DEUTERON MAGNETIC RESONANCE PROPERTIES

IN DEUTERATED MODIFICATIONS

OF METHANE

by

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ABSTRACT

Relaxation properties of the deuteron spin system in CD_4 and CD_3H were studied in the temperature range from $105°K - 57°K$. These results show that the intra-molecular quadrupole interactions dominate and the relaxation occurs through the molecular reorientations of the molecule.

The deuteron spin-lattice relaxation times are approximately temperature independent, except for a small contribution from the magnetic dipolar interactions near the melting point in CD_3H. From this data it is concluded that the reorientational correlation time is temperature independent.

The deuteron T_2 shows the same temperature dependence as the proton T_2; the deuteron T_2 can be accounted for on the basis of magnetic dipolar interactions alone.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

Nuclear magnetic resonance (N.M.R.) provides information on the properties of matter. Measurement of N.M.R. frequencies gives a measure of the time-averaged local magnetic fields at the nuclear sites, while observations on the approach to thermal equilibrium of the nuclear spin system (spin relaxation) give information on the fluctuations of the local fields. This thesis is only concerned with spin relaxation, as applied to liquid and solid methane.

Let $M_o \underline{k}$ be the macroscopic magnetization vector for a spin system in equilibrium with its surroundings (the lattice) at a temperature T in an external field $H_o \underline{k}$. If, initially, the spin system is not in equilibrium with the lattice, and has a magnetization $\underline{M}(o) = M_x(o) \underline{i} + M_3(o) \underline{k}$ it will approach equilibrium according to the following equation,

$$\underline{M}(t) = M_x(o) \left[\cos \omega_o t \; \underline{i} + \sin \omega_o t \; \underline{j} \right] F(t)$$
$$+ \left[M_o - (M_o - M_3(o)) G(t) \right] \underline{k}$$

where $\omega_o = \gamma H_o$ is the Larmor frequency of the nuclei having gyromagnetic ratio γ, F(t) and G(t) are the transverse and longitudinal relaxation functions respectively.

F(0) = G(0) = 1 and F(t), G(t) $\rightarrow$ 0 as t $\rightarrow \infty$.

Often, the approach to equilibrium is exponential. In those cases, the relaxation functions are completely specified by their time constants. The transverse or "spin-spin" relaxation time is usually denoted by T_2 and the longitudinal or "spin-lattice" relaxation time by T_1.

T_1 and T_2 have been previously measured for protons (see Appendix) in CH_4, CH_3D, CH_2D_2 and CHD_3 between $110°K$ and $55°K$ in an attempt to understand the basic relaxation mechanisms in methane through the dependence of T_1 and T_2 on the isotopes of hydrogen. There is a strong isotope effect because the deuteron has a magnetic moment about 1/7 of the proton magnetic moment, thereby producing weaker local fields and hence being far less effective than protons in causing spin relaxation of neighboring protons.

The three basic contributions to the local fields, (1) intra-molecular dipolar interactions, (2) inter-molecular dipolar interactions, (3) the influence of the rotational magnetic moments of the molecules, have different dependences on n, the number of deuterons in the $CH_{4-n}D_n$ molecule. The proton spin relaxation study was unable to provide a unique solution to the relative contributions of (1), (2) and (3) to the relaxation rate $1/T_1$, though it did give upper and lower limits for each of them. The simplest possible interpretation, namely that mechanism (2) predominates over the whole temperature range, is in conflict with the simplest theories which predict that mechanism (1) should be more important than

(2) in the liquid (90°K - 110°K) and the solid below about 65°K.

The results reported in this thesis are part of a program designed to further clarify the relaxation problem in methane. T_1 and T_2 have been measured for the deuterons in CD_4 and CHD_3 between 105°K and 57°K. Because of the smaller deuteron magnetic moment this study has been carried out at 4.3 megacycles per second, as compared with 30mc/sec. for the previous work on protons. To relate these measurements more clearly to the proton T_1 measurements, the proton T_1 in CHD_3 was also studied at 4.3 mc/sec.

The T_1 and T_2 measurements were performed using standard pulse techniques which are described briefly in Chapter 2, along with other experimental aspects of this work.

A new relaxation mechanism is introduced for deuterons since the deuteron spin is 1 (the proton spin is 1/2). The deuterons have quadrupole moments so that, in addition to effects produced by fluctuating magnetic fields, there is a contribution from (4) the fluctuating electric field gradient associated with the rotation of the molecules. The relationships between the proton and deuteron T_1 and T_2 as a function of n are discussed under Theory in Chapter 3. It is seen that mechanism (4) is closely analogous to mechanism (1) insofar as both mechanisms are governed by molecular rotation.

The experimental results are presented in Chapter 4. It is demonstrated clearly that as far as the deuteron T_1 is

concerned, mechanism (4) is dominant over the entire temperature range studied for CD_4 and CHD_3. In principle, these measurements should lead to an accurate calculation of the contribution of mechanism (1) to $1/T_1$ for protons. However, the quadrupole coupling constant, i.e. the magnitude of the electric field gradient at the deuteron, must be known first. Experiments are suggested to obtain this parameter.

On the other hand T_2 for the deuterons in solid methane is governed by (2) as is the case for the protons. The self-consistency between these measurements and the proton T_2 measurements is also discussed in Chapter 4.

The previously reported measurements on T_1 and T_2 for protons in $CH_{4-n}D_n$ have been performed by Bloom and Sandhu of this laboratory. Reprints of their papers are given in the Appendix for ready reference.

CHAPTER 2

EXPERIMENTAL APPARATUS AND TECHNIQUES

TEMPERATURE CONTROL:

The temperature control section of the apparatus was designed to cover a range of temperatures above the boiling point of the coolant used. Either liquid oxygen or liquid nitrogen was used in all the experiments. A continuous coverage from $77°K - 105°K$ was obtained. Moreover, by pumping on the liquid nitrogen, with a Hyvac no.7, the range was extended down to $57°K$.

Figure (1) shows schematically the dewars and the sample arrangement. There are three dewars, two glass dewars and a metal dewar. The procedure consisted essentially of cooling the whole system by filling the outer dewar with coolant, then evacuating the inner glass dewar to 0.1 micron of pressure, but leaving a few cm. of pressure inside the metal dewar. The heating rate of the sample was governed by the net heat input by conduction along the rods into the dewar, the heat supplied by the heater above the sample, and by the heat output, which was mainly caused by radiation to the coolant. To obtain lower temperatures both the outer and inner dewars were filled with liquid nitrogen, then the pressure in the inner glass dewar was reduced by pumping. The temperature was roughly controlled by
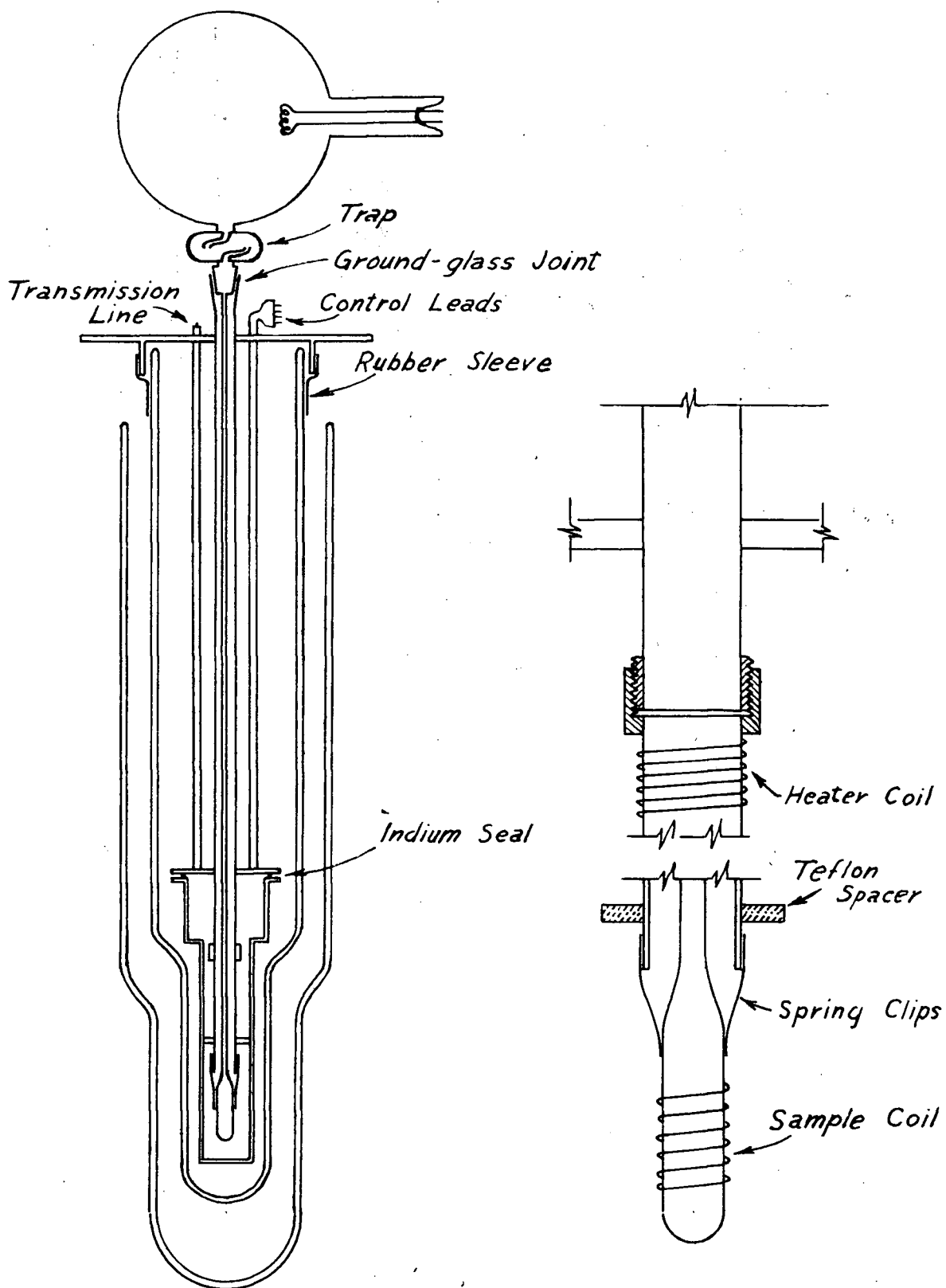
Figure 1. Diagram of the dewar and sample arrangement.

monitoring the vapor pressure inside the inner dewar using a
mercury manometer. The temperature was measured by means of
a platinum resistance thermometer previously calibrated using
the oxygen and nitrogen boiling points and the ice point.
The resistance was measured with a Rubicon Mueller Bridge.
The accuracy of the temperature measurements was $0.2°K$. Since
the purity of the liquid nitrogen was not known, the vapour
pressure readings were not used to measure the temperature,
but they did agree roughly with the published vapour pressure
versus temperature curves for nitrogen[2].

