \phi_1 - \sin \theta_2 \cos \phi_2 \right) \]

\[ y = a \left( \sin \theta_1 \sin \phi_1 - \sin \theta_2 \sin \phi_2 \right) \]

\[ z = R - a \left( \cos \theta_1 + \cos \theta_2 \right) \]

If we use the known crystal structure of CH\(_4\)\(^{(22)}\) and take the carbon-carbon separation \(R = 4.09 \, \text{Å}\), we get

\[ \sum \frac{1}{r^6} = 0.0057 \times 10^{48} \]

taking into account the nearest neighbours \((=12)\). Substituting this value in equation (5.6), we get

\[ (\omega_p^2)_n = 1.3 \times 10^9 (4 - n) + 0.036 \times 10^9 n \]

\[ = 5.2 \times 10^9 (1 - 0.24 n) \]

\[ \text{(5.7)} \]

In writing equation (5.7) we neglect isotopic changes in inter-molecular separations. Equation (5.7) predicts second moments for \(n = 0, 1, 2\) and \(3\) to be \(5.2, 3.95, 2.70\) and \(1.45\) in units of \(10^9 \, \text{sec}^{-2}\), corresponding to the ratios \(1:0.76:0.52:0.28\).

We can now evaluate the contribution to the second moments from intra-molecular interactions. These would contribute to the observable second moments only if the rate of reorientation of the molecules was slow compared with the Larmor periods of the nuclei in the local magnetic fields. Since \(\bar{F}\) is fixed, we have to average only \((1 - 3 \cos^2 \theta)^2\) over all spatial directions. Substituting the values of various quantities in equation (5.5), we get
FIG. 22  PLOT OF $\frac{\omega_n^2}{\omega_0^2}$ VERSUS NO. OF DEUTERONS IN RIGID LATTICE.
\[( \omega_p^2 )_n = 21.6 \times 10^9 (1 - 0.32 n) \]  \hspace{1cm} \text{(5.8)}

Equation (5.8) predicts second moments for \( n = 0, 1, 2 \) and 3 to be in the ratios of \( 1 : 0.68 : 0.36 : 0.04 \).

In Fig. 22, we show our results of the observable second moments calculated from equations (5.2), (5.7) and (5.8). We find that equation (5.8) gives much larger values of the observable second moments than our experimental values. It seems unlikely that intra-molecular interactions are contributing to the observable second moments. Since the ratios predicted by equation (5.7) agree with our experimental values to within a few percent, the contribution to the second moments comes from inter-molecular interactions. It seems that isotropic reorientation reduces the intra-molecular contribution to zero, intra-molecular local fields being averaged to zero. Local fields which are inter-molecular in origin do not average to zero so long as the centres of mass of the molecules remain fixed. It then follows that the observed change in \( T_2 \) with increase in temperature above 69\(^0\)K is associated with the inter-molecular interactions which become time-dependent due to self-diffusion. Therefore, the activation energy \( E_a \) associated with the variation of \( T_2 \) with temperature is a self-diffusion activation energy.

In the region where the line shape is Lorentzian, \( \tau_c \) can be evaluated from equation (5.3), which can be written as

\[
\frac{(\tau_c)_n}{(\tau_c)_0} = \frac{(\omega_p^2)_0}{(\omega_p^2)_n} \times \frac{(T_2)_0}{(T_2)_n} \hspace{1cm} \text{(5.9)}
\]
The ratios of \( \frac{\omega_p^2}{\omega_p^2} \) obtained from rigid lattice line-width data are 1 : 0.82 : 0.64 : 0.29. The ratios of \( \frac{T_2}{T_0} \) above 69°K (Fig. 20) are 1 : 0.75 : 0.54 : 0.31 for \( n = 0, 1, 2 \) and 3 respectively. Substituting these values in equation (5.9), the ratios of \( \frac{T_c}{T_{c_0}} \) for \( n = 0, 1, 2 \) and 3 are 1 : 0.92 : 0.86 : 1.0 respectively.

