# SPIN-LATTICE RELAXATION 

IN GASEOUS METHANE
by

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#### Abstract

The spin-lattice relaxation time $T_{1}$ has been measured in gaseous $\mathrm{CH}_{4}$ as a function of density at room temperature. The density region investigated is from 0.006 to 7.0 amagats and $T_{1}$ passes through a minimum near 0.04 amagats. The spin-rotation interaction is the dominant relaxation mechanism in gaseous $\mathrm{CH}_{4} \cdot$ Since the spin-rotation constants are accurately known for $\mathrm{CH}_{4}$, the results provide a check on the existing theory of spin-lattice relaxation for spherical top molecules. An interesting feature was the failure of commonly used theoretical expressions for the density dependence of $T_{1}$ to fit the experimental data. A reasonable explanation is that the centrifugal distortion of the $\mathrm{CH}_{4}$ molecule is indirectly contributing to the spin-lattice relaxation.


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## CHAPTER I

INIRODUCTION

The aim of this work is to investigate the mechanism or mechanisms which cause nuclear spin relaxation in gaseous tetrahedral molecules in the vicinity of the $T_{1}$ minimum. The technique is that of a pulsed nuclear magnetic resonance experiment. The spin-lattice relaxation time $T_{1}$ is obtained as a function of density at constant room temperature. It turns out that $T_{i}$ goes throuch a minimum at approximately 0.04 ainagats and the experiment is performed over the range of from 0.006 to to 7.0 amasats. The molecule being investigated is methane ( $\mathrm{CH}_{4}$ ) which has a spinless carbon nucleus $\left(1_{C}\right)$ at its centre and four spin $\frac{1}{2}$ protons at the corners of a tetrahedron.

Relaxation in $\mathrm{CH}_{4}$ has been investigated using these techniques by Dorothy (1967), Bloom and Dorothy (1967), Bloom, Bridges and Hardy (1967), Dong (1969) and Dong and Bloom (1970). The spin-rotation interaction which can be shown to be the most important cause of relaxation in $C_{4}$ (Bloom, Bridges and Hardy, 1967) has been investigated vsing molecular beam techniques by Anderson and Ramsey (1966), Yi (1967), Yi, Ozier, Khosiz and Ramsey (1967), Ozier, Crapo and Lee (1968) and Yi, Ozier and Ramsey (to be published). The experiment was originally intended to be a check on previously obtained results before
going on to tetrahedral molecules for which $\mathrm{T}_{1}$ had not been previously measured. However, with certain modifications to the already existing apparatus, greater accuracy was achieved as a result of greater signal to noise and many more runs were performed than in previous works. The results are more reliable and indicate the presence of some fine structure in the dependence of $T_{1}$ on density.

The remaining Chapters of this work are as follows. Chapter II involves basic concepts in nuclear magnetic resonance and spin-lattice relaxation. The only specialization is to the case of rare gases. Persons relatively new in the field are referred to the classic texts of Abragam (1961), Andrew (1955) and Slichter (1963).

Chapter III involves only the experiment; the procedures which are used to measure and calculate $T_{1}$ as a function of density. This does not involve any theoretical considerations other than those which have to be met in order to satisfactorily perform the experiment. In Chapter IV, the apparatus is discussed in detail and circuit diagrams for the pulse spectrometer may be found in the Appendix.

The concept of spin-lattice relaxation for $\mathrm{CH}_{4}$ through the spin-rotation interaction is discussed in Cnapter $V$ and the experimental data is interpreted using the existing theory.

The possibility of future fruitful work in the field is discussed, along with a summary of this thesis, in Chapter VI.

CHAPTER II
BASIC IDEAS

### 2.1. NUCLEAR MAGNETIC RESONANCE

Some nuclei possess an intrinsic magnetic property or observable called the magnetic moment $\bar{\mu}$ given by

$$
\begin{equation*}
\bar{\mu}=\gamma \hbar \bar{I} \tag{2.1}
\end{equation*}
$$

where $\bar{I}$ is the angular momentum of the nucleus and $\gamma$ is its gyromagnetic ratio.

$$
\gamma=\frac{g e}{m_{p} c}
$$

where $e$ and $m_{p}$ are the charge and mass of a proton and $g$ is the so-called g-factor. Gaussian units are used and $c$ is the speed of light. When a magnetic field $\bar{H}_{o}$ is applied, the projection of $\bar{I}$ along $\bar{H}_{0}$ is quantized and can only assume values $-I,-I+1$, ....., I-1, I.

The interaction between the field $\bar{H}_{0}$ and the spins (nuclei possessing a magnetic moment) is described by the Hamiltonian

$$
\begin{equation*}
W=-\bar{\mu} \cdot \bar{H}_{0} \tag{2.2}
\end{equation*}
$$

where $\bar{\mu}$ is understood to be a quantum mechanical vector operator. A laboratory coordinate system is partially defined by assuming that $\bar{H}_{O}=H_{0} \hat{k}$ where $\hat{k}$ is a unit vector in the $z$ direction. With the aid of equation (2.1), equation (2.2) becomes

$$
W=-\gamma \hbar H_{0} I_{2}
$$

The possible states of the system are denoted by $I m>$ and the observables associated with the operator $I_{z}$ are denoted by $m$.

$$
I_{z}|m>=m| m>
$$

The allowed energy values are

$$
\begin{aligned}
& W\left|m>=E_{m}\right| m> \\
& E_{m}=-\gamma \hbar H_{0} m
\end{aligned}
$$

Note that for $\gamma>0, m=-I$ has the highest interaction energy with the field whereas $m=+I$ has the lowest.

Any measurement made in an experiment will involve many spins and the parameter measured will be an average over an ensemble of spins. For a system of like spins in equilibrium with a bath at temperature $T$ it is convenient to use the

Canonical Ensemble where one knows the total volume, the total number of spins and the temperature of the bath with which they are in thermal contact. This bath or lattice as it is called can be taken to be associated with the other degrees of freedom of the molecule in which the nuclei exists. In the Canonical Ensemble, the probability of a spin being in the $\mathrm{m}^{\text {th }}$ state is given by

$$
P_{m}=\frac{\exp \left[-\frac{E_{m}}{k T}\right]}{\sum_{m=-I}^{+I} \exp \left[-\frac{E_{m}}{k T}\right]}
$$

In an equilibrium ensemble of $\mathbb{N}$ spins, there will be a net magnetization along the $z$ axis given by

$$
M_{0}=\sum_{\text {all } m \text { values }} \begin{gathered}
\text { (contribution of a } \\
\text { spin in } m \text { th state })
\end{gathered} \quad \times \quad \begin{gathered}
\text { (fraction of spins } \\
\text { in } m \text { th }
\end{gathered}
$$

The entire idea of our experiment is to measure how the system of spins returns to this value of $M_{0}$ if the system is perturbed. For completeness, we will briefly evaluate equation (2.3) even though we do not use it directly.

$$
M_{0}=\sum_{m=-I}^{+I} \mu_{z} N P_{m}
$$

$$
=\sum_{m=-I}^{+I} N \gamma \hbar m P_{m}
$$

Because the sum in the denominator of $\mathrm{P}_{\mathrm{m}}$ is independent of the total sum, we have

$$
M_{0}=\frac{\sum_{m=-I}^{+I} N \gamma \hbar m \exp \left[\frac{\gamma \hbar H_{0} m}{k T}\right]}{\sum_{m=-I}^{+I} \exp \left[\frac{\gamma \hbar H_{0} m}{k T}\right]}
$$

If one examines the magnitude of $\gamma_{\hbar H_{0} m / k T}$ for typical spins and laboratory conditions (room temperature), one finds that it is the order of $10^{-6}$ for a spin $\frac{1}{2}$ species in a field of 7 kilogauss. With this in mind, if one expands the exponentials and keeps terms of order $m$ (high temperature approximation) the result is the Curie Law:

$$
M_{0}=\frac{N \gamma^{2} \hbar^{2} I(I+1)}{3 k T} H_{0}
$$

Just as $M_{0}$ is a sum over the $\mu_{z}$ 's, the total magnetization $M$ is a vector sum over the individual $\bar{\mu}^{\prime}$ s. The equation of motion for $\bar{M}$ in a magnetic field results from the torque exerted on it by its interaction with the main field and is given by

$$
\begin{equation*}
\frac{d \bar{M}}{d t}=\gamma \bar{M} \times \bar{H}_{0} \tag{2.4}
\end{equation*}
$$

Note that $\bar{H}_{0}$ is in the $z$ direction and

$$
\begin{aligned}
& \frac{d M_{z}}{d t}=0 \\
& M_{z}=\text { constant }=M_{0}
\end{aligned}
$$

Equation (2.4) implies that the vector characterizing the magnetization is precessing about the $z$ axis. To see this, it is convenient to transform the equation of motion into a reference frame rotäting with an arbitrary angular frequency $W$ about the direction of the field $\bar{H}_{0}$. For our case the equation of motion in the rotating reference frame is given by

$$
\begin{equation*}
\frac{d \bar{M}}{d t}=\bar{M} \times\left(\gamma \bar{H}_{0}-\omega \hat{k}\right) \tag{2.5}
\end{equation*}
$$

Equation (2.5) is conveniently rewritten as

$$
\begin{equation*}
\frac{d \bar{M}}{d t}=\bar{M} \times\left(w_{0}-w\right) \hat{k} \tag{2.6}
\end{equation*}
$$

where $\omega_{0}=\gamma H_{0}$ defines the Larmor angular frequency. From equation (2.6) it is immediately obvious that in the reference frame rotating at $W=W_{0}$, the magnetization is static. Working backwards, it is evident that $\bar{M}$ is precessing about the $z$ axis in the laboratory frame with an angular frequency of magnitude $W_{0}$. Note that both frames of reference have the same $z$ axis. The next step in our development is to introduce an oscillating field in the $x$ (or $y$ ) direction of the laboratory frame. This is done by setting up an oscillating current in a solenoid, the sample under study being inside the solenoid. One can think of this field as being the vector sum of 2 circularly polarized fields with their polarizations in opposite senses. The rotating frame we use is defined by that one of these rotating fields which is constant in the wy plane of the rotating frame. If we define the $x$ direction in the rotating frame by the direction of the new field, we have

$$
\bar{H}_{1}=H_{1} \hat{i}
$$

and the equation of motion in the rotating reference frame becomes

$$
\begin{equation*}
\frac{d \bar{M}}{d t}=\bar{M} \times\left[\left(w_{0}-w\right) \hat{k}+w_{1} \hat{i}\right] \tag{2.7}
\end{equation*}
$$

where $W_{1}=\gamma_{H_{1}}$ defines $W_{1}$. We have ignored the other component of the original oscillating field which is rotating with an angular frequency $-2 \omega$ with respect to the rotating frame we
have chosen. In practice, $\mathrm{H}_{1} \ll \mathrm{H}_{\mathrm{O}}$ and Abragam (1961) shows that this field causes very small effects which we can neglect. Equation (2.7) can be misleading at first sight and one must remember the following. The magnitude of a field rotating with an angular frequency $W$ with respect to the laboratory frame is described by Lh. The magnitude of the constant magnetic field is described by $W_{0}$. If we write equation (2.7) as

$$
\frac{d \bar{M}}{d t}=\gamma \bar{M} \times \bar{H}_{e f f}
$$

the magnetization is now precessing about an effective field in the rotating frame given by

$$
H_{e f f}=\frac{1}{\gamma}\left[\left(w_{0}-w\right)^{2}+w_{1}^{2}\right]^{\frac{1}{2}}
$$

Because $W_{1}$ is very small, for most values of $W h, W_{1}^{2} \ll$ $\left(\boldsymbol{W}_{0}-\boldsymbol{W}\right)^{2}$ and the magnetization is almost unaffected by $H_{1}$. That is, the solution to equation (2.7) is not very different from the solution to equation (2.6).