Because of the poor thermal conductivity of glass,
precautions were taken to avoid thermal gradients, and to ensure
correct temperature measurements. For these reasons, the
pressure inside the metal dewar was kept at a few centimeters,
and copper spring fingers were used to provide as large an
area of contact with the glass as possible. The fact that the
melting point transition temperature, as noted from the
experimental results, agrees to within at least $.5°K$ with that
given in the literature[3], shows that the temperature control
was sufficiently accurate for this experiment.

SAMPLE PREPARATION:

The samples were prepared according to the procedure
developed by H. Sandhu, J. Lees, and M. Bloom[4]. The problem is
to completely remove any paramagnetic impurities, which are

normally present in commercially prepared methane samples.
The purification is accomplished by a gettering technique; a
diffuse layer of misch metal is deposited on a spherical bulb
at the top of the sample tube (figure 1). The procedure is
as follows, a tungsten coil containing some pieces of misch
metal is sealed into the glass bulb. The whole assembly is
evacuated to 1 micron of pressure. In order to obtain a
diffuse layer of the deposit, the sample tube is filled with
Argon up to about 2mm. of pressure. The reason for this step
is that a diffuse deposit has a larger absorption capacity.
The getter is flashed, the Argon is pumped out, the methane is
introduced, and the sample is sealed off. The slight enlarge-
ment at the end of the sample tube, around which the sample
coil fits, is to increase the sample volume and hence to
improve the signal to noise ratio.

ELECTRONICS:

The electronics is that of a standard pulsed N.M.R.
spectrometer. It consists of a timing section, which generates
gating pulses of definite width and at definite times; a
transmitter section, which produces sharp pulses of r.f. power;
a sample circuit and a receiver. The timing section is built
up from three Tektronix units, two pulse generators (type 163)
and one sawtooth generator (type 162). The sawtooths produced
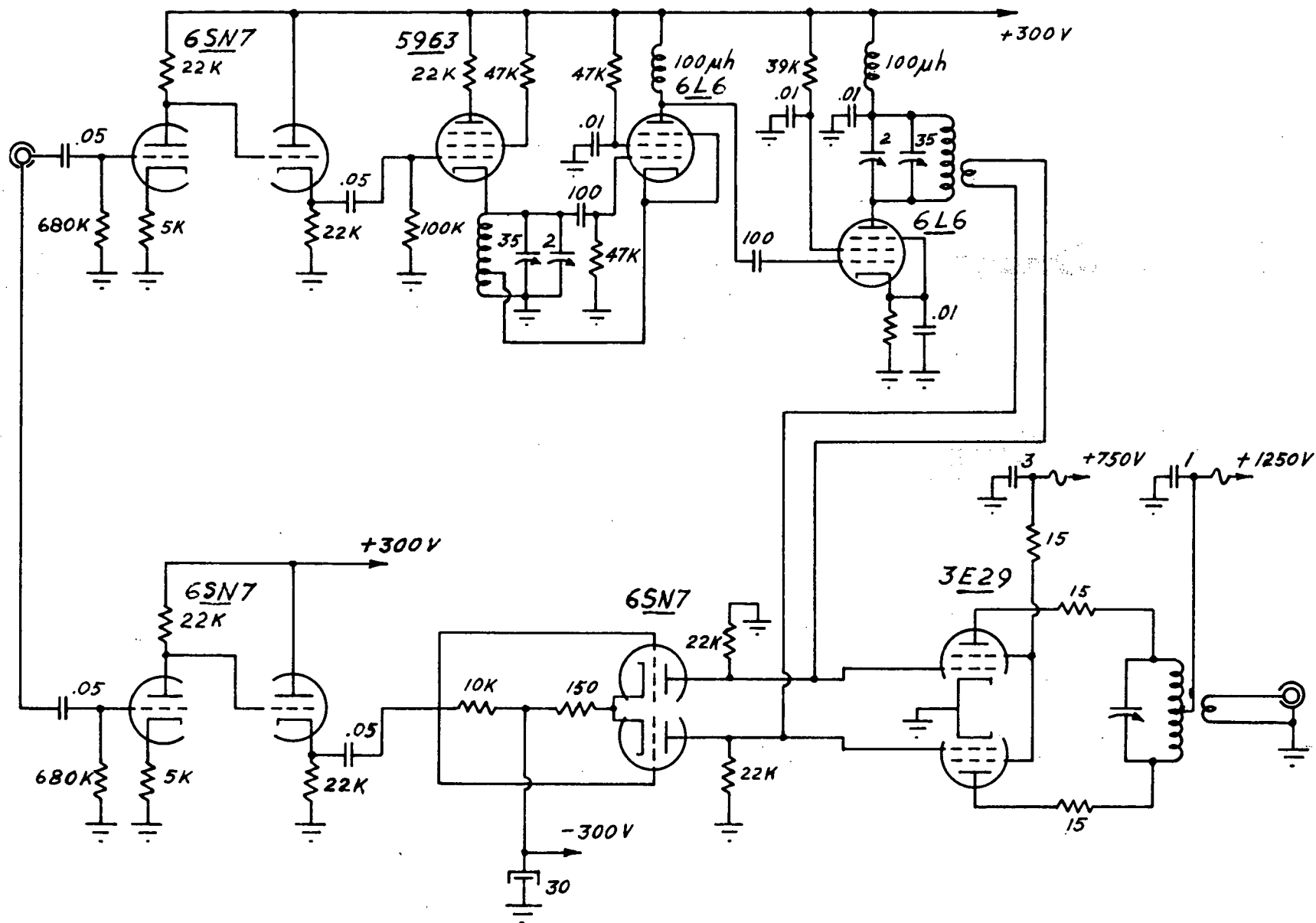by the sawtooth generator, either singly or repetitively, are

Figure 2.   Schematic diagram of the transmitter.

used to trigger the pulse generators at predetermined times on the sawtooth. This timing circuit works very well, the jitter is less than 0.5%. The transmitter, see figure 2, (on previous page) is basically a gated Hartley oscillator followed by buffer stage, and a power amplifier. The rise and fall times of the edges of the r.f. pulses are approximately 1-2 microsec; the peak-to-peak voltage across the sample circuit is 800 volts. The receiver is a high gain wide-band I.F.I. receiver type SPC.-230. The recovery characteristics, as well as its stability against self-oscillation were very poor; consequently a number of changes were made. The schematic in figure 3 shows the modified circuit. The signal-to-noise ratio for the deuteron resonance was approximately 100:1 for maximum signal; the non-linearity of the amplifier was found to be negligible for the signal amplitudes obtained and no corrections were found to be necessary.

THE MEASUREMENT OF RELAXATION TIMES:

T_1 and T_2 measurements were accomplished by standard N.M.R. techniques. For long T_1 (4 sec. and up) the sample is saturated with r.f. at time t=0 by a train of closely spaced 90° pulses; this produces the initial non-equilibrium condition $M_x(0) = M_y(0) = M_z(0) = 0$. Then at a definite time t later a single 90° pulse is applied; i.e. $M_3(t) = M_o \left[1 - e^{-t/\tau} \right]$ is rotated into the x-y plane by the pulse. The amplitude A(t)
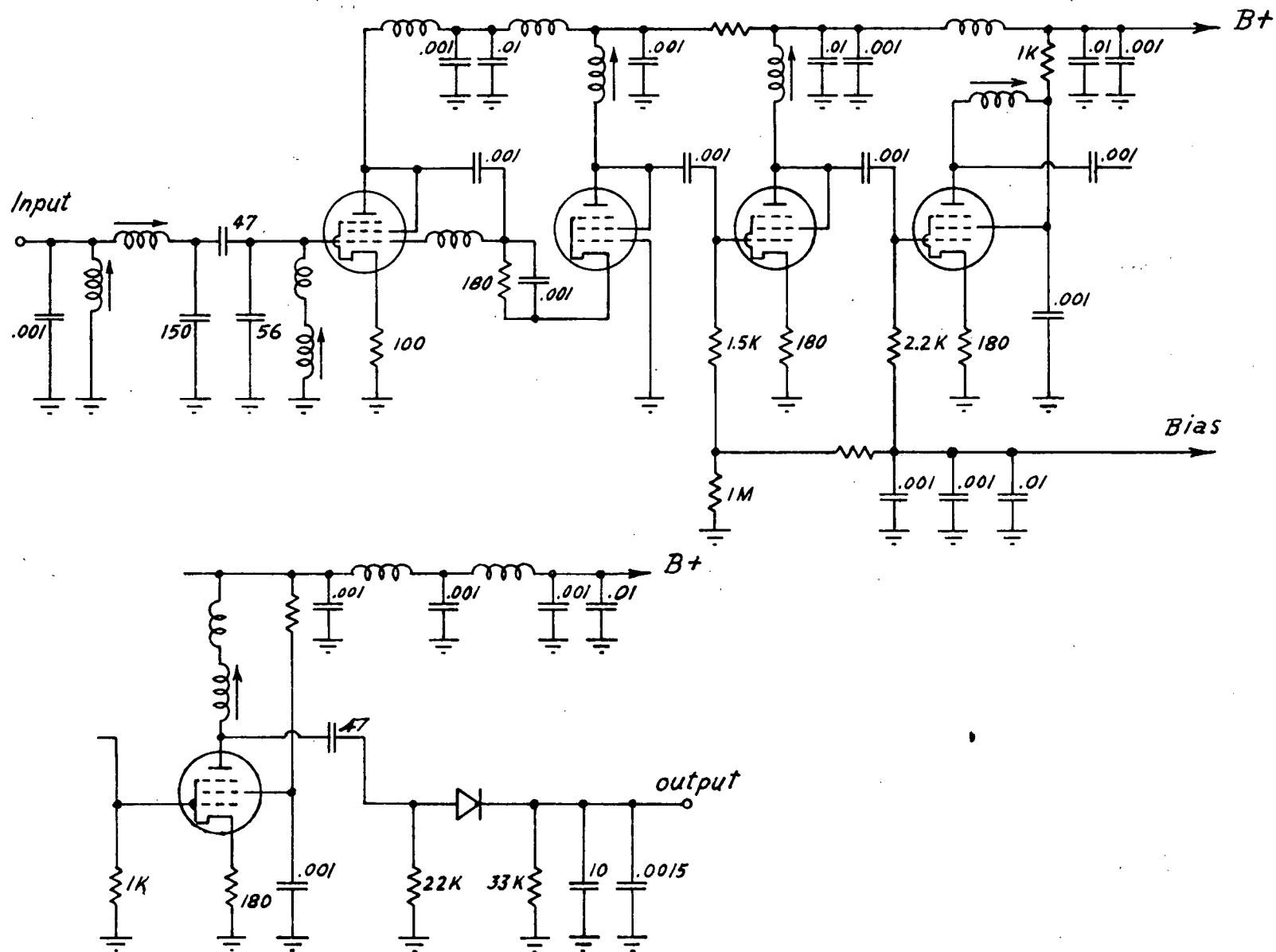
Figure 3. Modified receiver circuit diagram.