Since our values of activation energies from \( T_2 \) measurements agree with the values obtained from \( T_1 \) measurements and we have shown that inter-molecular interactions contribute to the line-width, we can say that \( T_1 \) between 80°K and 90°K is predominantly due to inter-molecular interactions. This result has been used in Chap. IV.
CHAPTER VI

SUMMARY AND CONCLUSIONS

The work described in the preceding chapters may be regarded as a part of a program for the study of proton and deuteron nuclear magnetic resonances in methane. Our chief aim is to explore the various possible mechanisms that cause spin-lattice relaxation. In addition, one can obtain information on the liquid and solid-state properties of the system being investigated.

Our work has been concerned with the measurements of $T_1$ from $110^0 \text{K}$ to $56^0 \text{K}$ and $T_2$ from $90^0 \text{K}$ to $56^0 \text{K}$ in samples of $\text{CH}_4$, $\text{CH}_3\text{D}$, $\text{CH}_2\text{D}_2$ and $\text{CHD}_3$. We have been able to show that:

1. $T_1$ in a pure sample of $\text{CH}_4$ is more than 1000 times longer than the previous reported values. Our measurements have shown that $T_1$ is very sensitive to small amounts of oxygen and the previously reported shorter values of $T_1$ may be attributed to dissolved oxygen.

2. We have been able to develop a very simple technique for the removal of oxygen from our samples. This technique is well suited for the removal of oxygen from other gases and has already been extended to liquids. On the basis of our $T_1$ measurements in $\text{CH}_4$, we are probably justified in saying that our purification procedure resulted in oxygen $\leq 2.6 \times 10^{-4}$ %.

3. Our measurements of $T_1$ in samples of $\text{CH}_4$ with different concentrations of oxygen have confirmed that $T_1$ is
inversely proportional to oxygen concentration.

(4) Contrary to the observations of Thomas, Alpert and Torrey\(^4\), we have been able to observe a marked discontinuity in \(T_1\) across the melting point in all our samples.

(5) Johnson and Waugh\(^3\) have predicted that in liquids, spin-rotational interactions may be contributing to the relaxation process, but in our case we find that inter-molecular dipolar interactions probably play a predominant role in liquids and solids, and the contribution to relaxation from spin-rotational interactions appears to be small. There is additional evidence that the inter-molecular dipolar interactions are predominant in the region just below the melting point, since we get the same value of activation energies from our \(T_1\) and \(T_2\) measurements.

(6) At lower temperatures (\(\leq 80^\circ K\)), it seems that relaxation is caused by inter-molecular dipolar interactions modulated by the reorientation of the molecules. Our results are in conflict with the conventional theory which predicts that intra-molecular interactions should be more important in liquids and in solids below \(65^\circ K\).

(7) The line shape is Lorentzian in the region just below the melting point which changes to Gaussian at lower temperatures. The line shape is predominantly due to inter-molecular interactions.

It would, however, be most valuable to extend the present work in several directions:

(1) One would like to have data on \(T_1\) and \(T_2\) over
the entire range extending down to liquid helium temperatures so as to get a complete picture of the various mechanisms that cause relaxation.

(2) Since we have only been able to predict the most predominant mechanism causing relaxation and we cannot exclude completely the possibility of others, as predicted by conventional theory, it would be useful to perform some more experiments by mixing CH₄ and CD₄ in different concentrations to obtain more precise values of inter-molecular and intra-molecular interactions.

(3) It may be of interest to study proton resonance at some other frequency (say 4-5 Mc/sec.) . The results should show the same dependence in temperature as do our results. This will provide a check on our results.

(4) Our activation energies are in disagreement with previous measurements for CH₄. This lack of agreement between our values and those obtained by Professor Waugh from the line-width data of Thomas, Alpert and Torrey is probably due to the change in line shape with temperature, which is not taken into account in their data. However, steady state experiments on methane should be repeated to check whether or not this conjecture is true. If it is true, many of the published activation energies derived from line-width measurements may have to be re-examined.

We have shown that, with the equipment constructed for n.m.r. work, we have been able to gain insight into some aspects of relaxation mechanisms in methane and its
deuterated modifications. Some work along the suggested lines is already being done by students under the supervision of Dr. M. Bloom but further work will have to be done to get a clear picture of the problem.
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