The interesting case is when we apply the rotating field at $\boldsymbol{\omega}=\boldsymbol{\omega}_{0}$. Equation (2.7) becomes

$$
\begin{equation*}
\frac{d \bar{M}}{d t}=\bar{M} \times w_{1} \hat{i} \tag{2.8}
\end{equation*}
$$

The magnetization now precesses about the field $H_{1} \hat{i}$ in the rotating frame. This is a resonance phenomenon and is appropriately
named nuclear magnetic resonance. If we pulse the field $H_{1}$ at the resonance frequency for a predetermined time, $\bar{M}$ can be left at any orientation with respect to the $z$ axis. A $\pi$ pulse of the field $\mathrm{H}_{1}$ rotates $\overline{\mathrm{M}}$ by $180^{\circ}$ about the x axis and takes $\mathrm{M}_{z}$ into $-M_{Z}$. A $\pi / 2$ pulse effectively puts the magnetization in the $x y$ plane and so on.

The effect of the pulsed radio frequency is to cause the spin system to depart from its equilibrium position providing the angle of rotation is not a multiple of $2 \pi$. Then it will tend to relax back to its equilibrium value. Another way of stating this is that we have perturbed the system from its lowest energy configuration and it will strive for its equilibrium situation by giving up energy to the other molecular degrees of freedom which comprise the "lattice" or "bath".

### 2.2. SPIN-LATTICE RELAXATION

Some kind of model is required to explain the approach to equilibrium of the spin system after it has been perturbed. The spin-lattice relaxation time $T_{1}$ is loosely defined as a characteristic time for the component of the magnetization along the field direction to approach its equilibrium value. $A T_{1}$ mechanism involves an exchange of energy between the spins and the lattice. There may be interactions between spins which redistribute energy among the spin system but do not change the total energy. For simple systems this relaxation is described by a single constant $T_{2}$, the spin-spin relaxation time and involves relaxation of the components of $\bar{M}$ perpendicular to the
constant field. Although $T_{2}$ is not the subject of our discussion we must later consider its effects when we perform the pulsed nuclear magnetic resonance experiments.

The microscopic mechanisms for spin-lattice relaxation for the special case of spherical top molecules such as $\mathrm{CH}_{4}$ are discussed in Chapter V. In our present discussion, the aim is to obtain a general formula for $T_{1}$ in terms of the total magnetization $\overline{\mathrm{M}}$ which is a macroscopic and measureable observable. The $\mathrm{T}_{1}$ expression we develop in the microscopic theory in Chapter $V$ will be used to interpret the experimental data which is obtained by applying the expression for $T_{1}$ we now develop using the macroscopic theory.

We can modify the equation of motion (2.7) to include relaxation after a perturbation. The modified equation of motion which holds very well for gases along with the concepts of $T_{1}$ and $T_{2}$ are phenomenological in nature and are due to Bloch (1946).

$$
\begin{align*}
\frac{d \bar{M}}{d t} & =\bar{M} \times\left[\left(w_{0}-w\right) \hat{k}+w_{1} \hat{i}\right] \\
& +\frac{M_{0}-M_{z}}{T_{1}} \hat{k}-\frac{M_{x} \hat{i}+M_{y} \hat{j}}{T_{2}} \tag{2.9}
\end{align*}
$$

Starting with the general equation (2.9) in the rotating frame, we can specialize it for our pulse techniques. Starting with the equilibrium situation where $W_{1}$ has not been introduced, we have

$$
\frac{d \bar{M}}{d t}=\bar{M} \times\left(w_{0}-w\right) \hat{k}
$$

$$
\frac{d M_{z}}{d t}=0
$$

$$
M_{z}=M_{0}
$$

The system is perturbed at the resonant frequency in a time short enough that relaxation effects are negligible.

$$
\begin{equation*}
\frac{d \bar{M}}{d t}=\bar{M} \times \omega_{1} \hat{i} \tag{2.10}
\end{equation*}
$$

As discussed previously, this means that $\bar{M}$ precesses about the x direction in the rotating frame. Rather than solve equation (2.10) directly, we just leave $W_{1}$ on long enough to take $M_{z}$ from its equilibrium value of $M_{0}$ to a non equilibrium value of $M_{z}(0)$. In the experiment, the special case of a $\pi$ pulse is used which means $M_{Z}(0)=-M_{0}$. This is as much as the system can be perturbed. After the pulse, the equation of motion in the frame rotating at the Larmour angular frequency becomes

$$
\begin{equation*}
\frac{d \bar{M}}{d t}=\frac{M_{0}-M_{2}}{T_{1}} \hat{k}-\frac{M_{x} \hat{i}+M_{y} \hat{j}}{T_{2}} \tag{2.11}
\end{equation*}
$$

Note that in the laboratory frame, the $\mathrm{T}_{2}$ part of equation (2.11) will have factors involving $\sin \left(W_{0} t\right)$ and $\cos \left(W_{0} t\right)$ but in both frames

$$
\begin{equation*}
\frac{d M_{z}}{d t}=\frac{M_{0}-M_{z}}{T_{1}} \tag{2.12}
\end{equation*}
$$

Equation (2.12) is easily solved and $M_{z}(t)$ is given by

$$
\begin{equation*}
M_{z}(t)=M_{0}-\left[M_{0}-M_{z}(0)\right]\left[\exp \left(-\frac{t}{T_{1}}\right)\right] \tag{2.13}
\end{equation*}
$$

and with the initial condition, $M_{z}(0)=-M_{0}$ imposed by a $\pi$ pulse we have

$$
\begin{equation*}
M_{z}(t)=M_{0}\left[1-2 \exp \left(-\frac{t}{T_{1}}\right)\right] \tag{2.14}
\end{equation*}
$$

Thus from a measurement of $M_{z}$ as a function of time after a suitable perturbation, we can uniquely determine $T_{1}$.

## CHAPTER III

THE EXPERIMENT
3.1

SIGNAL DETECTION

The same coil is used to deliver the radio frequency pulse and detect the nuclear magnetic resonance signal. A time dependent net magnetization $\bar{M}(t)$ for the sample in the coil will be proportional to a time dependent magnetic induction $\bar{B}(t)$. The signal voltage induced in the coil will be

$$
\begin{equation*}
V_{S}(t)=-\frac{d \Phi(t)}{d t} \tag{3.1}
\end{equation*}
$$

where the total magnetic flux $\Phi(t)$ is given by

$$
\begin{equation*}
\Phi(t)=A B_{x}(t) \tag{3.2}
\end{equation*}
$$

The cross section area of the coil is $A$ and we have assumed the coil is wound around the x axis in the laboratory frame.

The reference sine wave $\mathrm{V}_{\mathrm{R}}\left(\boldsymbol{W}_{0}\right)$ from the reference amplifier is used for phase sensitive detection in the tuned amplifier. Taking care to adjust $V_{R}\left(W_{0}\right)$ such that the amplifier is linear over all desired amplification regions, the output will
be proportional to the magnitude of $V_{S}\left(\omega_{0}\right)$ at time $t$. (See figure 4.4.) The signal $V_{S}\left(W_{0}\right)$ is proportional to the magnitude of the $W_{0}$ component of the flux $\Phi(t)$. From equations (3.1) and (3.2) and the previous discussion in this section it is clear that $V_{S}\left(\omega_{0}\right)$ is proportional to the magnitude of the component of $M_{x}(t)$ with $\boldsymbol{W}=\boldsymbol{W}_{0}$. To summarize, we can measure a voltage proportional to the Larmor frequency component of the magnetization in the $x y$ plane.

### 3.2 PULSED N. M. R. EXPERIMENTS

The information we wish to obtain concerns $M_{z}$ as a function of time after a suitable perturbation. However, we can only measure a net magnetization in the xy plane. We can prepare a net magnetization in the $x y$ plane which is proportional to an initial $z$ component of the magnetization by using pulse techniques. We will examine the- two types of pulse techniques used in our experiments by examining some simple models.

### 3.2.1 FREE INDUCTION DECAY

Starting with the magnetization in the equilibrium position with $M_{z}=M_{o}$, the application of an r. f. pulse will take $M_{z}$ into $M_{z}(0)$. Figure 3.1 shows the special case used in our experiments where a $\pi$ pulse gives $M_{Z}(0)=-M_{0}$. In terms of figure 3.1 , we have $A \rightarrow B$. (The primed and double primed letters in figure 3.1 correspond to the same event for a second and third time.) The spins will now relax according to equation (2.13)
figure 3.1 free induction decay


which reduces to equation (2.14) for the special case of a $\pi$ pulse. In a time $t$ we have $B \rightarrow C$ in figure 3.1. At this time $t$, a $\pi / 2$ pulse will rotate $M_{Z}(t)$ into the $y$ direction indicated by $C \longrightarrow D$ in figure 3.1. We are. in the rotating frame and the perturbing field is in the $x$ direction. From Chapter 3.1, we have the result that a signal is now detected. After the $\pi / 2$ pulse, the signal will be positive or negative depending on whether $M_{z}(t)$ was positive or negative. This magnetization in the xy plane will decay according to the $T_{2}$ part of equation (2.11). If a measurement is made a constant time after the $\pi / 2$ pulse, the factor which describes the loss of signal due to $T_{2}$ effects in a rigorous expression for the amplitude of the signal becomes a constant and the measured voltage $V_{S}(t)$ discussed in Chapter 3.1 becomes proportional to $M_{z}(t)$. The signal is sampled by a measuring pulse indicated by $E$ in figure 3.1. Figure 3.1 shows three measurements for increasing values of $t$, namely $t, t^{\prime}$ and $t^{\prime \prime}$ and indicates how the signal decays from $-M_{0}$ to $+M_{0}$ as $t$ is varied from 0 to $t_{R}$, the repetition rate of the pulse sequence.
3.2.2. SPIN-ECHO

The spin-echo technique makes use of the fact that after the $\pi / 2$ pulse discussed in the previous section, the loss of signal in the $x y$ plane is, in part, reversible. Under general conditions, the decay of the $x$ and $y$ components of $\bar{M}$ through the mechanism of mutual spin flips resulting from the dipolar interaction is irreversible. However, that part of the decay arising from the fact that the spins precess at slightly different
angular frequencies because of slightly different constant local fields is certainly reversible. For our case, this variation in local fields is chiefly due to the inhomogeneity of the magnet. The spin-echo effect is shown in figure 3.2 using three spins; $S_{1}, S_{2}$ and $S_{3}$, for simplicity. The positions $A, B, C$ and $D$ are the same as for the free induction decay situation described in the last section. At $E$, the spins are in the position shown because the angular frequency of $S_{3}$ is greater than the angular frequency of $S_{2}$, which in turn has an angular frequency greater than $S_{1}$. The application of another $\pi$ pulse at this time will flip the spins to position $F$ with the "fastest" spin now behind the others. As should be obvious with this simple model, the spins will reunite at position $G$ and "pass through each other". The result is a spin-echo which is in effect two induction decays back to back. A measurement at the echo peak will again give a signal proportional to $M_{Z}(t)$.