of the induction tail following this 90° pulse is recorded.
It can be shown from the definition of T_1 that

$A(t) = A_\infty \left[1 - e^{-t/T_1} \right]$; thus T_1 can be obtained from a series
of amplitude measurements at different times t. A stop watch
was used for timing; the induction tails were recorded on
film with a Du Mont Scope camera type 2620. For shorter
spin-lattice relaxation times a 90°- 90° pulse sequence was
used. Again the amplitude after the second pulse should vary
in the same manner. In this case, the time interval between
pulses was measured using a Hewlett-Packard frequency meter
model 524C with a time interval plug-in unit model 526B. On
the average, the reproducibility of the deuteron T_1
measurements was approximately 5%; this was arrived at by
measuring T_1 a number of times at the same temperature. But
a large source of error is introduced, if the sample itself
(the lattice) has not yet attained thermal equilibrium at
the time of measurement. This time could be quite long
(an hour or so) if the sample has been cycled through the
melting point. The proton T_1 measurements had a lower accuracy
because of a lower signal to noise ratio. The spin-spin
relaxation was measured using a 90° - 180° pulse sequence. For
two such pulses separated by a time T a spin echo appears at
2T with an amplitude $A(2T) = A_o \exp \left[\dfrac{-2T}{T_2} \right]$ (see Hahn[5]).

In the liquid state the decay of the induction tail is
governed by the distribution of values of the main magnetic

field over the sample. In the solid the local magnetic
fields inside the sample due to the distribution of the
nuclear magnetic moments can be much larger than the magnet
inhomogeneity. Under those conditions the distributions is
approximately Gaussian and it can be shown that the induction
tail has the form $A(t) = A(o) \exp\left[-\frac{1}{2} \langle\omega^2\rangle t^2\right]$ (see next
chapter). By fitting the induction tail the second moment
$\langle\omega^2\rangle$ can be obtained.

CHAPTER 3

THEORY

In this section the theory relevant to this experiment will be discussed. For a spin system consisting of two spin species, one of which has $I=1/2$ and the other $I>1/2$ and a quadrupole moment Q, the general Hamiltonian including the quadrupole and spin-rotation interactions, is:

$$\mathcal{H} = \gamma \hbar H_0 \sum_j I_{3j} + \gamma' \hbar H_0 \sum_{j'} I_{3j'}$$

$$+ \sum_{i<k} \sum_{q=-2}^{2} F_{ik}^{(q)} A_{ik}^{(q)} + \sum_{i,\ell'} \sum_{q=-2}^{2} F_{i\ell'}^{(q)} A_{i\ell'}^{(q)}$$

$$+ \sum_{k'<\ell'} \sum_{q=-2}^{2} F_{k'\ell'}^{(q)} A_{k'\ell'}^{(q)}$$

$$+ \sum_i \sum_{q=-2}^{2} (-1)^q Q_{qi} E_q \tag{1}$$

$$+ \sum_i A \underline{I}_i \cdot \underline{J}_i + \sum_{j'} A \underline{I}_{j'} \cdot \underline{J}_{j'}$$

where primed symbols refer to the spin species with $I=1/2$. The first two terms are the Zeeman energy terms; the next three terms are magnetic dipole interaction terms; the fifth represents the quadrupole energy; the last two terms represent the spin-rotation interaction terms

where

$$F_{ij}^{(o)} = \frac{1 - 3\cos^2\theta_{ij}}{r_{ij}^3}$$

$$F_{ij}^{(\pm 1)} = \frac{\sin\theta_{ij}\, e^{\pm i\varphi_{ij}}\cos\theta_{ij}}{r_{ij}^3}$$

$$F_{ij}^{\pm 2} = \frac{\sin^2\theta_{ij}\, e^{\pm 2\varphi_{ij}}}{r_{ij}^3}$$

$$A_{ik}^{o} = -\frac{3}{2}\,\gamma_i\,\gamma_k\,\hbar^2\left[-\frac{3}{2}\,I_{3i}\,I_{3k} + \frac{1}{6}\left(I_{+i}\,I_{-k} + I_{-i}\,I_{+k}\right)\right]$$

$$A_{ik}^{\pm 1} = -\frac{3}{2}\,\gamma_i\,\gamma_k\,\hbar^2\left[I_{3i}\,I_{\pm k} + I_{\pm i}\,I_{3k}\right]$$

$$A_{ik}^{\pm 2} = -3\,\gamma_i\,\gamma_k\,\hbar^2\,I_{+i}\,I_{+k}$$

$$Q_{oi} = \frac{eQ}{I(2I-1)}\left(3\,I_{3i}^2 - \underline{I}_i^2\right)$$

$$Q_{\pm i} = \frac{\sqrt{3}\,eQ}{I(2I-1)}\left[I_{\pm i}\,I_{3i} + I_{3i}\,I_{\pm i}\right]$$

$$Q_{\pm 2i} = \frac{\sqrt{6}\,eQ}{I(2I-1)}\left(I_{\pm i}\right)^2$$

$$E_o = \frac{eq}{2}\,\frac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$E_{\pm 1} = \mp\frac{\sqrt{6}}{4}\,eq\,\sin\theta\,\cos\theta\,e^{\pm i\phi}$$

$$E_{\pm 2} = \frac{\sqrt{6}}{8}\,eq\,\sin^2\theta\,e^{\pm 2i\phi}$$

where the symmetry axis of the molecule is défined by θ and ϕ with respect to the main magnetic field .

The physical picture underlying the description of relaxation phenomena was first proposed by Bloembergen, Purcell and Pound[6]. The Fourier spectrum of the time-dependent local fields acting on the nucleus may have components at the frequency corresponding to the energy difference between a pair of levels of the nuclear spin system; there exists then a finite probability of a spin transition being induced by the fluctuating field. The energy required for this transition is provided by the lattice. Since the lattice is in thermal equilibrium, these transitions are weighted by the appropriate Boltzman factors and the effect of these transitions is to bring the nuclear spin system into thermal equilibrium with the lattice.

To be able to describe the above ideas mathematically a correlation function $G(\tau)$ of a function f(t) is introduced; by definition $G(\tau) = \langle f(t) \, f^{*}(t+\tau) \rangle$ where $\langle \; \rangle$ denotes an ensemble average. The assumption is usually made that the distribution is stationary, in other words, one which does not depend upon the origin in time. In this case the correlation function depends only on τ. For most physical quantities a certain amount of correlation exists between the values of a physical quantity within a small interval of time, i.e. $G(\tau)$ is in general non-zero for a finite range of values of τ. The length of time in which some correlation persists is called the correlation time; for example, τ_c could be defined by $G(\tau_c) \approx \dfrac{G(o)}{e}$.

The above Hamiltonian describes four contributions to changes in the local magnetic field each with a correlation function. The dipole-dipole interactions can be expressed as a sum of terms involving $F^k = \dfrac{a_k \, Y_{2k}(\theta, \varphi)}{r^3}$, where $k = 0, 1, 2$, the a_k are constants and the Y_{2k} are spherical harmonics. Thus the correlation functions which appear in the expression for the transition probability between nuclear spin states and hence in the expressions for $1/T_1$ and $1/T_2$ are of the form $\langle F^k(t) \, F^{k*}(t+\tau) \rangle$, which depend on the motions of the neighboring spins. It is convenient to separate this interaction into inter- and intra-molecular contributions. The reorientational motions of the molecule give an intra-molecular correlation function

$$G^{(m)}(\tau) = \frac{A}{r^6} \left\langle Y_{2m}(t) \, Y_{2m}^{*}(t+\tau) \right\rangle \tag{2}$$

(where A/r^6 is a constant) which has a correlation time of the order of the average time for appreciable reorientations τ_{cr}. For a spin transition involving an energy change $\Delta E = \hbar \omega$, the intramolecular contribution to T_1, can thus be written in terms of the spectral densities

$$J^{(m)}(\omega) = \int_{-\infty}^{\infty} G^{(m)}(\tau) \, e^{-i\omega\tau} \, d\tau \tag{3}$$

The complete expression for the intra-molecular contribution to $1/T_1$ is (Abragam[7] page 291)

$$\left(\frac{1}{T_1}\right)_{intra} = \frac{3}{2} \gamma_I^4 \hbar^2 I(I+1) \sum_k' \left[J_{Aik}^{(1)}(\omega_I) + J_{Aik}^{(2)}(2\omega_I) \right]$$

$$+ \gamma_I^2 \gamma_S^2 S(S+1) \sum_\ell \left[\frac{1}{12} J_{Ai\ell}^{(0)}(\omega_I - \omega_S) \right. \tag{4}$$

$$\left. + \frac{3}{2} J_{Ai\ell}^{(1)}(\omega_I) + \frac{3}{4} J_{Ai\ell}^{(2)}(\omega_I + \omega_S) \right]$$

where i and k spins are similar, but the l spins are dis-
similar.