### 3.3 EXPERIMENTAL PROCEDURE

There are several experimental parameters to be set in performing a measurement of $T_{1}$. In order that signal to noise be maximized and signal distortion be prevented, one must inflict limits on some variables and preserve relationships between others. The following is a discussion of a typical run which will lead to the determination of $\mathrm{T}_{1}$ for a given pressure.

Approximately 100 p. s.i. g. of $\mathrm{CH}_{4}$ is used to tune the signal. The phase of the r. f. pulses relative to the reference voltage is adjusted to give a negative free induction
figure 3.2 spin-echo

decay and if the three pulse sequence is used, a positive spinecho is obtained. A negative induction decay is used because it is easier to differentiate between the indistinct end of the large $\pi / 2$ pulse and the beginning of the signal. The signal is tuned by maximizing the amplitude of the induction decay. The echo is also maximized in the same way, taking care not to disturb the induction decay. The pressure is then reduced to the desired value.

One must now decide on the values of five parameters: $t_{R}$ is the repetition rate of the $t w o$ or three pulse sequence, $t_{S}$ is the width of the sampling pulse, and $R C$ is the value of the boxcar integrating constant. These three parameters along with the positioning of $t_{S}$ and the rate at which $t$ is varied must be determined. This last point decides how long a run will take and places an upper limit on the effective measuring time constant. This is so, because the recorded signal must not lag behind the detected signal. However, the longer the effective time constant is, the better the signal to noise will be. As discussed in Chapter 4.3, the effective time constant $\tilde{\mathcal{T}}$ is given by

$$
\tilde{\tau}=\frac{t_{R}}{t_{S}} R C
$$

For a typical run of about 30 minutes, a value of 5 to 15 seconds seemed to be an optimum value for $\tilde{\mathcal{T}}$. Theoretically, the longer the time taken for a run, the larger the $\tilde{\tau}$ that may be used and the better the resulting signal to noise. However, long term
drifts in $M_{O}$ often make it better in practice to put up with poorer signal to noise and use a shorter run time.

Normally, one fixes $t_{R}$ and $t_{S}$ independently and uses an RC necessary to give an optirnum $\tilde{\mathcal{T}}$. The time $t_{R}$ must be long enough that $M_{z}\left(t_{R}\right) \approx M_{0}$ or, in other words, the spins must be very close to equilibrium before the next pulse sequence begins. Within the sensitivity of the experiment, $t_{R} \geq 10 T_{1}$ is a reasonable choice. For higher values of $t_{R}$, signal to noise is proportional to $t_{R}^{1 / 2}$ (among other things) so one does not wish to make it arbitrarily long. The width of $t_{S}$ depends on the width of the signal being sampled, (induction decay or echo). For the echo, one centres $t_{S}$ symmetrically about the peak and adjusts the width until signal to noise is maximized; all other parameters being held constant. For the induction decay, the sampling pulse is positioned as close as possible to the $\pi / 2$ pulse. This limit ( about 20 microseconds from the end of the $\pi / 2$ pulse) is set by the recovery time of the amplifier after the $\pi / 2$ pulse. Signal to noise is then maximized by adjusting the width. Note that the width of either signal is proportional to $T_{2}$ which in turn is approximately proportional to density . As a result, the lower the density is, the smaller $t_{S}$ must be. Signal to noise is proportional to density, but because this $T_{2}$ narrowing effect places an upper limit on $t_{S}$, there is a further decrease in signal to noise at lower densities. At densities lower than about 0.03 amagats for $\mathrm{CH}_{4}$, signal to noise must be maximized on the chart recorder without seeing the signal, because it is completely buried in noise. It should be noted that at several densities
runs were performed sampling the echo and then the induction decay and in each case, $T_{1}$ was well within the scatter of surrounding points.

Attenuation occurs at three stages; the tuned amplifier, the oscilloscope and the boxcar integrator output. The time $t$ is varied manually hetween 0 and almost $t_{R}$ and the three amplifiers are set to give full scale deflection on the chart recorder. Note that $M_{z}(\sim 0)=-M_{0}$ is the minimum signal and $M_{z}\left(\sim t_{R}\right) \approx$ $M_{z}(\infty)=M_{0}$ is the maximum signal. The only time full scale deflection was not used was for very low densities where nothing was gained by using full scale deflection because of the very poor signal to noise. The maximum signal to noise, $\frac{M_{Z}(\infty)-M_{z}(0)}{N}$ $\approx \frac{2 M_{0}}{N}$ varied depending on how much time was taken for various runs, but typical signal to noise ratios on the chart records were 3 at 0.006 amagats, $?$ at 0.01 amagats, 13 at 0.02 amagats, 20 at 0.04 amagats and 50 for densities above 0.1 anagats. The optimum bandwidth and d. c. amplification are determined by maximizing signal to noise and depend on the characteristics of the individual amplifiers. This is a matter of trial and error and because the tuned amplifier has a maximum amplification of about $10^{6}$, one must take care that the signal does not saturate its final stage.

The sampling time $t$ is set as close to $t_{R}$ as possible and $M_{z}(\infty) \approx M_{o}$ is recorded. An ultra-slow sweep (see next chapter) which automatically varies from 0 to about 2 or 3 T (or until the signal becomes too close to $M_{0}$ to be useful) is
used to measure $M_{z}(t)$. The ultra-slow sweep is then turned off and $M_{0}$ is again recorded. If $M_{0}$ has varied more than about $5 \%$ of full scale deflection, the run is rejected. This might happen if a temperature change during the run changes the constant magnetic field or temperature dependent components of the electronic system. The equilibrium magnetization Mo before and after the run is joined by a straight line to enable one to compute $M_{z}(t)-M_{0}$ as a function of $t$, which is indicated by an event marker.

If systematic errors are present, one must try to account for and eliminate as many as possible. One effect definitely present is an exponential signal superimposed on the induction decay resulting from the amplifier's recovery after the first $\pi$ pulse. The signal is sampled a constant time after the $\pi / 2$ pulse and because only the differences $M_{z}(t)-N_{0}$ are involved in the computation of $T_{1}$, the constant voltage added to the signal due to the amplifier's recovery after the $\pi / 2$ pulse may be neglected. However, as the time between the first $\pi$ pulse and the $\pi / 2$ pulse is varied, the boxcar sampling pulse effectively sweeps the distortion signal associated with the amplifier's recovery after the first $\pi$ pulse. For all runs, the bomb was evacuated and a normal run performed to obtain this correction.

### 3.4 T1 CALCULATION

Having measured a voltage $V_{S}(t)$ proportional to
$M_{z}(t)-M_{0}$, one has from equation (2.14)

$$
\begin{equation*}
V_{\mathbf{S}}(t) \quad \propto \quad 2 M_{0}\left[\exp \left(-\frac{t}{T_{1}}\right)\right] \tag{3.3}
\end{equation*}
$$

A smooth curve is drawn through the signal and equation (3.3) is fitted on semi-log graph paper.

$$
\begin{equation*}
\ln \left[V_{S}(t)\right]=-\frac{t}{T_{1}}+\text { constant } \tag{3.4}
\end{equation*}
$$

$T_{1}$ is then calculated from the slope. This was performed manually rather than using a least squares fit (for equation 3.4) because of the author's belief that the experimenter can thus study each plot carefully and take into account more reliably certain problems which may arise. For example, when a curved line results from plotting $\ln \left[V_{S}(t)\right]$ against $t$ over the entire range of $t$, it could always be traced to a poor choice of $V_{S}(\infty)$, usually because $M_{o}$ was not recorded long enough. A scatter of points significantly greater than that obtained from other runs in similar density regions could usually be attributed to equipment instability. In both cases, the runs were rejected. If there is a slight error $\Delta M_{0}$ in $M_{0}$ the curve might deviate slightly from a straight line in the high $t$ regions because $\frac{\Delta\left[M_{o}-M_{z}(t)\right]}{\left[M_{O}-M_{Z}(t)\right]}$ may be so small as to be unnoticeable at low values of $t\left[\right.$ large $\left.M_{z}(t)-M_{0}\right]$, but exceedingly large at high values of $t\left[s m a l l M_{z}(t)-M_{0}\right]$. In such a case, the high $t$ points were not used if there was a considerable straight line
region for lower $t$ values. Of about 300 runs, 294 satisfied the condition that the change in $M_{0}$ before and after the run was less than $5 \%$ (discussed in the previous section). Of these 294 runs, nine failed to meet the criteria discussed in this section which means the experimental points in figure 5.3 (Chapter V) number 285.

In the higher density regions, the relaxation was exponential within experimental error over 2 orders of magnitude, 2 decades being all that could be measured reasonably with the available equipment. For one value of pressure near the $T_{1}$ minimum, a very lengthy run was performed using a Fabri-Tek Instrument Computer and the relaxation was found to be exponential within experimental error over almost 3 orders of magnitude $[$ in $\left.M_{Z}(t)-M_{0}\right]$. It should be noted that the Fabri-Tek, which is a digital signal averager, was not used for very low pressure runs because; a) it takes much longer to both perform the run and calculate $T_{1}$ and b) $T_{2}$ becomes so short that the smallest time per channel over which the instrument averages was too long to detect the signal.

### 3.5 ERROR ANALYSIS

The results of the experiment appear in figure 5.3 . This graph of $T_{1}{ }^{-1}$ vs $\rho$ has the following special features. Firstly, all the experimental points appear as opposed to a few representative points and secondly, no error bars appear. This latter point requires an explanation and upon giving this, the reasoning behind the first point will become obvious.

In most error analysis, one computes a probable error
from a least squares fit or some other well defined procedure. The error analysis presented here differs from the normal procedure in that rather than calculating probable errors, the experimenter attempts to determine meaningful "possible errors". The meaning of the term "possible error" will become clear in the following paragraph.

There are two quite different procedures one can use to obtain a reasonable estimate of the error in $T_{1}$ for a given run. A. One can draw maximum and minimum slopes through the points on the $\ln \left[V_{S}(t)\right]$ vs $t$ graph and call these limits "the error in $T_{1}$ ". B. One can go back to the trace from the chart recorder and from signal to noise considerations put an error bar on each point of the $\ln \left[V_{S}(t)\right]$ vs $t$ curve. Both these procedures were carried out for several runs in all density regions. For $\rho>0.2$ amagats, the error determined in both ways was less than $1 \%$. In the region $0.02<\rho<0.2$, the first procedure yielded errors of about $5 \%$ and the second procedure yielded errors of about $3 \%$ For the region $\rho<0.02$ anagats, a separate discussion is given later in this section. Because the drawing of extreme lines (first method) always gave an error larger than the second method, this procedure was adopted in the earlier stages of the experiment. To make sure we were not "biased line drawers", the following experinent was performed. Ten persons in the Physics department (who knew nothing of the experiment) were given 3 Xerox copies of each of 3 different runs ( 9 graphs). They were asked to draw what they thought to be the best line, the line of minimum reasonable slope and the line of
maximum reasonable slope. They were not given runs with a curved departure from linearity at high $t$ values because they would have no doubt used these high t points. (See Chapter 3.4.) The results were the following; all the best lines (including the author's) were within $1 \%$ of each other and the maximum and minimum slopes were "inside" the author's in every case. Satisfied that errors were not being underestimated, this method was used to determine errors. That is to say, if anything, the errors were overestimated. (This is the author's philosophy.) It should be noted that this error is certainly larger than the probable error resulting from a least squares fit analysis.

With the exception of a very few cases, the errors computed in this manner were smaller than the spread in points on the $T_{1}^{-1}$ vs $\rho$ graph. This implies that for some unknown reason, there is a "systematic" error associated with each run which is "random" when considered over several runs. For instance, the error resulting from the spread in points near the maximum is about $20 \%$ whereas the error determined for each $T_{1}^{-1}$ by using the preceding procedure is about $5 \%$. Because the systematic approaches used in determining a possible error for each $T_{1}$ give errors smaller than the spread in points on the $T_{1}^{-1}$ vs $\rho$ graph, it seems reasonable to associate the spread in points with the probable error.

For the low density results ( $\rho<0.02$ anagats) the preceding arguments would probably hold if many more runs were performed; namely the spread would increase considerably. Because there are not many points in this region (relative to the other
regions) the low density results look better than they probably are. If one were to use the maximum-minimum slope method to determine errors for each $T_{1}$ in this region, the resulting errors would probably exceed the spread in points. This would certainly be the case for $\rho<0.01$ amagats. For instance, the lowest density point ( 0.006 amagats) has 2 points, 4.24 and 5.26 msec . These two points result from the same trace calculated by two people, Dr. Burnell and myself. One might suspect that a least squares fit of the $\ln \left[V_{S}(t)\right]$ vs $t$ graph resulting from a smooth curve drawn through the trace might be significant for this point. However, the possibility of a large error has already been removed when the $\ln \left[V_{S}(t)\right]$ vs $t$ plot has been made, namely other smooth curves that could be drawn through the signal on the chart record. Errors determined from the methods already discussed would certainly be larger and in the author's opinion more meaningful than a least squares fit approach. Because only very general remarks will be made concerning this low density region, the errors are not included in the experimental plot of $T_{1}^{-1}$ vs $\rho$ 。

## CHAPTER IV

THE APPARATUS

The apparatus used in these experiments can be divided into two parts, the nuclear magnetic resonance pulse spectrometer and the gas handling system. The original apparatus was built by John D. Noble (1964). Since that time, additions and improvements have been made by Hardy (1964), Dorothy (1967), Lalita (1967), Dong (1969), Burnell and myself.
4.1 N. M. R. PULSE SPECTROMETER

The spectrometer can be conveniently divided into three stages; the transmission stage, the tuned circuit stage and the receiving stage. The transmitter delivers radio frequency pulses to the coil in the tuned circuit. The same coil receives the nuclear induction signal. This signal is then detected, amplified, displayed and recorded by the receiving stage. Figure 4.1 shows these three parts of the spectrometer. Circuit details for all the non commercial components can be found in the Appendix. We now consider the spectrometer in greater detail.

### 4.1.1 TRANSMISSION STAGE

Components of the transmitter are designated by upper case Arabic letters whereas pulses and waveforms are indicated by underlined lower case Arabic letters. The reader may follow the analysis more clearly by referring to fiçures 4.1 and 4.2.

A Tektronix 162 vaveform generator, A, delivers a pulse, a, and a sawtooth, $\underline{b}$, of period $t_{R}$ to different channels at the sane time. That is, pulse a coincides with the leading edge of sawtooth $\underline{b}$, indicated by lines 1 and 2 of figure 4.2. Another Tektronix 162, B, is modified to deliver an ultra-slow (or long period) sawtooth, $c$, indicated by line 2 of figure 4.2. The repetition rate $t_{R}$ is typically in the millisecond range while the period of the ultra-slow is usually about an hour. These two sawtooths, $\underline{b}$ and $\underline{c}$, are fed into a Tektronix 163 wave generator, C. C produces a square pulse, $d$, of width $t_{E}$ when the voltages of the two sawtooths crossover, indicated by lines 2 and 3 of figure 4.2.

The result is a pulse, $\mathfrak{a}$, on one channel which defines the beginning of a sequence of pulses of period $t_{R}$. On another channel there is a square pulse of widh $t_{E}$ which starts a time $t$ after the initial pulse, a. As dicussed in Chapter 3.3, $t_{R}$ and $t_{E}$ are fixed and $t$ increases automatically as the ultra-slow sawtooth decreases in amplitude.

The square pulse, $\frac{\alpha}{\alpha}$, is differentiated, D, producing a positive pulse, $\underline{e}$, from the leading edge of $\underline{\alpha}$ and a negative pulse, $f$, from the trailing edge of $d$, indicated by line 4 of figure 4.2. The two pulses are channeled separately and the sign

figure 4.2 pulse sequences

of the negative pulse is reversed, indicated by lines 5 and 6 of figure 4.2. Pulse a from $A$ and pulse $f$ from $D$ are mixed, $E$, and channeled into a pulse width generator, $F$, where they trigeer 2 square waves, $\underline{d}^{\prime}$ and $\underline{f}^{\prime}$ ' respectively. This is indicated by lines 7 and 8 of figure 4.2. This unit is called a $\pi$ pulse generator because $\underline{a}^{\prime}$ and $\underline{I}^{\prime}$ will eventually be $\pi$ pulses. Pulse efrom D triggers another square pulse, éin the $\pi / 2$ pulse width generator G, indicated by line 9 of figure 4.2. The three pulses are mixed, $H$, and amplified, $I$, indicated by line 10 of figure 4.2 .

The three pulse sequence, $\underline{a}^{\prime}, \underline{e}^{\prime}$ and $\underline{f}^{\prime}$ is repeated with period $t_{R}$. The widths of the first and third may be varied independently from the width of the second. The time between $\underline{a}^{\prime}$ and $\underline{e}^{\prime}$ is $t$ and the time between $\underline{e}^{\prime}$ and $\underline{f}^{\prime}$ is $t_{E}$. Depending on which pulse sequence is desired (see Chapter 3.2) pulse f'can be turned on or off.

A 10 MHz crystal oscillator, $J$, provides the radio frequency sine wave which is amplified, $K$, and superimposed on the three gating pulses, $\underline{a}^{\prime}, \underline{e}^{\prime}$ and $\underline{f}^{\prime}$ in a gated oscillator, L. The three radio frequency pulses pass through a phase shifter, M, where the phase of the radio frequency voltage can be adjusted relative to the original oscillator, J. Finally, the frequency is tripled, $N$, and the pulses are amplified to about 1000 volts peak to peak, O. A reference signal from the oscillator, J, is amplified, $K$, tripled, $P$, and amplified again, Q. This signal is used for phase sensitive detection in the receiving stage.

Having superimposed the radio frequency voltage on the three gating pulses, we rename them to be consistant with the
former discussions in this work. That is, the pulses $\underline{a}^{\prime}, \underline{e}^{\prime}$ and $\underline{I}^{\prime}$ plus the radio frequency sine wave become $\pi_{1}, \pi / 2$ and $\pi_{2}$. The transmitter's output, then, is these three r. $f$. pulses on one channel and a reference $r$. $f$. on another channel.
4.1.2 TUNED CIRCUIT STAGE

The physics takes place in the tuned circuit stage. This is perhaps the most important part of the apparatus and it is here where advances in signal to noise have been made which yielded the lower density results.

The lead from the transruitter to the tuned circuit is one-half wavelength to reduce the loss of r. f. power. A 4.7 picofarad capacitor decouples the transmission and tuned circuit stages. The tuned circuit itself entails a coil of fixed inductance and a variable capacitor to meet the resonance condition, $\omega_{0}=$ $(L C)^{-\frac{1}{2}}$. A factor of at least 2 in signal to noise has been gained over previous experiments by having the tuning capacitor as close to the coil as physically possible. $\omega_{0}\left(=\gamma_{H_{0}}\right)$ is fixed by the permanent magnetic field, $H_{0}$, of about 7000 gauss which may be varied anout $\pm 25$ gauss with a set of d. c. coils. A diagram of the tuned circuit stage is shown in figure 4.3. A general discussion of the tuned circuit stage for an N. M. R. spectrometer is given by Clark (1964). Clark's excellent discussion on "coil strategy" explains how one goes about optimizing signal to noise which is dependent on several factors.

The coil in this particular experiment was made from 10 turns of \#14 guage copper wire with a diameter of $3 / 4$ " and a
figure 4.3 tuned circuit stage

length of $1 \frac{1}{2}$ ". The wire was well cleaned, including removal of the enamal and surrounded by a 26 rm . outside diameter glass cylinder to prevent breakdown between the coil and the bomb. The coil and glass were placed in the pressure tight brass bomb with the r. f. lead coming through a kovar seal. The glass was fixed to the bomb with epoxi, which extended to the kovar seal, again to prevent breakdown. The gas enters the system at the other end of the bomb.

The inductance of the coil was 2 microhenries and at 30 MHz the circuit tuned at 15 picofarad. The output signal passes through a 4.7 picofarad decoupling capacitor en route to the receiving stage.

### 4.1.3 THE RECEIVING STAGE

The receiving stage detects, amplifies, displays and records the signal. - As discussed in Chapter 3.2, the signal is an induction decay immediately following the $\pi / 2$ pulse and, if desired, an echo following the second $\pi$ pulse $\left(\pi_{2}\right)$.