The inter-molecular contribution is more complicated,
because the $F^k(r,\theta,\varphi)$ of neighboring spins are determined
by the orientations as well as the relative spatial locations
of the molecules. Consequently the spectral density is in
general a function of two correlation times, one associated
with molecular reorientation and the other with translational
motion. If the assumption is made that the reorientations
occur much faster than the translational motions, then the
spectral density and the correlation function can be written
as the sum of two independent terms. The perturbation
Hamiltonian $\mathcal{H}_1$ is a function of the vector $\underline{R} = (R, \Theta, \phi)$
between the centers of the molecules, and the vectors

$\underline{r}_i = (r_i, \theta_i, \varphi_i)$ where i=1, 2, specifying the positions of
each of the two interacting nuclei with respect to the centers
of the two molecules. Now write the identity

$$\mathcal{H}_1 = \mathcal{H}_r + \mathcal{H}_t \tag{5}$$

$$= \left[\mathcal{H}_1 - \langle \mathcal{H}_1 \rangle_{\substack{\theta_1,\varphi_1 \\ \theta_2,\varphi_2}} \right] + \langle \mathcal{H}_1 \rangle_{\substack{\theta_1,\varphi_1 \\ \theta_2,\varphi_2}}$$

where $\langle\ \rangle_{\theta_1, \varphi_1 \atop \theta_2, \varphi_2}$ represents an average over all orientations of each of the molecules. The time dependence of $\mathcal{H}_r$ is primarily due to reorientations of the molecules and $\mathcal{H}_t$ depends only on the relative positions of the two nuclei, so that its time dependence is due to translational motions. Now the correlation function has the form from equation (5)

$$\langle \mathcal{H}_i(t)\ \mathcal{H}_i(t+\tau)\rangle = \langle \mathcal{H}_r(t)\ \mathcal{H}_r(t+\tau)\rangle + \langle \mathcal{H}_t(t)\ \mathcal{H}_t(t+\tau)\rangle$$

$$+ \langle \mathcal{H}_r(t)\ \mathcal{H}_t(t+\tau)\rangle + \langle \mathcal{H}_t(t)\ \mathcal{H}_r(t+\tau)\rangle \qquad (6)$$

The last two terms average to zero, if the translational and rotational motions are uncorrelated, i.e.

$$\langle \mathcal{H}_r(t)\ \mathcal{H}_t(t+\tau)\rangle = \langle \mathcal{H}_t(t)\ \mathcal{H}_r(t+\tau)\rangle = 0$$

The spectral density $J_B(\omega)$ will be the sum of two terms

$$J_B(\omega) = J_{Bt}(\omega) + J_{Br}(\omega)$$

one of which $J_{Bt}(\omega)$ involves the translational correlation time, $J_{Br}(\omega)$ is a function of the rotational correlation time. The contribution to $1/T_1$ will have the same form as equation (4) with $J_B(\omega)$ substituted for $J_A(\omega)$.

$$\left(\frac{1}{T_1}\right)_{inter} = \frac{3}{2} \gamma_I^4 \hbar^2 I(I+1) \sum_k{}' \left[J_{Bik}^{(1)}(\omega_I) + J_{Bik}^{(2)}(2\omega_I)\right]$$

$$+ \gamma_I^2 \gamma_S^2 S(S+1) \sum_\ell \left[\frac{1}{12} J_{Bi\ell}^{(0)}(\omega_I - \omega_S)\right.$$

$$\left. + \frac{3}{2} J_{Bi\ell}^{(1)}(\omega_I) + \frac{3}{4} J_{Bi\ell}^{(2)}(\omega_I + \omega_S)\right] \tag{7}$$

As methane is a molecular crystal, it will be assumed that the electric field gradient at the nuclear site due to the neighbors is negligible. Consequently the quadrupole relaxation mechanism can be expressed in terms of molecular reorientations only; the field gradient being fixed with respect to the molecular body axis. The Hamiltonian, equation (1), shows that the quadrupole interaction can be expressed in terms of the Y_{2m}. Thus the correlation functions $\langle Y_{2m}(t) \, Y_{2m}^*(t+\tau)\rangle$ involved are the same as those for the intra-molecular dipole-dipole interaction equation (2). The spin lattice relaxation time for I=1 and for an axially symmetric field inside the molecule (Abragam page 314)

$$\frac{1}{T_1} = \frac{3}{80} \left[\frac{eQ}{\hbar} q\right]^2 \left[J_A^{(1)}(\omega_I) + J_A^{(2)}(2\omega_I)\right] \tag{8}$$

where eQ is the nuclear electric quadrupole moment and q is the electric field gradient at the nucleus.

The Hamiltonian describing the interaction between the spin and the rotational magnetic moments is

$$\mathcal{H} = A \, \mathbf{I} \cdot \mathbf{J}$$

$$= A \left[I_3 J_3 + \tfrac{1}{2} \left(I_+ J_- + I_- J_+ \right) \right]$$

where A is a constant. The rotational quantum state m_J of
the molecule changes due to collisions. The resulting
changes in the local magnetic field induce spin transitions.
For this type of perturbation Abragam, page 309, shows that
the contribution $\dfrac{1}{T_1} = 2 \, J_J^{(1)}(\omega_x)$

where $\quad J_J^{(1)}(\omega) = \displaystyle\int_{-\infty}^{\infty} G^{(1)}(\tau) \, e^{i\omega\tau} \, d\tau$ (9)

and $\quad G^{(1)}(\tau) = \dfrac{1}{4} A^2 \left\langle J_+(0) \, J_-(\tau) \right\rangle$

The complete expression for $1/T_1$ is the sum of the contri-
butions given by equations (4), (7), (8) and (9).

This expression is correct only if the spin temperature
of the coupled spin system is independent of time. If this
condition is not satisfied the relaxation function will not
be described by a single relaxation time, there would be two
exponential terms. In the experimental results reported here,
the relaxation function was always a single exponential
within experimental error.

If exponential correlation functions are assumed, then
the spectral density has the following form $J(\omega) \propto \dfrac{\tau_c}{1 + \omega^2 \tau_c^2}$.
For translational and rotational diffusion it can be shown

that $J^{(0)}: J^{(1)}: J^{(2)} = 6:1:4$. The above expressions for the inter-
and intra-molecular dipolar contributions to the spin-lattice
relaxation times can be simplified for the case $\omega \tau_c \gg 1$. In
this limit J can be approximated by $J \propto \dfrac{1}{\omega^2 \tau_c}$.

For the intra-molecular interactions alone the expression,
equation (4), becomes

$$\frac{1}{T_1} = \frac{3}{2} \gamma_I^4 \hbar^2 I(I+1) \sum_k A_k$$

$$+ \gamma_I^2 \gamma_S^2 S(S+1) \sum_l B_l$$

Upon evaluation of the expressions for A_k and B_l one finds
that $1.6 A_k = B_l$. For a $CD_{4-n} H_n$ molecule

$$\sum_k A_k = \left(1 - \frac{m}{3}\right) A \qquad \text{and} \qquad \sum_l B_l = \frac{m}{3} B$$

$$\left(\frac{1}{T_1}\right)_{intra} = \left[\left(1 - \frac{m}{3}\right) + 1.6 \frac{m}{3}\right] R_A \tag{10}$$

Where the functions R_A depends upon the rotational correlation
time, the gyromagnetic ratios, lattice parameters, etc.

For the inter-molecular dipole-dipole interaction the
relative contributions of the two spin species will be the
same; except the absolute value is determined by different
functions R_B and R_C, which are dependent on the rotational
and translational correlation times respectively

$$\left(\frac{1}{T_1}\right)_{inter} = \left[\left(1 - \frac{m}{4}\right) + 1.6 \frac{m}{4}\right] (R_B + R_C) \tag{11}$$

Johnson and Waugh[8] have suggested that the relaxation rate due to the spin rotation interaction is proportional to $\langle J(J+1)\rangle \propto T I_o$; if this is valid the dependence of the spin rotation mechanism on n takes the form

$$\left(\frac{1}{T_1}\right)_{spin-rot} = \left[2(4-n) + n\right] R_D \qquad (12)$$

where R_D will be a function of the correlation time for changes in the m_J values.

The quadrupole relaxation mechanism of the deuteron spin system is independent of the isotopic constitution of the molecule, in so far as the molecular wave functions remain unchanged. It can be described by a function R_E, which is dependent on the rotational correlation time.

It should be remarked that R_A, R_B, R_C and R_E are strictly speaking functions of n too, because the correlation times are functions of the mass of the molecule through the diffusion coefficients.

The complete expression for $(1/T_1)_n$ from (10), (11) and (12)

$$\left(\frac{1}{T_1}\right)_n = \left[1.6\,\frac{n}{3} + \left(1 - \frac{n}{3}\right)\right] R_A + \left[2(4-n) + n\right] R_D$$
$$+ \left[1.6\,\frac{n}{4} + \left(1 - \frac{n}{4}\right)\right]\left(R_B + R_C\right) + R_E \qquad (13)$$

In the interpretation some of the results of the theory

of the influence of motion of the spins on line width are
utilized (Abragam Chapter 10), thus a few comments are in
order. The development of the adiabatic case $\omega_o \tau_c \gg 1$ by
Abragam is a semi-classical one, where the matrix elements
of the spin-spin interactions are assumed to be random
functions of time. At each instant the microscopic distri-
bution of local fields throughout the sample is assumed to
be of a stationary character and is the same as that for a
rigid lattice (assumed to be Gaussian), but the local field
at each point is assumed to fluctuate at a rate described by
the correlation function $G_\omega(\tau) = \langle \omega(t) \, \omega(t+\tau) \rangle = \langle \omega^2 \rangle g_\omega(\tau)$,
where $\langle \omega^2 \rangle$ is the second moment of the rigid lattice resonance
line. Abragam obtains the final expression for the Fourier
transform of the absorption line shape

$$G(t) = e^{i \omega_o t} \exp\left[- \langle \omega^2 \rangle \int_o^t (t - \tau) \, g_\omega(\tau) \, d\tau \right] \qquad (14)$$

Without making any explicit assumptions about $g_\omega(\tau)$ the
following extreme cases can be considered:

1) Long correlation time limit:

The correlation time is so long that $\langle \omega^2 \rangle \tau_c^2 \gg 1$
i.e. for $\tau \leq t \ll \tau_c$ can approximate $g_\omega(\tau) \approx 1$, thus

$$G(t) = e^{i \omega_o t} \exp\left[- \tfrac{1}{2} \langle \omega^2 \rangle t^2 \right] \qquad (15)$$

In other words, the shape of the transverse relaxation function is Gaussian.

2) Short correlation time limit:

If τ_c is so short that $\langle \omega^2 \rangle \tau_c^2 \ll 1$ for $t \gg \tau_c$ it is permissible to write

$$\langle \omega^2 \rangle \int_0^t (t-\tau) \, g_\omega(\tau) \, d\tau$$
$$\doteq \langle \omega^2 \rangle \, t \int_0^\infty g_\omega(t) \, d\tau = \langle \omega^2 \rangle \, t \, \tau_c'$$

the definition of τ_c' as used here $\tau_c' = \int_0^\infty g_\omega(t) \, d\tau$ is of the order of τ_c . Then

$$G(t) \doteq e^{-i\omega_0 t} \, e^{-\langle \omega^2 \rangle |t| \tau_c'} = e^{-i\omega_0 t} \, e^{-t/T_2}$$

and $\quad \dfrac{1}{T_2} = \langle \omega^2 \rangle \, \tau_c' \qquad\qquad (16)$

The above formulae hold for any correlation function, in particular for the cases of Brownian motion and self-diffusion. In those instances for which the self-diffusion mechanism is dominant, the expression

$$\text{Log } T_2 = - \frac{E_a}{kT} - \text{Log } \tau_0 \langle \omega^2 \rangle \qquad\qquad (17)$$

is obtained using the fact that for self-diffusion $\tau_c' = \tau_0 \, e^{E_a/kT}$, where E_a is called the activation energy.