The signal from the coil would look something like the picture in figure 4.4A. A set of crossed diodes to ground cuts the high voltage pulses down to the back voltage of the diodes. The signal is very small ( 1 microvolt) and is unaffected. Quarter wavelength leads join the diodes to the tuned circuit and to the preamplifier, $R$, and cut down the loss of the radio frequency ( 30 MHz ) signal. The reader is again referred to figure 4.1. The 2 stage preamplifier, $R$, has crossed diodes between its stages which cut the voltages of the pulses to the point where the main
figure 4.4 free induction signal

( not to scale)

amplifier, $S$, can recover in about 20 microseconds. As discussed in Chapter 3.3 the recovery time of the tuned amplifier, $S$, is important at low densities where $T_{2}$ is short because this limits how close to the $\pi / 2$ pulse the signal can be measured. The main amplifier, $S$, is a commercial, low noise L. E. L. amplifier, model 21B.S. This is a multi-staged tuned amplifier with a bandwidth of 2 MHz centred around 30 MHz at 3 db . The r. f. signal is amplified in the first 3 stages where the reference voltage from the reference amplifier, $Q$, in the transmitter is introduced for phase sensitive detection. The reference voltage was kept at about 2 volts (d. c. level) and the output from the 30 MHz amplifier was kept below 0.2 volts in order that the amplifier operate in its linear region. After phase sensitive detection, the signal becomes the r. f. envelope shown in figure 4.4B.

The signal from the tuned amplifier is again amplified by, and displayed on a Tektronix 531A oscilloscope, $T$, with a type $z$ plug-in. It should be noted that this combination of oscilloscope and plug-in is a very low noise wideband amplifier. The signal from the oscilloscope is fed into a boxcar integrator, U. A pulse from the $\pi / 2$ pulse generator, $G$, triggers a Tektronix 162 waveform generator, $V$, which produces a sawtooth. At a set time after its beginning, this sawtooth triggers positive and negative square pulses of duration $t_{S}$ in a modified Tektronix 161 pulse generator, W. These square pulses, or sample pulses, gate the signal from the oscilloscope in the boxcar integrator. The boxcar accepts the signal over the time $t_{S}$ and then averages using
an RC integrating circuit. The effective time constant of the boxcar is $\tilde{\mathcal{T}}=\left(t_{R} / t_{S}\right)$ RC. An excellent account of the theoretical aspects and experimental techniques involved in the boxcar integrator may be found in Hardy (1964). The output of the boxcar is displayed on a Varian strip chart recorder, $Z$.

The time $t$ between the first $\pi$ pulse and the $\pi / 2$ pulse is measured by a Hewlett Packard Electronic Counter, X, with a time interval unit plug-in. The count starts on a trigger pulse from the $\pi$ pulse generator, $F$, and stops on a trigger pulse from the $\pi / 2$ pulse width generator, $G$. At convenient times, a Hewlett Packard Digital Recorder, Y, indicates the time $t$ on a printed output and at the same time triggers an event marker on the strip chart recorder, $Z$.

The input of the receiving stage is an r. f. signal detected by the coil and the output is the measured signal on a chart recorder.

### 4.2 THE GAS HANDLING SYSTEM

Methane is a relatively easy gas to work with because it may be expelled into the air as long as the ventilation in the room is reasonable and there is no flame near the punp outlet. The schematic diagram shown in figure 4.5 is self explanatory. For pressures greater than 2 amagats, a calibrated 0 to 100 pounds per square inch guage was used. In the region from 1 to 2 amagats, the mercury manometer was used with stopcock 1 open and stopcock 2 closed. Atmospheric pressure was added to the pressure in the system to get the absolute pressure. For pressures below 1
figure 4.5
gas handling system

amagat, stopcock 1 was closed and stopcock 2 opened in order to pump out the right hand side of the manometer. The pressure of the system is then determined (with stopcock 2 closed) absolutely with no addition or subtraction due to atmospheric pressure. Note that this latter method reduces the possible error in pressure by a factor of $\sqrt{2}$. The probable error in pressure is completely negligible down to 0.01 amagats and for the points below 0.01 amagats the probable error is small compared with the spread ( in $T_{1}{ }^{-1}$ ) in points.

All pressures in mm Hg were converted to density in amagats which is the ratio of the density at a particular temperature and pressure to the density at standard temperature and pressure. The maximum density, 7 amagats, is well below the density where 3 body collisions become significant and the Perfect Gas Law is an excellent approximation.

$$
\begin{gathered}
P V=n k T \\
d=\frac{n}{V}=\frac{P}{k T} \\
\rho \text { (amagats) }=\frac{d}{d_{0}}=\frac{P T_{0}}{P_{0} T}
\end{gathered}
$$

where the subscript zero refers to standard temperature and pressure. Amagats are obviously dimensionless.

Although temperature differences for different runs will not affect the computation of density in amagats, they will
affect $T_{1}$ by changing the constant of proportionality between $\mathcal{T}_{c}$ and $\rho^{-1}$ as discussed in the next chapter. For this reason, no runs were performed if the temperature in the magnet gap was outside the limits $20^{\circ} \mathrm{C}<\mathrm{T}<23^{\circ} \mathrm{C} \quad\left(1 \%\right.$ change in $\left.{ }^{\circ} \mathrm{K}\right)$.

## CHAPTER V

SPIN-LATTICE RELAXATION IN $\mathrm{CH}_{4}$ AND THE INTERPRETATION OF THE

EXPERIMENTAL DATA

In the following discussion, the possible mechanisms for nuclear spin relaxation are considered with emphasis placed on the spin-rotation interaction which is the dominant relaxation mechanism in $\mathrm{CH}_{4}$. The relaxation rate $1 / \mathrm{T}_{1}$ is then formulated in terms of the combined effects of the spin-rotation interaction and the molecular motion. Finally, having reviewed the microscopic theory for relaxation, we use the theory to interpret the experimental data. -

### 5.1 NUCLEAR INTERACTIONS

The nuclear hyperfine interactions for spherical top molecules such as $\mathrm{CH}_{4}$ are discussed in considerable detail by Yi, Ozier and Anderson (1967). In the following discussion, we pick out those interactions which play a role in the theory of spinlattice relaxation.

## 5.1 .1 <br> ZEEMAN LEEVELS

A discussion has been given in Chapter 2.1 of the Zeeman energy levels arising from the interaction of a free spin with a constant magnetic field. Of the many possible modifications to these levels resulting from the molecular environment of the nuclei, only the effect of the rotational moment is important. This is an interaction between the molecular magnetic moment associated with the rotational angular momentum $\bar{N} \bar{J}$ and the constant field $\bar{H}_{0}$ and must be added to the Zeeman Hamiltonian. As discussed by Gordon (1966), the molecular rotation is very fast compared with the Larmor precession and although several J states are occupied in $\mathrm{CH}_{4}$ at room temperature, the rotation has only on averege (onnstent) offect. The modificetion (i.e the effect on the N.M.R. experiment) amounts to changing the Zeeman splittings from $\pi W_{0}$ to $\hbar\left(W_{0}-W_{J}\right)$. The parameter $W_{J}$ has been measured by Anderson and Ramsey (1966) to be $0.056 W_{0}$. Note that this does not concern the interaction between the nuclear spins and a field associated with the molecular rotation, but rather the effect on the N.M.R. experiment of the interaction between the rotational monent and the field.

Although there are other interactions which have to be taken into account for certain work with molecular beams (Yi, Ozier and Anderson, 1967) they can be neglected in our case in which the Zeeman levels already discussed completely dominate in determining
the unperturbed ener\&y levels of the spin system.

### 5.1.2 PERTURBATION INTERACTIONS

The following interactions are denoted as perturbations because in a general discussion, they all may link the spins with the lattice and, therefore, represent possible mechanisms for nuclear spin relaxation.

As a result of its importance, we consider the spinrotation interaction in somewhat more detail. The rotation of a free $\mathrm{CH}_{4}$ molecule will result in a magnetic field at the site of a nuclear spin because of the periodic motion of the other three spins in the tetrahedron. The general Hamiltonian describing this interaction may be written

$$
\begin{equation*}
W_{S R}=-\sum_{i=1}^{4} \bar{\mu}_{i} \cdot \bar{H}_{i}^{(r o t)} \tag{5.1}
\end{equation*}
$$

where we must sum over the 4 spins in the molecule and include the possibility that each may see different fields. The rotational fields are related to the rotational state by

$$
\begin{equation*}
\bar{H}_{i}^{(r o t)}=\frac{2 \pi}{\gamma} \underline{C}_{i} \cdot \bar{J} \tag{5.2}
\end{equation*}
$$

which defines the spin-rotation tensor $\mathbb{C}$. Substituting equation (5.2) into equation (5.1) yields

$$
\begin{equation*}
W_{S R}=-2 \pi \hbar \sum_{i=1}^{4} \bar{I}_{i} \underline{C}_{i} \bar{J} \tag{5.3}
\end{equation*}
$$

It is convenient to simplify this Hamiltonian by considering the restrictions required by the tetrahedral symmetry. This is done in detail by Anderson and Ramsey (1966). There are two physically different contributions to $W_{S R}$ given by equation (5.3). The first is the average interaction between the spins and the rotation and can be written $-2 \pi \pi C_{a} \bar{I} \cdot \bar{J}$ which implies that all 4 spins see a constant field $2 \pi C_{a} \bar{J} / \gamma$. The second term, denoted by $C_{d}$ is an anisotropic tensor interaction and may be described as the departure from the average. The exact form is somewhat complicated and does not concern us directly; it may be found in Anderson and Ramsey (1966). For reasons discussed later, if the $C_{a}$ and $C_{d}$ terms can not be separated in the relaxation experiments, one speaks of an effective spin-rotation coupling constant, $C_{e f f}$. For purposes of data analysis, the numerical values for $C_{a}, C_{d}$ and $C_{e f f}$ are taken from the molecular beam experiments of Yi, Ozier, Khosla and Ramsey(1967). These values have been verified by Wofsy, Muenter and Klemperer (1970) and Yi, Ozier and Ramsey (to be published).

There will, in general, be a magnetic dipolar interaction. The intermolecular dipolar interaction can be completely neglected because of the effect of the $r^{-3}$ factor in the Hamiltonian. Bloom, Bridges and Hardy (1967) investigated the intramolecular
dipolar interaction's contribution to the relaxation and found it to be about $5 \%$ of the spin-rotation interaction's contribution. With this in mind, we neglect this contribution to the relaxation and assume the spin-rotation interaction is dominant. It should be noted that this assumption is made purely on the theoretical evidence of Bloom, Bridges and Hardy (1967) because there is no information in the experimental results concerning the contribution of the intramolecular dipolar interaction.