In the non-adiabatic approximation the restriction $\omega_0 \tau_c \gg 1$ is removed, it can be shown that there exists a unique spin-spin relaxation time, i.e. the absorption curve is Lorentzian; the result of the derivation is (Abragam p.292)

$$\frac{1}{T_2} = \gamma^4 \hbar^2 \, I \, (I+1) \left[\frac{3}{8} \, J^\circ(0) \; + \; \frac{15}{4} \; J^{(1)}(\omega) \; + \frac{3}{8} J^{(2)}(2\omega_0) \right] \tag{18}$$

If $\omega_0 \tau_c \gg 1$ only the $J^{(0)}(0)$ term is important and equation (18) gives the same result as equation (16).

CHAPTER 4

RESULTS AND DISCUSSION

Measurements of spin-lattice T_1 and spin-spin T_2 relaxation times of the deuteron resonance in CD_4 and CD_3H, and T_1 of the proton resonance in CD_3H were carried out at 4.3 mc/sec. as a function of temperature in the range from 105°K to 57°K. The results are shown in figures 4 - 7.

Upon comparison of the proton measurements at 30 mcs (see Appendix) with the deuteron measurements some observations can be made. First of all, the strong temperature dependence exhibited in the proton T_1 measurements is completely absent in the deuteron measurements for both CD_4 and CD_3H (see figures 4 and 5). Moreover, the values of T_1 in most of the temperature range are shorter for the deuteron resonance, whereas they are expected to be longer if the relaxation is due to magnetic dipolar interactions, especially in the liquid state 90°K - 105°K. In the liquid, $\omega_o \tau_c \ll 1$, thus $J^{(o)}(o) = J^{(m)}(\omega_r) = J^{(m)}(2\omega_r)$ and from equation (7)

$$\left(T_1\right)_{deuteron} = \frac{\gamma_p^4 \, I_p (I_p + 1)}{\gamma_D^4 \, I_D (I_D + 1)} \left(T_1\right)_{protons} \approx 690 \left(T_1\right)_{proton}$$

These observations allow one to conclude that either the coupling between the nuclei is of a different nature or the random motions of the molecules are of an entirely different
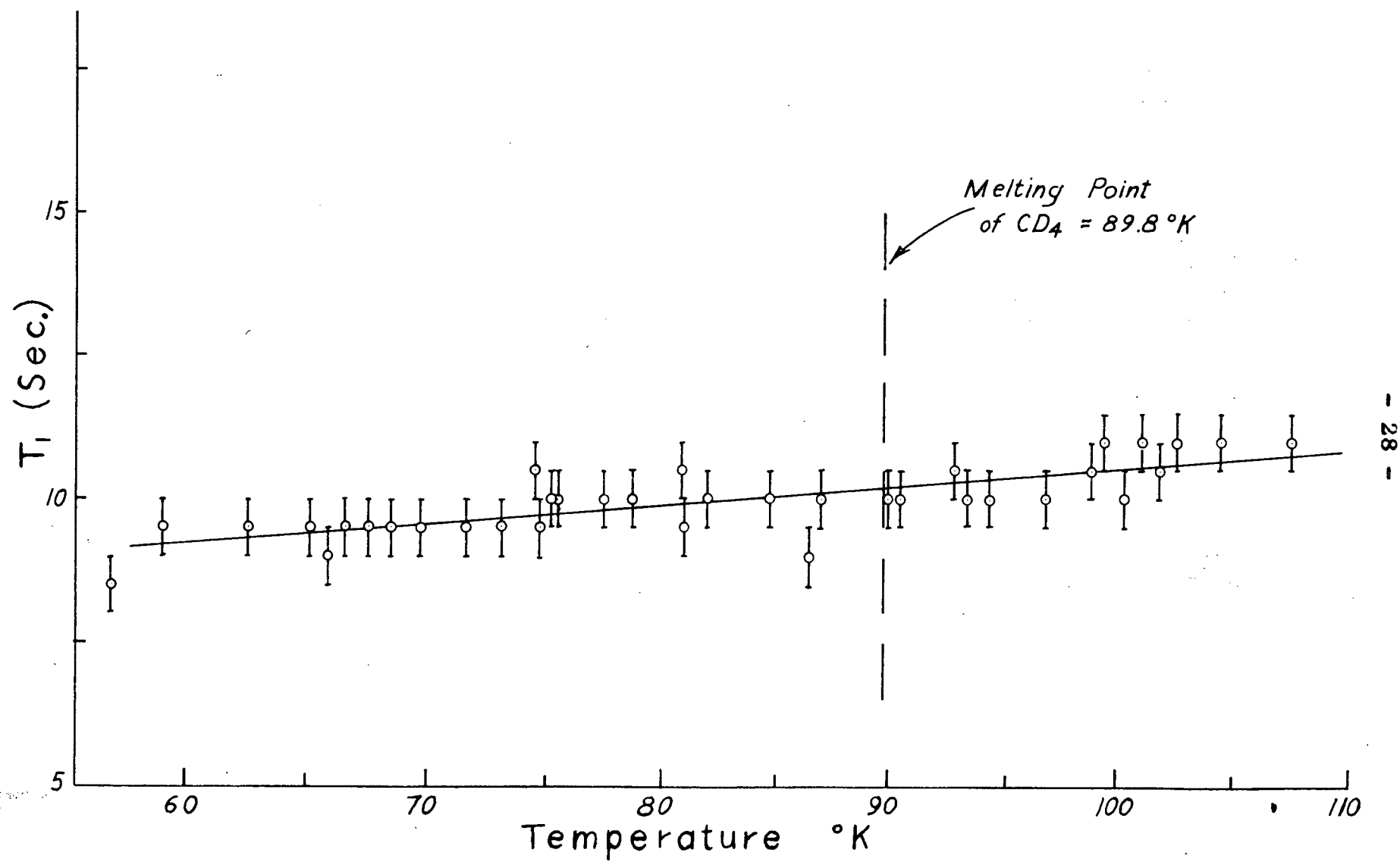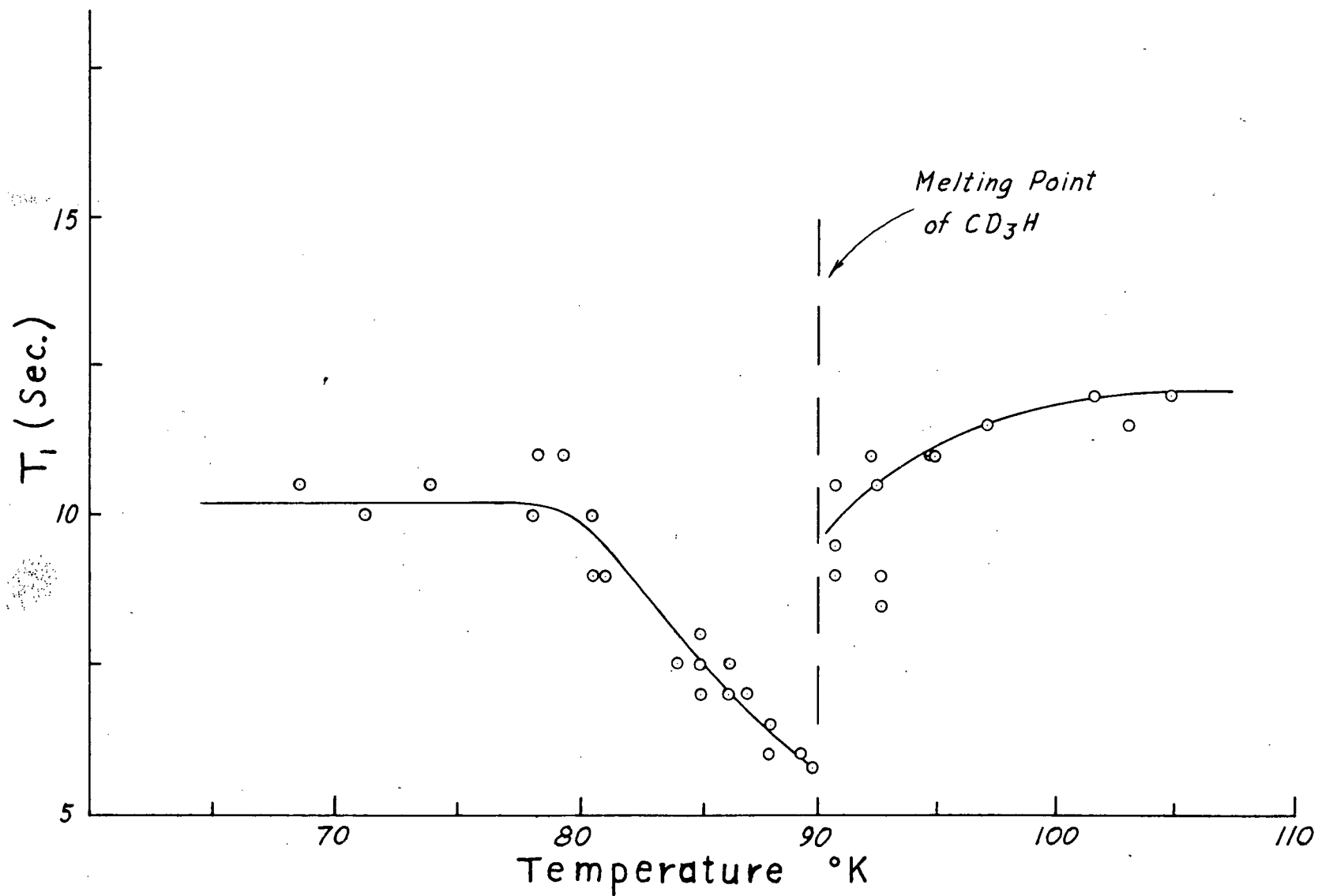
Figure 4.   Deuteron T_1 of CD_4 versus temperature.

Figure 5.   Deuteron T_1 of CD_3H versus temperature.

character, which would effect changes in the spectral densities governing the relaxation times.