## $5.2 \quad \mathrm{~T}_{1} \mathrm{INCH}_{4}$

Nuclear spin relaxation in spherical top molecules due to the spin-rotation interaction has been investigated quite thoroughly and we give here only a brief review yith an emphasis on the physical processes involved. The interested reader is referred to the following six publications. Hubbard (1963) and Blicharski (1963) arrived at expressions for $T_{1}$ in liquids for symmetric top molecules. Bloom, Bridges and Hardy (1967) extended this to the case of gases for symmetric top and spherical top molecules. These papers use the treatment of relaxation in the classic text of Abragam (1961) as the starting point. Dong (1969) and Dong and Bloom (1970) simplified the expression for $T_{1}$ for $\mathrm{CH}_{4}$ using the experimental evidence that the same correlation time could be associated with both the $C_{a}$ and $C_{d}$ terms.

The relaxation rate will involve the probability per unit time that a transition between spin states will occur in the spin system. In order that energy be conserved, we must consider the lattice as well as the spins because a change of state of the
latter implies a change of state of the former. If the lattice states are denoted by $|I\rangle$ and the spin states by $|s\rangle$, the unperturbed energies are given quite generally by

$$
\begin{aligned}
& W_{1}\left\|>=E_{1}\right\|> \\
& W_{S}\left|s>=E_{S}\right| s>
\end{aligned}
$$

In a rigorous treatment, $E_{1}$ will involve the rotational and translational energies and $E_{S}$ the nuclear Leman levels. If we consider the case of a free molecule and assume the spin-rotation interaction is a small perturbation on the unperturbed levels, we can use first order perturbation theory to determine the probability per unit time that the system goes from a state ils> to a state $\mid I^{\prime}, s^{\prime}>$. This probability will contain terms of the form

$$
\frac{2 \pi}{\hbar}|<l, S| \bar{W}_{S R}\left|l^{\prime}, s^{\prime}>\right|^{2} \delta\left[\left(E_{s^{\prime}}-E_{s}\right)+\left(E_{l}-E_{l}\right)\right]
$$

where $W_{S R}$ is the perturbing spin-rotation Hamiltonian and as usual the unperturbed energies are used. The transition probability per unit time for the spin system will involve an ensemble average over the lattice states and will give terms of the form

$$
\sum_{l^{\prime}} \sum_{l} P_{l} W_{l, s \rightarrow l^{\prime}, s^{\prime}}
$$

where $W_{l, s \rightarrow I^{\prime}, s^{\prime}}$ contains terms like those given in expression (5.4) and the $P_{1}$ are the normal exponential factors in the Canonical Ensemble. Using the integral form of the $\mathcal{O}$-function for expression (5.4), an expression for the relaxation rate will involve terms like

$$
\begin{equation*}
\sum_{l^{\prime}} \sum_{l} P_{1}|<l, s| W_{s p}\left|l^{\prime}, s^{\prime}>\right|^{2} \int_{-\infty}^{+\infty} \exp \left[i\left(w_{s s^{\prime}}+w_{11}\right) t\right] d t \tag{5.5}
\end{equation*}
$$

where $\hbar \boldsymbol{W}_{1 I^{\prime}}=E_{I^{\prime}}-E_{1}, \quad \hbar \boldsymbol{W}_{S S^{\prime}}=E_{S^{\prime}}-E_{S}$ and constants have been dropped. Noting that $W_{S S^{\prime}}$ must be $W_{0}-W_{J}$ because the unperturbed spin states are equally spaced, expression (5.5) may be expressed as a sum over lattice transitions rather than initial and final states. With this in mind, we write $1 / T_{1}$ as a sum over the physical causes of the $\boldsymbol{W}_{11}$.

$$
\begin{equation*}
\frac{1}{T_{1}} \propto \sum_{k} G_{k}(0) \int_{-\infty}^{+\infty} \exp \left[i\left[\left(w_{0}-w_{j}\right)+w_{k}\right] t\right] d t \tag{5.6}
\end{equation*}
$$

A great deal has been omitted in the transition from expression (5.5) to equation (5.6), but what equation (5.6) effectively says is that one can associate an amplitude $G_{k}(0)$ with each lattice frequency component $W_{k} \cdot G_{k}(0)$ is called the time independent correlation function and it is the sum of squares of matrix elements of the spin-rotation Hamiltonian between lattice states separated by energy $\hbar \boldsymbol{W}_{k}$. Each matrix element squared is weighted by an appropriate Boltzmann factor.

Equation (5.6) must be modified to include the effect of collisions. The "effective lattice states" take into account all the lattice degrees of freedom and may be thought of as the discrete rotational states, each of which is broadened into a band by the translational energies associated with the Boltzmann distribution of velocities. During a collision, a molecule will experience anisotropic forces which will change the fields associated with molecular rotation at a nuclear spin site. We can include the effect of this collisional modulation by associating a "reduced correlation function" $\mathrm{g}_{k}(\mathrm{t})$ with each term in equation (5.6).

$$
\frac{1}{T_{1}} \propto \sum_{k} G_{k}(0) \int_{-\infty}^{+\infty} \exp \left[i\left[\left(w_{0}-w_{j}\right)+w_{k}\right] t\right] g_{k}(t) d t
$$

This will, perhaps, become clearer if one defines the spectral density $j_{k}(W)$ as

$$
\begin{equation*}
j_{k}(w)=\int_{-\infty}^{+\infty} \exp \left[i\left(w+w_{k}\right) t\right] g_{k}(t) d t \tag{5.7}
\end{equation*}
$$

and interprets this as the frequency distribution of local fields provided by the broadening due to collisions. The relaxation rate then becomes proportional to the components of this field distribution with $\omega=\omega_{0}-\omega_{J}$.

$$
\begin{equation*}
\frac{1}{T_{1}} \propto \sum_{k} G_{k}(0) j_{k}\left(w_{0}-w_{j}\right) \tag{5.8}
\end{equation*}
$$

The time independent correlation function $G_{h}(0)$ and the constants of proportionality in equation (5.8) are known and it remains to obtain an expression for $\mathrm{g}_{\mathrm{k}}(\mathrm{t})$ in order to solve equation (5.7). If one associates a correlation time $\tau_{k}$, which describes a characteristic time for the effect of a collision, with each interaction and assumes that the collisions are random, $\mathrm{E}_{\mathrm{k}}(\mathrm{t})$ may be written

$$
\begin{equation*}
g_{k}(t)=\exp \left[-\frac{|t|}{\tau_{k}}\right] \tag{5.9}
\end{equation*}
$$

Theoretically, one can only say that $g_{k}(t)$ must be a monotomically decreasing function of time at long times and the form given in equation (5.9) must be interpreted as a reasonable attempt to explain the data. This is discussed by Dong and Bloom (1970). If we perform the integration in equation (5.7), using equation (5.9), equation (5.8) becomes

$$
\begin{equation*}
\frac{1}{T_{1}} \propto \sum_{k} G_{k}(0) \frac{\tau_{k}}{1+\left[\left(w_{0}-w_{j}\right)+w_{k}\right]^{2} \tau_{k}^{2}} \tag{5.10}
\end{equation*}
$$

It is interesting to look at some special cases of equation (5.10). If centrifugal distortion is negligible but we
must associate different correlation times with the $C_{a}$ and $C_{d}$ terms, we have

$$
\begin{align*}
\frac{1}{T_{1}}= & \frac{4 \pi^{2}}{\alpha} C_{a}^{2} \frac{\tau_{1}}{1+\left(\omega_{0}-\omega_{j}\right)^{2} \tau_{1}^{2}} \\
& \vdots  \tag{5.11}\\
& +\frac{4}{45} \frac{4 \pi^{2}}{\alpha} C_{d}^{2} \frac{\tau_{12}^{\prime}}{1+\left(\omega_{o}-\omega_{j}\right)^{2}\left(\tau_{12}^{\prime}\right)^{2}}
\end{align*}
$$

The constants in equation (5.11) are taken from Dong and Bloom (1970) and the choice of notation for the $\mathcal{T}$ 's is in keeping with the literature. The parameter $\alpha$ is given by

$$
\alpha=\frac{\hbar^{2}}{2 I_{0} k T}
$$

where $I_{0}$ is the moment of inertia for the spherically symmetric molecule.

If the same correlation time may be associated with both terms, equation (5.11) reduces to

$$
\begin{equation*}
\frac{1}{T_{1}}=\frac{4 \pi^{2}}{\alpha} C_{\text {eff }}^{2} \frac{\tau_{1}}{1+\left(w_{0}-w_{j}\right)^{2} \tau_{1}^{2}} \tag{5.12}
\end{equation*}
$$

where

$$
C_{e f f}^{2}=C_{a}^{2}+\frac{4}{45} C_{d}^{2}
$$

If centrifugal distortion is not negligible, the anisotropic $C_{d}$ contribution to the relaxation rate may have non zero $W_{k}$ 's and we can write

$$
\begin{aligned}
\frac{1}{T_{1}}= & \frac{4 \pi^{2}}{\alpha} C_{0}^{2} \frac{\tau_{1}}{1+\left(w_{0}-w_{j}\right)^{2} \tau_{1}^{2}} \\
& +\frac{4}{45} \frac{4 \pi^{2}}{\alpha} C_{d}^{2} \sum_{k} \frac{\tau_{k}}{1+\left[\left(w_{0}-w_{j}\right)+\omega_{k}\right]^{2} \tau_{k}^{2}} F_{k}
\end{aligned}
$$

where $F_{k}$ is a normalized function and the sum over $k$ includes $k=0$.

$$
\sum_{k} F_{k}=1
$$

A superficial examination of the experimental results given in figure 5.3 indicates that $1 / T_{1}$ is of the form given by equation (5.12). This implies that the relaxation rate $1 / T_{i}$ is described by; A) equation (5.12), or B) equation (5.i1) with $\tau_{12}^{\prime}$ not very different from $\tau_{1}$, or $C$ ) equation (5.13) with one term dominant. If the relaxation rate were given by, say, two equally dominant, but very different terms, we would expect to
see another maximum or at least a bump where the second term has its maximum. If the spectral densities $j_{k}(W)$ associated with the centrifugal distortion are centred around $W_{k}{ }^{\prime} s$ which are "far away" from $W_{0}-W_{J}$ we can certainly imagine their contribution to the relaxation rate being very small. This is shown schematically in figure 5.1 where only a single distortion frequency is shown for simplicity. The dominant $C_{a}$ term is described by $j_{1}(W)$ and the distortion term is described by $j_{12}^{\prime}(W)$. As is evident in equation (5.12) or a dominant term in equations (5.11) and (5.13), the fastest relaxation rate occurs when $\tau_{1}^{-1} \approx W_{0}-W_{J}$. This is the characteristic $1 / T_{1}$ maximum or $T_{1}$ minimum and manifests itself in the experimental results in figure 5.3. The relaxation rate then decreases monotomically as; A) $\tau_{1}$ decreases in the region $\tau_{1}^{-1}>W_{0}-W_{J}$ and, B) $\tau_{1}$ increases in the region $\tau_{1}{ }^{-1}<W_{0}-W_{J}$. Case $A$ is considered the high density region and case $B$ the low density region. The maximum relaxation along with the two extreme cases are shown schematically in figure 5.2 for the case of the $j_{j}(\boldsymbol{W})$ term completely dominant.

Experimentally, one measures the density $\rho$ which is related to the correlation times $\tau_{k}$ by

$$
\begin{equation*}
\frac{1}{\tau_{k}}=\rho<\sigma_{k} \vee> \tag{5.14}
\end{equation*}
$$

where $\sigma_{k}$ is an effective collision cross section for the particular interaction and $v$ is the speed of a molecule. The Canonical Ensemble average $\left\langle\sigma_{k} v\right\rangle$ depends only on the mean

figure 5.2 collision induced fields


velocity which, in turn, is a function of the temperature of the lattice. If temperature is held constant, we can write

$$
\begin{equation*}
\tau_{k}=\frac{A_{k}}{\rho} \tag{5.15}
\end{equation*}
$$

where we allow different constants, $A_{k}$, for the different cross sections associated with each interaction.

For purposes of analysing the experimental data it is convenient to express the relaxation rate as a function of density through equation (5.15) and furthermore noting that the density $\rho_{\mathrm{k}}$ at which the expression

$$
\frac{\tau_{k}}{1+\left[\left(w_{0}-w_{j}\right)+w_{k}\right]^{2} \tau_{k}^{2}}
$$

is a maximum occurs when

$$
\left[\left(w_{0}-w_{j}\right)+w_{k}\right] \tau_{k}=1
$$

Using equation (5.15), we have

$$
\left[\left(w_{o}-w_{j}\right)+w_{k}\right] \frac{A_{k}}{\rho_{k}}=1
$$

which can be taken as the definition of $\boldsymbol{\rho}_{\mathrm{k}}$. We have then

$$
\begin{equation*}
\tau_{k}=\frac{\rho_{k}}{\left[\left(w_{0}-w_{j}\right)+w_{k}\right]} \frac{1}{\rho} \tag{5.16}
\end{equation*}
$$

' and by substituting equation (5.16) into the three possible cases for $1 / T_{1}$ given by equations (5.11), (5.12) and (5.13) we obtain the following formulae.

Case 1. If centrifugal distortion is negligible and the same correlation time may be associated with the $C_{a}$ and $C_{d}$ terms, the relaxation rate is given by

$$
\begin{equation*}
\frac{1}{T_{1}}=\frac{4 \pi^{2} \mathrm{C}_{\mathrm{eff}}^{2}}{\alpha\left(\omega_{0}-\omega_{\mathrm{J}}\right)} \frac{\frac{\rho_{1}}{\rho}}{1+\frac{\rho_{1}^{2}}{\rho^{2}}} \tag{5.17}
\end{equation*}
$$

where $\rho_{1}$ is given by equation (5.16) with $\omega_{1}=0$.

$$
\begin{equation*}
\tau_{1}=\frac{\rho_{1}}{\left(\omega_{0}-\omega_{j}\right)} \frac{1}{\rho} \tag{5.18}
\end{equation*}
$$

Case 2 If centrifugal distortion is negligible, but different correlation times are required for the $C_{a}$ and $C_{d}$ terms, the relaxation rate is given by

$$
\frac{1}{T_{1}}=\frac{4 \pi^{2} C_{0}^{2}}{\alpha\left(w_{0}-W_{j}\right)} \frac{\frac{\rho_{1}}{\rho}}{1+\frac{\rho_{1}^{2}}{\rho^{2}}}
$$

$$
\begin{equation*}
+\frac{4}{45} \frac{4 \pi^{2} \mathrm{C}_{d}^{2}}{\alpha\left(\omega_{0}-\omega_{j}\right)} \frac{\frac{\rho_{12}}{\rho}}{1+\frac{\left(\rho_{12}^{\prime}\right)^{2}}{\rho^{2}}} \tag{5.19}
\end{equation*}
$$

where $\rho_{1}$ is given by equation (5.18) and $\rho_{12}^{\prime}$ is given by equation (5.16) with $W_{12}^{\prime}=0$.

$$
\tau_{12}^{\prime}=-\frac{\rho_{12}^{\prime}}{\left(w_{0}-w_{j}\right)} \frac{1}{\rho}
$$

Case 3 If relaxation due to centrifugal distortion is small but not negligible (i.e. measurable), the relaxation rate is given by

$$
\begin{align*}
& \frac{1}{T_{1}}=\frac{4 \pi^{2} C_{0}^{2}}{\alpha\left(\omega_{0}-w_{j}\right)} \frac{\frac{\rho_{1}}{\rho}}{1+\frac{\rho_{\rho}^{2}}{\rho^{2}}}  \tag{5.21}\\
& +\frac{16 \pi^{2}}{45} \frac{C_{d}^{2}}{\alpha} \sum_{k} \frac{F_{k}}{\left[\left(w_{0}-\omega_{j}\right)+w_{k}\right]} \frac{\frac{\rho_{k}}{\rho}}{1+\frac{\rho_{k}^{2}}{\rho^{2}}}
\end{align*}
$$

with $\boldsymbol{\rho}_{\mathrm{k}}$ given by equation (5.16).
5.3 DATA ANALYSIS

The experimental data shown in figure 5.3 is the relaxation rate $1 / T_{1}$ as a function of density $\rho$. The simplest fit of the data is to assume that the relaxation rate is given by equation (5.17). Equation (5.17) can be subjected to a least squares fit using

$$
\begin{equation*}
\frac{T_{1}}{\rho}=a \frac{1}{\rho^{2}}+b \tag{5.22}
\end{equation*}
$$


where

$$
\begin{aligned}
& a=\frac{\alpha\left(w_{0}-w_{j}\right) \rho_{1}}{4 \pi^{2} C_{e f f}^{2}} \\
& b=\frac{\alpha\left(w_{0}-w_{j}\right)}{4 \pi^{2} C_{e f f}^{2} \rho_{1}}
\end{aligned}
$$

or

$$
\begin{aligned}
\rho_{1} & =\sqrt{\frac{a}{b}} \\
C_{e f f}^{2} & =\frac{\alpha\left(w_{o}-w_{j}\right)}{4 \pi^{2}} \frac{1}{\sqrt{a b}}
\end{aligned}
$$

A determination of $\bar{a}$ and $b$ will give values for $c_{e f f}^{2}$ and $\rho_{1}$. The most fruitful approach is to fit over a certain region and note the fit for the rest of the curve. Several plots were performed in this manner and the agreement in the regions outside the fit was very poor in each case. Figure 5.4 is an example of such a fit. The errors for the theoretical curves such as in figure 5.4 are very small because of the fact that the region fit contains many points. If $\mathrm{C}_{\mathrm{eff}}{ }^{2}$ and $\rho_{1}$ are both considered unknown, one can not fit the linear high density region because in terms of equation $(5.22), b \gg a / \rho^{2}$ and the least squares fit does not contain sufficient information. However, because

$C_{\text {eff }}{ }^{2}=137.60 \mathrm{kHz}^{2}$ is accurately known, we can use the fact portrayed in figure 5.5 that for $\rho>1$ amagats, $\frac{T_{1}}{\rho}$ is constant.
In terms of equation (5.17), thisimplies that $\frac{\rho_{1}^{2}}{\rho^{2}} \ll 1$ with the result that $\frac{T_{1}}{\rho}$ is given by $b$ in equation (5.22). The experimental result that

$$
\begin{equation*}
\frac{T_{1}}{\rho}=21.9 \pm 0.4 \frac{\mathrm{msec}}{\text { amagats }} \tag{5.23}
\end{equation*}
$$

uniquely determines $\rho_{1}$ with the result that equation (5.17) can now be plotted. This is done in figure 5.6. The theoretical value of $\rho_{1}$ agrees very well with the experimental value, but the theoretical curve gives far too strong relaxation in the region of the maximum. This high density fit of the data using equation (5.17) provides the logical conclusion that whatever interactions contribute to the relaxation at higher densities there are some effects which do not contribute as much in the region of the maximum.

Having eliminated equation (5.17) as a reasonable fit of the data (but none the less having gained considerable insight into the problem) the next step is to allow two correlation times. Using the accepted values of $C_{a}=10.4 \mathrm{kHz}$ and $C_{d}=18.2 \mathrm{kHz}$, equation (5.19) contains two unknowns; $\rho_{1}$ and $\rho_{12}^{\prime}$. This is the same as saying that the two correlation times are unknown (given by equations (5.18) and (5.20) ). Rather than randomly picking
figure $\quad 5.5$


values for these two parameters it is reasonable to fit the high density region under the assumption that $\rho>\rho_{1}, \rho_{12}^{\prime}$ and investigate the consequences in the area of the maximum. For the region $\rho>1$ amagats, equation (5.19) reduces to

$$
\begin{equation*}
\frac{1}{T_{1}}=\frac{4 \pi^{2}}{\alpha\left(w_{0}-w_{j}\right)}\left[C_{0}^{2} \rho_{1}+\frac{4}{45} C_{d}^{2} \rho_{12}^{\prime}\right] \frac{1}{\rho} \tag{5.24}
\end{equation*}
$$