The second of the two alternatives can be ruled out, because the temperature dependences of the proton T_1 in CD_3H and the deuteron T_2 in CD_4 are similar to those at 30 mcs. In the range of $105°K - 90°K$ the sample is a liquid, below $90°K$ it is a solid but the behaviour of the proton T_1 and T_2 indicate that translational motions associated with self-diffusion are important down to approximately $65°K$ (Waugh[9]). Despite this large change in the molecular mobility, there is no indication of it in the deuteron T_1 measurements for CD_4 and is only slightly noticeable for CD_3H; it is therefore concluded that intra-molecular interactions dominate the spin-lattice relaxation. The proton relaxation measurements at 30 mcs. indicate that the magnetic intra-molecular relaxation mechanism is very inefficient; it is suggested that the molecules are undergoing rapid reorientations (Bloom and Sandhu). As the deuteron magnetic moment is 1/7 of the proton magnetic moment, the magnetic intra-molecular interactions are expected to be even less efficient for the deuteron spin system and can thus be disregarded.

The interaction of the deuteron quadrupole moment with the electric field gradient is suggested as a possible intra-molecular interaction to account for the above results. The contribution to the relaxation is through the modulation of

the electric field by the molecular reorientations. The temperature independence of the deuteron T_1's shows that the correlation time for molecular reorientation is independent of temperature.

The T_2 measurements for CD_4 can be explained if the above model is used, and if the reorientations occur at a sufficiently high frequency. Under these circumstances the contribution to the line shape from the quadrupole interaction will have a Lorentzian character with a long decay constant, equation (18) $\frac{1}{T_2} = \langle\omega^2\rangle\tau_c$, this is the behaviour characteristic of extreme motional narrowing. The effect of the quadrupole interaction is unobservable, because the induction decay is dominated by the inter-molecular dipolar interactions; the effect would only be observable far out in the induction tail, where it is inseparable from the noise.

If the above considerations are correct, the values of the deuteron T_2 should be calculable from the values of the proton T_2 at 30 mcs. The expression for T_2 for a system of identical spins is, equation (18)

$$\frac{1}{T_2} = \gamma^4 I(I+1)\hbar^2\left[\frac{3}{8}J^o(o) + \frac{15}{4}J^{(1)}(\omega_r) + \frac{3}{8}J^{(2)}(2\omega_r)\right] \tag{19}$$

In the range of temperatures just below the M.P. the spectral densities are dominated by the self-diffusion and can be approximated by $J^{(i)}(\omega) = \frac{a_i\tau_c}{1+\omega^2\tau_c^2}$ where $a_o:a_1:a_2 = 6:1:4$
The values of τ_c in this region can be obtained from the values

of the proton T_2 and the line shape given by equation (16)

$A \propto e^{-\langle \omega^2 \rangle t \tau_c}$ for $t > \tau_c$, thus T_2 can be written as

$T_2 = \left[\langle \omega^2 \rangle \tau_c \right]^{-1}$. Using these values for τ_c, one finds that

$\omega \tau_c \geqslant 3$ in the range of temperatures $90°K - 70°K$, thus

$J(\omega) \propto \dfrac{1}{\omega^2 \tau_c}$ and equation (19) is dominated by the $J^0(o)$

term and

$$\frac{1}{T_2} \approx \frac{3}{8} \gamma^4 \hbar^2 I(I+1) \tau_c$$

The same approximations are also correct for the proton
resonance. Using the values of the proton T_2 at 30 mcs.,
one can predict those for the deuteron resonance $(T_2)_D$

$$(T_2)_D = \frac{\gamma_P^4 \, I_P (I_P+1)}{\gamma_D^4 \, I_D (I_D+1)} \, (T_2)_P$$

The predicted values are shown in figure 6; the agreement
between the predicted and experimental values is reasonable;
the difference in activation energies accounts for the
systematic deviation of the slopes of the two lines. The
above result implies that the quadrupole interaction has no
effect on T_2.

In order to obtain significant results it is of the
utmost importance, that all paramagnetic oxygen impurities
have been removed. In the paper by H. Sandhu, J. Lees and
M. Bloom[4] it is shown that an almost temperature independent
result is obtained, if the oxygen impurity concentration is
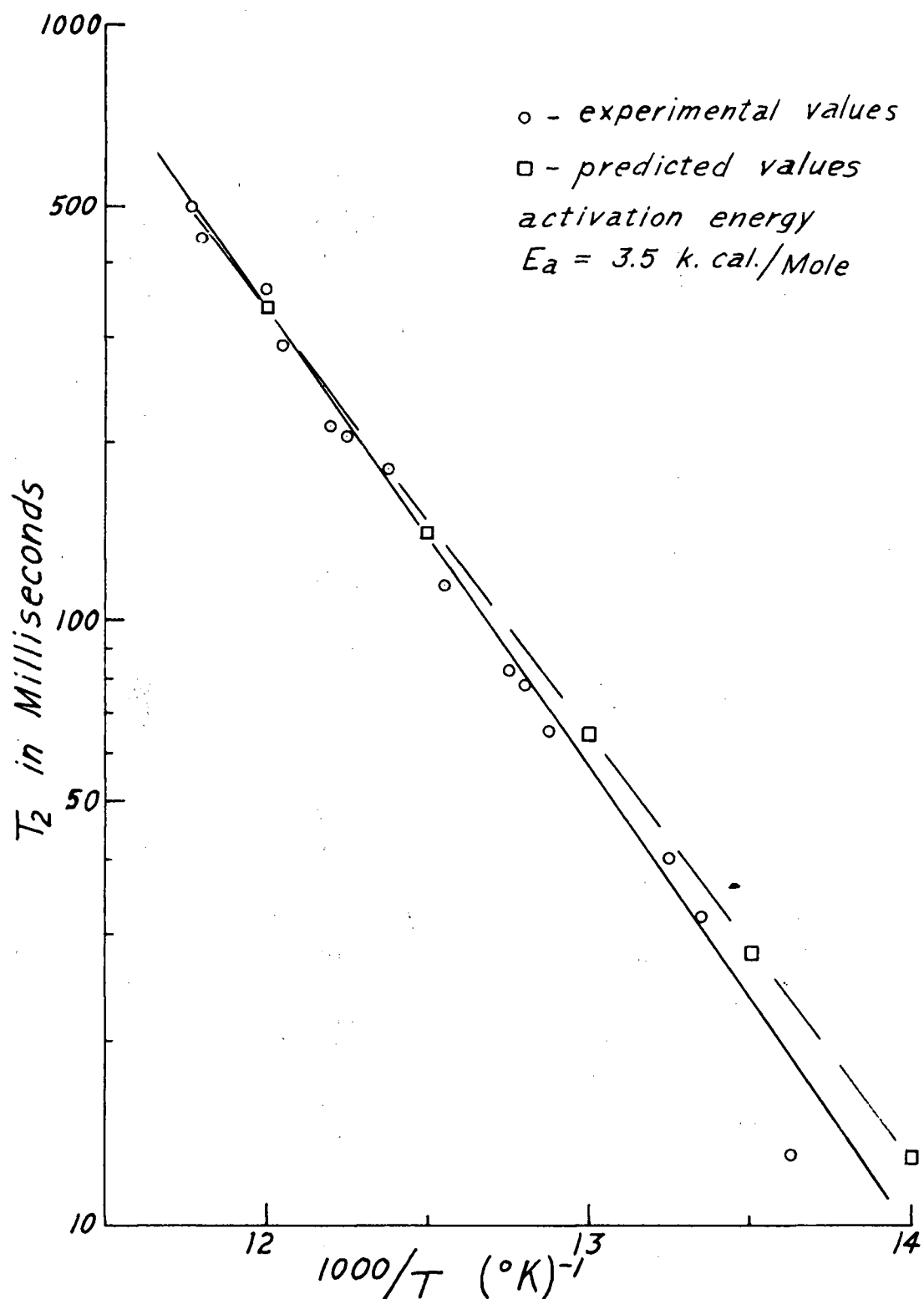1% or more, but effects of the magnetic interactions with

Figure 6. Deuteron T_2 in CD_4 versus the reciprocal of temperature.

other methane molecules start to be observed for lower concentration. When the relaxation effects are dominated by the oxygen impurities T_1 should equal T_2. A value for T_1 of 34 milli seconds is obtained for an oxygen concentration of 1%.

Convincing proof that the CD_4 sample used was free from impurities is the fact that the values of $(T_2)_D$ can be predicted from the values for $(T_2)_p$, as is discussed above. The CD_3H must also be free from oxygen impurities, because the values of $(T_1)_p$ at 4.3 mcs. show the characteristic temperature dependence of inter-molecular dipolar interactions modulated by self-diffusion, (see below).

The activation energy for the self-diffusion process as obtained from the $(T_2)_D$ temperature dependence is 3.5 kcal. per mole for CD_4, as compared with 3.2 kcal/mole for CH_4 obtained from the proton measurements at 30 mcs. The 10% increase in the activation energy can possibly be attributed to the 25% increase in the mass of the molecule.