Using equations (5.23) and (5.24), equation (5.19) can be written with only one variable. That is to say $\rho_{12}^{\prime}$ becomes a function of $\rho_{1}$. Equation (5.19) was then plotted for a range of values for $P_{1}$. It was absolutely impossible to fit the data adequately, for in all cases there is too strong relaxation in the region of the maximum. We do not give an example of such a fit because a typical fit looked something like figure 5.6. If we had decided to force a fit in the region of the maximum, we would certainly be left too weak relaxation in the region of $\rho>1$ amagats. We are left with the task of interpreting the data in terms of a measurable contribution to the relaxation rate by centrifugal distortion effects. We now want to analyse the data in terms of equation (5.13) whose independent variables are the $\tau_{k}$, or the identical equation (5.21) whose independent variable is $\rho$. Bloom and Ozier (private communication) maintain that one can calculate the $\boldsymbol{W}_{\mathrm{k}}$ and $\mathrm{F}_{\mathrm{k}}$ but that it is, perhaps, a lengthy and time consuming procedure. Certainly, the experimental data should be re-analysed when this is done, but we can arrive at reasonable qualitative results by approximating equation (5.13)
(or 5.21). First we assume that the spectral densities $j_{k}(\boldsymbol{W})$ associated with each peak frequency $W_{k}$ add in such a way at $\boldsymbol{W}_{0}-\boldsymbol{W}_{J}$ that we can approximate them by one spectral density which we denote by $j_{12}^{\prime}(W)$ peaked around $W_{12}^{\prime}$. That is to say, in terms of equation (5.13) (or 5.21), $F_{k}=1$ for $W_{k}=W_{12}^{\prime}$ and $F_{k}=0$ for all other $\omega_{k}$. Also, we assume that the angular frequency $W_{12}^{\prime}$ is sufficiently high that $\left(\omega_{12}^{\prime}\right)^{2} \approx\left[\left(w_{0}-w_{J}\right)\right.$ $\left.+W_{12}^{\prime}\right]^{2}$. Finally, we assume that both the $C_{a}$ term and the now single $C_{d}$ term may be analysed in terms of a single correlation time $\boldsymbol{\tau}_{1}$. With these approximations and assumptions, equation (5.13) becomes

$$
\begin{align*}
\frac{1}{T_{1}} & \approx \frac{4 \pi^{2} C_{0}^{2}}{\alpha} \frac{\tau_{1}}{1+\left(\omega_{0}-\omega_{j}\right)^{2} \tau_{1}^{2}} \\
& +\frac{16 \pi^{2} C_{d}^{2}}{45 \alpha} \frac{\tau_{1}}{1+\left(w_{12}^{\prime}\right)^{2} \tau_{1}^{2}} \tag{5.25}
\end{align*}
$$

with the variable parameters $\mathcal{T}_{1}$ and $\mathcal{W}_{12}^{\prime}$ and equation (5.21) becomes

$$
\begin{align*}
& \frac{1}{T_{1}} \approx \frac{4 \pi^{2} C_{0}^{2}}{\alpha\left(w_{0}-\omega_{j}\right)} \frac{\frac{\rho_{1}}{\rho}}{1+\frac{\rho_{1}^{2}}{\rho^{2}}} \\
& +\frac{16 \pi^{2} C_{0}^{2}}{45 \alpha \omega_{12}} \frac{\frac{\rho_{12}^{\prime}}{\rho}}{1+\frac{\left(\rho_{12}\right)^{2}}{\rho^{2}}} \tag{5.26}
\end{align*}
$$

with the variable parameters $\rho_{1}, \rho_{12}^{\prime}$ and $W_{12}^{\prime}$ and the restriction given by $\tau_{12}^{\prime}=\tau_{1}$ and equation (5.16)

$$
\begin{equation*}
\frac{\rho_{1}}{\rho_{12}^{\prime}}=-\frac{\left(w_{0}-w_{\mathrm{J}}\right)}{w_{12}^{\prime}} \tag{5.27}
\end{equation*}
$$

We now utilize another restriction; namely the slope of the high density region. For $\rho \gg \rho_{1}, \rho_{12}^{\prime}$, which is assumed to be satisfied for $\rho>1$ amagat, equation (5.26) becomes

$$
\frac{1}{T_{1}} \approx\left[\frac{4 \pi^{2} C_{o}^{2}}{\alpha\left(w_{0}-\omega_{j}\right)} \rho_{1}+\frac{16 \pi^{2} C_{d}^{2}}{45 \alpha w_{12}^{\prime}} \rho_{12}^{\prime}\right] \frac{1}{\rho}
$$

and using equation (5.27)

$$
\begin{aligned}
\frac{1}{T_{1}} & \approx \frac{4 \pi^{2}}{\alpha} \frac{\rho_{1}}{\left(w_{0}-w_{j}\right)}\left[C_{a}^{2}+\frac{4}{45} C_{d}^{2}\right] \frac{1}{\rho} \\
& \approx\left[\frac{4 \pi^{2}}{\alpha} \frac{C_{\mathrm{eff}}^{2}}{\left(w_{0}-\omega_{j}\right)} \rho_{1}\right] \frac{1}{\rho}
\end{aligned}
$$

Using the numerical value given in equation (5.23), we have the following result

$$
\begin{aligned}
& \rho_{1}=0.039 \text { amagats } \\
& \rho_{12}^{-}=\left(2.2 \times 10^{-10} \text { sec amagats) } W_{12}^{\prime}\right.
\end{aligned}
$$

Having determined all the parameters for the $C_{a}$ contribution to equation (5.26) we write equation (5.26) as

$$
\begin{equation*}
\frac{1}{T_{1}} \approx\left[\frac{1}{T}\right]_{C_{a}}+\left[\frac{1}{T}\right]_{C_{d}} \tag{5.29}
\end{equation*}
$$

and $\left[\begin{array}{c}1 \\ T_{1}\end{array}\right]_{C_{a}}$ is plotted in figure 5.7. As expected, the $C_{a}$ contribution to the relaxation rate is dominant and as proposed by figure 5.7 it is the only mechanism that is important at the maximum. We now have a reasonable explanation of why the theoretical curve for a single term fit shown in figure 5.6 gives too strong relaxation in the region of the maximum, namely the $C_{d}$ contribution to $C_{e f f}{ }^{2}$

is not present. Having accounted for the $C_{a}$ contribution to $1 / T_{1}$ we now plot

$$
\begin{equation*}
\left[\frac{1}{T}\right]_{\text {exp. }}-\left[\frac{1}{T}\right]_{C_{a}} \text { vs } \rho \tag{5.30}
\end{equation*}
$$

and attempt to interpret it in terms of

$$
\begin{align*}
{\left[\frac{1}{T}\right]_{C_{d}} } & \approx \frac{16 \pi^{2} C_{d}^{2}}{45 \alpha w_{12}^{\prime}} \frac{\rho_{12}^{\prime}}{1+\frac{\left(\rho_{12}^{\prime}\right)^{2}}{\rho^{2}}}  \tag{5.31}\\
\rho_{12}^{\prime} & =\left(2.2 \times 10^{-10} \mathrm{sec} \text { amagats }\right) \omega_{12}^{\prime} \tag{5.32}
\end{align*}
$$

The plot given by equation (5.30) is given in figure 5.8. The fact that the $C_{a}$ term is dominant accounts for the large apparent spread in points in figure 5.8. There is a maximum somewhere in the region between 0.1 and 0.4 amagats. If the low density results are reliable there seems to be another $C_{d}$ term which peaks at a density lower than we are presently able to observe. If we neglect the very low density results momentarily, we can analyse figure 5.8 in terms of equation (5.31) and (5.32).

Instead of randomly varying $\rho_{12}^{\prime}$ and $W_{12}^{\prime}$ with the restriction given by equation (5.32), we note that the best fit will occur when the maximum of equation (5.31) corresponds to a possible maximum of figure 5.8. To find where this might be, the

locus of maxima given by

$$
\begin{equation*}
\left[\frac{1}{T}\right]_{C_{d}, \max }=\frac{1}{2} \frac{16 \pi^{2} C_{d}^{2}}{45 \alpha w_{12}^{2}} \tag{5.33}
\end{equation*}
$$

and equation (5.32) is plotted in figure 5.9 as a function of $W_{12}^{\prime}$. We have omittod tho low density region in order to magnify the region of interest. Surprisingly enough, this loci of maxima do pass through possible candidate points for the experimental maxima. Highly quantitative conclusions are impossible because of the spread"in points, but the allowed range of $W_{12}^{\prime}$ can be narrowed by plotting equation (5.31) for a few reasonable values of $W_{12}^{\prime}$. This is done in figure 5.10. Noting that the top and bottom curves in figure 5.10 can probably be ruled out, it seems reasonably safe to say that $5\left(W_{0}-W_{J}\right)<W_{12}^{\prime}<8\left(W_{0}-W_{J}\right)$. If the low density effect is real, we can not say anything about it. The tremendous spread in points alone with the fact that a maximum has not been reached does not permit any way of putting limits on another $W_{k}$ for this effect. It should be noted, however, that if the effect is real, the limis set on $W_{12}^{\prime}$ will be slightly inodified because $F_{k}$ for $W_{12}^{\prime}$ will be slightly less than 1 . It would not be surprising, then, if the theoretical plots in figure 5.10 should be slightly lowered.



## CHAPTER VI

## SUMAREY AND SUGGESTIONS FOR FURTHER WORI

Using nuclear magnetic resonance pulse techniques, the spin-lattice relaxation time $T_{1}$ in gaseous methane has been measured as a function of density at constant temperature. The experimental results could not be interpreted in terms of the simplest theoretical framework which suggests that the relaxation rate $1 / T_{1}$ is a Lorentzian function of $1 / \rho$ where $\rho$ is the density. The "fine structure" which upsets the simple theoretical model has been attributed to a contribution to the relaxation rate by centrifugal distortion. In arriving at this conclusion several assumptions have been made. The important resuit is that a more rigorous approach would probably affect the results in a quantitative and not qualitative manner.

The qualitative conclusions of this thesis should be checked with other tetrahedral molecules and this is presently being done with $\mathrm{SiH}_{4}$ (silane). A study of the relaxation as a function of temperature would also be a useful experiment.

A rigorous theoretical treatment should involve a study of relaxation effects arising from the intranolecular dipolar interaction and spin diffusion in and out of the solenoid. spin symmetry effects, which have been completely neglected in the
conventional theory have been introduced in this thesis as the high frequency $W_{k}(k \neq 0)$ terms. Whereas a proper treatment of the intramolecular dipolar interaction and spin diffusion would probably not affect the conclusion concerning relaxation due to centrifugal distortion, spin symmetry effects are central to this conclusion and an expression for $1 / \mathbb{T}_{1}$ should be developed which includes the higher order distortion frequencies in the rotational states. In principle, one could calculate the spectral densities for all the distortion frequencies and as a result their contribution to the relaxation could be determined (i.e. their contribution at the Larmor frequency). The rigorous results would be similar to equation (5.13) in form with the $F_{k}$ 's and $W_{k}$ 's calculated exactly. In the analysis presented here we have assumed oniy one distortion frequency simply because of lack of information. A re-analysis of the experimental data on completion of these theoretical suggestions would certainly reveal fruitful information.

The most fruitful approach is, probably, to search for similar effects in other spherically symmetric gaseous molecules and to engage in a theoretical programme of some rigour in order to pinpoint the origin of the experimentally observed effect which we have attributed to centrifugal distortion of the molecule.

## APPENDIX

CIRCUIT DIAGRAMS

Some of the original components have been changed in a trivial fashion since they were first assembled in the early 1960's and some components have been recently added. Although some of the circuit diagrams may be found in their original form in previously published theses, the following diagrams represent the spectrometer in its entirety. Only the commercial equipment has been omitted. The upper case Arabic letters refer to the description of the apparatus in Chapter IV.


figure A 2
pulse width generator $F$ (or $G$ )

figure A3
mixer $H$

figure A4 gating pulses amplifier I

figure A5
10 mhz crystal oscillator J

figure A6 wide band amplifier $K$

figure A7
coherent gated oscillator

from gating pulses amplifier I

figure A9 gated power amplifier 0



figure A12 preamplifier $R$

figure A13 boxcar integrator $U$


figure A15 power supply for J,K and $P$

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