The $(T_1)_p$ results for CD_3H at 4.3 mcs., see figure 7, show some interesting features. They can be calculated approximately using equation (7) and the $(T_1)_p$ results at 30 mcs., as before it is assumed that $J(\omega) \propto \frac{1}{\omega^2 \tau_c}$. Then the predicted value of $(T_1)_p$ at 4.3 mcs. is approximately 2.1×10^{-2} $(T_1)_p$ as 30 mcs., i.e. the $(T_1)_p$ results at 4.3 mcs. should show the same dependence on temperature, as do the $(T_1)_p$ results at 30 mcs. However, the predicted results are smaller than the experimental values by as much as a factor
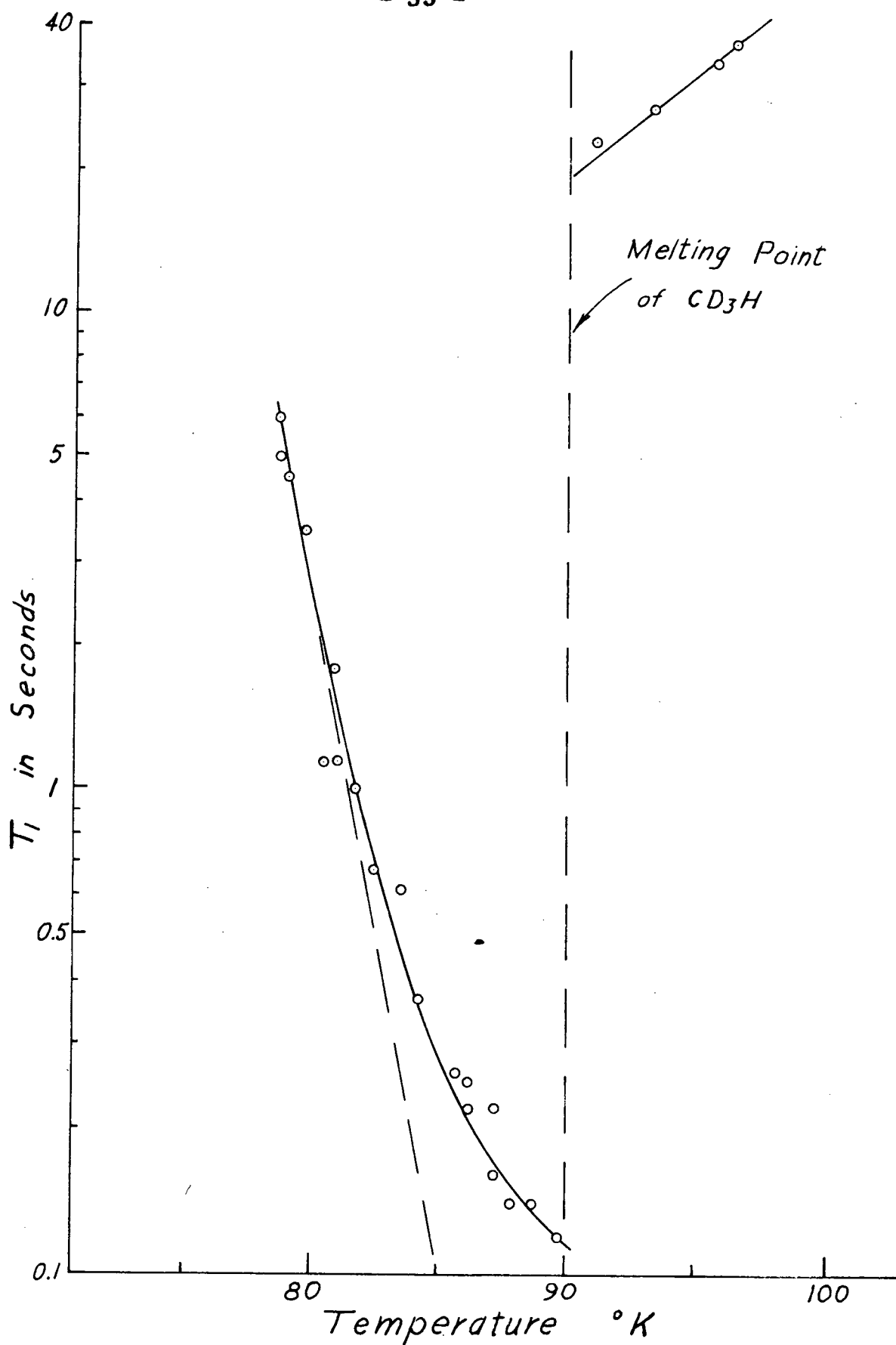
Figure 7.   Proton T_1 in CD_3H versus temperature.

of three at the highest temperatures, though they agree at the lower temperatures. The assumption of a single correlation time for self-diffusion, which leads to $\omega_o \tau_c \geqslant 3$ for 4.3 mcs. below the melting point, may be an oversimplification. Perhaps a more detailed model, Torrey's model[10] for example, should be employed, but this has not yet been attempted.

The dip in the deuteron T_1 results near the melting point for CD_3H can be explained qualitatively, if the dipolar interactions are taken into account. The contribution to $1/T_1$ due to dipolar interactions can be obtained using equation (7) and the T_1 results for CH_4 at 30 mcs. The same approximations regarding $J(\omega)$ will be made as above.
For example at 89°K, the contribution to T_1 due to dipolar interaction is approximately 24 sec. for CD_3H, if the quadrupole contribution is assumed to be 10 sec., then the observed T_1 should be approximately 7.1 sec. as compared with an experimental value of 6.0 sec. Again this result may possibly be improved through the use of a more accurate spectral density.

The quadrupole contribution to the relaxation of the spin system can only be interpreted, if somehow a value for the quadrupole coupling constant can be obtained. One possibility is from the line shape of a poly-crystalline sample at helium temperatures. If the quadrupole coupling is sufficiently strong and if the internal motions are completely quenched, then the absorption line shape will exhibit two

peaks. The distance between the peaks is a function of the coupling constant. Another possibility is to calculate the field gradient from Hartree-Fock approximate wave functions for the molecule (e.g. Krause[11]).

To obtain the absolute magnitude of the inter-molecular contribution to T_1, the following experiment is suggested. If the spin lattice relaxation times of mixtures of CH_4 and CD_4 are measured, then the term $(R_B + R_C)$ in equation (13) will be replaced by $\left[(1-x) + Ax\right](R_B + R_C)$ where x is the concentration of CD_4 molecules and A is a constant which describes the relative strength of the inter-molecular inter-actions of the two types of molecules. If the relaxation time is measured for a number of concentrations at each temperature, then $(R_B + R_C)$ can be evaluated as a function of temperature. In conjunction with the proton results at 30 mcs, it may be possible to provide a unique solution to the relative contributions to the relaxation rate $1/T_1$.

APPENDIX

Proton Relaxation Data at 30 mcs:

i)   "Proton Spin-Lattice Relaxation in Pure Methane and its Deuterated Modifications."

      M. Bloom and H. S. Sandhu
      Can. J. Phys. **40**, 289 (1962).

ii)   "N.M.R. Line-shape Studies in Methane Using Pulse Techniques."

      M. Bloom and H. S. Sandhu
      Can. J. Phys. **40**, 292 (1962).

NOTES

PROTON SPIN-LATTICE RELAXATION IN PURE METHANE AND ITS DEUTERATED MODIFICATIONS*

M. Bloom† AND H. S. Sandhu

We report here measurements of the proton spin–lattice relaxation time T_1 using pulse techniques (Hahn 1950) in liquid and solid CH_4, CH_3D, CH_2D_2, and CHD_3 between 57° K and 110° K. By varying the isotopic form of methane in this way it is possible to obtain information on the nature of the interactions contributing to spin–lattice relaxation. Reliable measurements were made possible by the use of a purification technique reported previously (Sandhu, Lees, and Bloom 1960). When this technique is used, T_1 in liquid and solid CH_4 is found to be about 1000 times longer than previously reported (Thomas, Alpert, and Torrey 1950), presumably because of O_2 contamination of the samples used previously. The detailed interpretation of T_1 by Tomita (1953) must therefore be reconsidered.

The interactions governing T_1 for spin $\frac{1}{2}$ nuclei in polyatomic molecules such as methane are: (A) intramolecular dipolar interactions, (B) intermolecular dipolar interactions, (C) $A\mathbf{I}.\mathbf{J}$ type interactions between the nuclear spin $\mathbf{I}$ and the rotational angular momentum of the molecules $\mathbf{J}$.

There has been some evidence recently that mechanism (C) is probably predominant for fluorine nuclei in systems such as liquid CHF_3 (Gutowsky, Lawrenson, and Shimonura 1961). Recently Johnson and Waugh (1961) have suggested that it is also important for liquid CH_4. They estimate a contribution to T_1^{-1} of approximately $0.02\ \text{sec}^{-1}$ at its normal boiling point. In making this suggestion Johnson and Waugh have surmised that the relaxation rate due to mechanism (C) is proportional to $\langle J(J+1) \rangle \cong TI_0$, where T is the absolute temperature and I_0 is the moment of inertia of the molecule. If we accept this assumption, T_1 in the molecule $CH_{4-n}D_n$ has the following dependence on n, the number of deuterons, at constant temperature

$$(1) \qquad \left(\frac{1}{T_1}\right)_n = \left\{\left(1-\frac{n}{3}\right)+\frac{4.1\times10^{-2}}{3}n\right\}R_A$$

$$+\left\{\left(1-\frac{n}{4}\right)+\frac{4.1\times10^{-2}}{4}n\right\}R_B+\left(1+\frac{n}{4}\right)R_C$$

where R_A, R_B, and R_C are the contributions to T_1^{-1} for $n = 0$ due to mechanisms A, B, and C respectively. In writing equation (1) we neglect the changes in the correlation functions appearing in R_A, R_B, R_C due to the changes in n. In the conventional theories of T_1 (Abragam 1961, pp. 300 and 302), R_A and R_B would depend on the diffusion coefficient and if the diffusion coefficient were proportional to $M^{-1/2}$, R_A and R_B would be multiplied by $[1+(n/16)]^{1/2}$, having at most an influence of 9% for CHD_3.

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

$$(2a) \qquad \left(\frac{1}{T_1}\right)_0 = R_A + R_B + R_C,$$

$$(2b) \qquad \frac{\partial}{\partial n}\left(\frac{1}{T_1}\right)_n = -0.32R_A - 0.24R_B + 0.25R_C.$$

Although one cannot obtain a unique solution to equations (2), the fact that R_A, R_B, and R_C must all be positive enables us to establish upper and lower bounds for R_A, R_B, and R_C.

The Liquids

A reasonable fit of the experimental data given in Fig. 1 over the entire *liquid* range is obtained for

$$(3) \qquad \frac{\partial}{\partial n}\left(\frac{1}{T_1}\right)_n = -0.2\left(\frac{1}{T_1}\right)_0 \qquad \text{within } \pm 10\%.$$
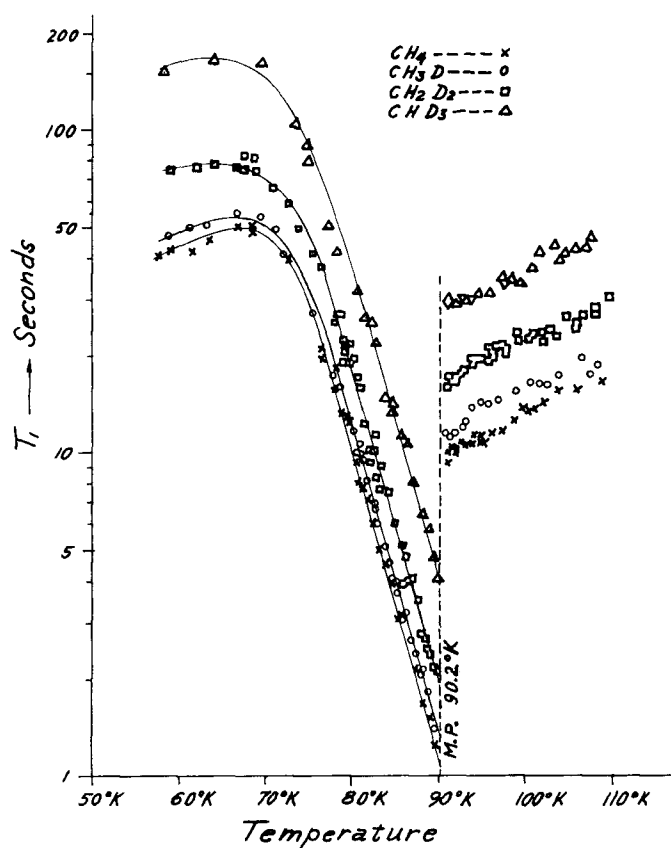

FIG. 1. Plot of T_1 versus temperature for the proton resonances in liquid and solid CH₄, CH₃D, CH₂D₂, and CHD₃ between 56° K and 110° K.

$R_A, R_B \geq 0$ give the following approximate limits for R_C:

$$0.08\left(\frac{1}{T_1}\right)_0 \leq R_C \leq 0.22\left(\frac{1}{T_1}\right)_0$$

where limits on R_A and R_B are obtained as follows.
For

$$R_C = 0.08\left(\frac{1}{T_1}\right)_0, \qquad R_A = 0, \qquad R_B = 0.92\left(\frac{1}{T_1}\right)_0$$

$$R_C = 0.22\left(\frac{1}{T_1}\right)_0, \qquad R_A = 0.78\left(\frac{1}{T_1}\right)_0, \qquad R_B = 0.$$

If the correction factor $[1+(n/16)]^{1/2} \cong 1+0.03n+ \ldots$ mentioned above for R_A and R_B is applied, the limits are changed to

$$0.02\left(\frac{1}{T_1}\right)_0 \leq R_C \leq 0.17\left(\frac{1}{T_1}\right)_0.$$

More precise values can be obtained by performing double resonance experiments on the proton–deuteron systems, which we plan to carry out. We may conclude, however, that Johnson and Waugh are correct in predicting that $R_C \neq 0$ but the experimental upper 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 the rotational angular momentum.

The Solids

Here we obtain

(4)
$$\frac{\partial}{\partial n}\left(\frac{1}{T_1}\right)_n = -0.24\left(\frac{1}{T_1}\right)_0$$

which provides the limits

$$0 \leq R_C \leq 0.14\left(\frac{1}{T_1}\right)_0.$$

The simplest interpretation of the results in both the liquids and solids is that $R_A = R_C \cong 0$, i.e. that the contributions to proton spin–lattice relaxation due to all intramolecular interactions is negligible compared with the intermolecular dipolar interactions. The conventional theory for R_A and R_B in the liquid (Abragam 1961) would predict that they are of comparable orders of magnitude. This possibility is not excluded by our results.

In the solid, it is expected that mechanism (B) is predominant in the region just below the melting point since a plot of $\ln T_1$ versus $1/T$ gives the same activation energy, 3.2 kcal/mole, as obtained from line-width measurements (Bloom and Sandhu 1961). The line width is predominantly due to intermolecular interactions.

If mechanism (B) is predominant at lower temperatures ($\leq 70^\circ$ K), the mechanism is associated with dipolar intermolecular interactions modulated

by the reorientations of the molecules. Using the rigid-lattice line widths (Bloom and Sandhu 1961), the correlation times for molecular reorientation required to give these results are found to be reasonable ($\approx 10^{-12}$ seconds). However, the conventional theory would predict that for such reorientational motions R_A should be several times larger than R_B. It may be that mechanism (A) is sensitive to the influence of the crystalline electric fields on the rotational states of the molecules (Tomita 1953).

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N.M.R. LINE-SHAPE STUDIES IN METHANE USING PULSE TECHNIQUES[*]

M. BLOOM[†] AND H. S. SANDHU

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 is often closely approximated by a Gaussian function, i.e. $I(\omega) \sim \exp[(\omega - \omega_0)^2/2\omega_p^2]$, where $\omega_0 = \gamma H_0$ is the Larmor frequency of the nuclear spins in the external field H_0 and ω_p^2 is the second moment of the line.

The free induction signal observed in a pulse experiment (Hahn 1950) is proportional to the "relaxation function" $G(t)$ which is the Fourier transform of $I(\omega)$, i.e. $G(t) \sim \exp[-\omega_p^2 t^2/2]$ for a Gaussian line shape (Abragam 1961, p. 114).

With the onset of rapid molecular motion the observable line shape or relaxation function changes to a Lorentzian form, $G(t) \sim \exp[-\omega_p^2 \tau_c t]$, where τ_c is the correlation time for changes in local fields due to translational motions with $\omega_p^2 \tau_c^2 \ll 1$.

Under very general assumptions the relaxation function for all times is predicted to be (Abragam 1961, p. 439)

$$(1) \qquad G(t) \sim \exp[-\omega_p^2 \tau_c^2 \{ \exp(-t/\tau_c) - 1 + t/\tau_c \}].$$

The general form of $G(t)$ in (1) has not been extensively used in evaluating experimental results. Normally, in order to obtain τ_c as a function of temperature in a system where diffusion takes place, one works in a region where τ_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 τ_c can be obtained.

Abragam (1961, p. 456) has pointed out that it may be fruitful to use the general form for $G(t)$ in (1) to interpret experimental results. In fact, we have found in studying the proton resonance in CH_4, CH_3D, CH_2D_2, and CHD_3 that the use of the pulse technique enables the direct study of (1) over a range of τ_c not usually accessible to absorption methods.

When τ_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. In the pulse experiment, $G(t)$ is Gaussian for $t \ll \tau_c$, enabling one to study the (temperature-independent) second moment. However, the proton induction signals in such systems are so large that one can also study $G(t)$ for $t \gg \tau_c$. Here, the line shape is indeed found to be Lorentzian.

The corresponding observation in absorption experiments is that $I(\omega)$ is Lorentzian for $(\omega-\omega_0)^2\tau_c^2 \ll 1$. 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.

The results are shown in Fig. 1 where T_2 is plotted versus temperature. The crosses show T_2 evaluated from signals observed at $t \ll \tau_c$ fitting the curve $G(t) \sim \exp[-t^2/2T_2^2]$. The circles are obtained from spin echo experiments at higher temperatures where τ_c is short. The squares are obtained from free precession signals for $t \gg \tau_c$ fitting $G(t) \sim \exp[-t/T_2]$. The results show that for the molecules $CH_{4-n}D_n$, the correlation times accurately follow activation energy curves over the entire temperature range.

$$(2) \qquad (\tau_c)_n = (\tau_0)_n \exp[-E_a/RT].$$

The activation energies E_a are found to be 3.2 kcal/mole independent of n, in disagreement with previous measurements for CH_4 (Waugh 1957).

Professor Waugh's estimates are based on the line-width data of Thomas, Alpert, and Torrey (1950). 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. This is not taken into account in the line-width data. 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.

The second moments are, in units of 10^9 sec^{-2}, 4.8, 3.95, 3.1, and 1.4 for $n = 0, 1, 2,$ and 3 respectively, corresponding to the ratios $1:0.8:0.63:0.28$.
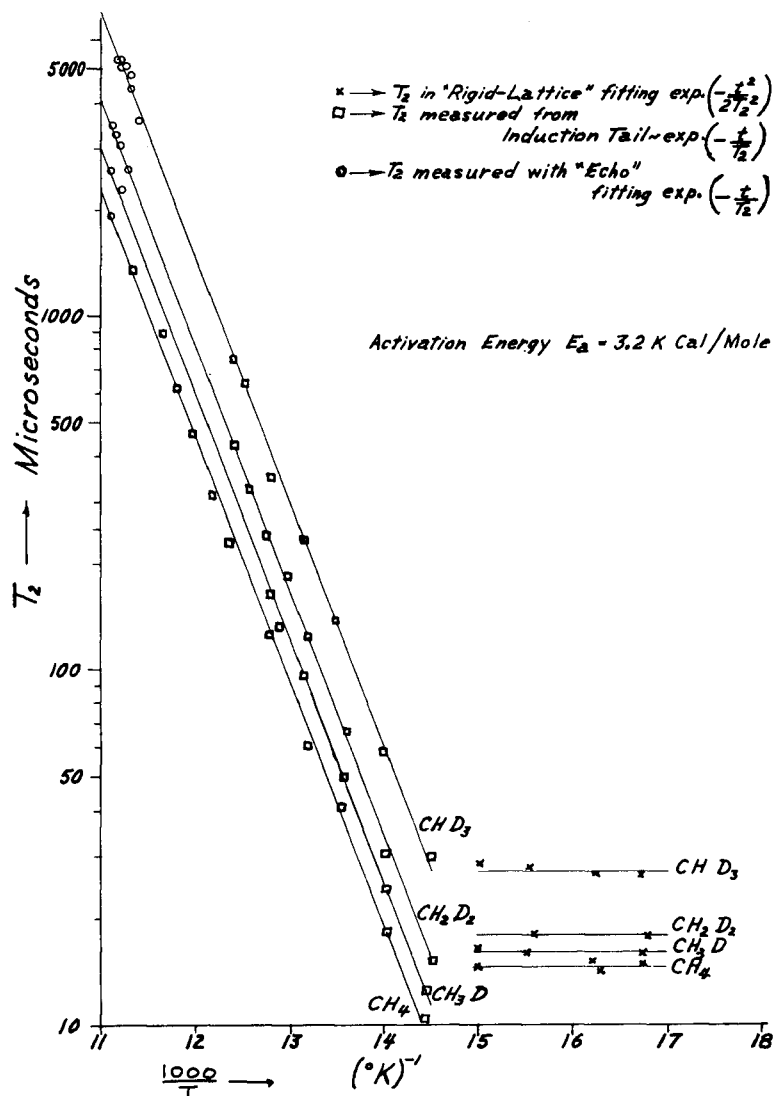
FIG. 1. Plot of T_2 versus the reciprocal of temperature for solid CH_4, CH_3D, CH_2D_2, and CHD_3 between 56° K and 90° K. As indicated in the figure and discussed in the text, two different types of time constants are plotted, one associated with the approximately Gaussian shape of the relaxation function at short times and the other with the approximately Lorentzian shape at long times.

These ratios are to be compared with the ratios predicted for intermolecular interactions (Bloom and Sandhu 1961; Abragam 1961)

$$(3) \qquad\qquad (\omega_p^2)_n = (\omega_p^2)_0(1-0.24n)$$

which predicts $1:0.76:0.52:0.28$. In using (3), we neglect isotopic changes in intermolecular separations and assume that the molecules are undergoing such rapid *reorientations* that the intramolecular interactions do not contribute to the observable second moments.

NOTES ■■■

If one assumes a uniform distribution of protons or deuterons on a sphere of radius given by the C–H distance in CH_4, and if one uses the known crystal structure of CH_4 (see, for example, James and Keenan 1959), the predicted second moments agree with the experimental values within a few per cent.

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