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AN N.M.R. INVESTIGATION OF THE REORIENTATION PROCESSES
OF SOME SMALL HYDROCARBON MOLECULES
IN THE SOLID STATE

A Thesis

presented by

Michael J. R. Hoch, M.Sc.

to the

University of St. Andrews

in application for the Degree

of Doctor of Philosophy.



Th 5120

DECLARATION

I hereby certify that this thesis has been composed by me, and is a record of work done by me, and has not previously been presented for a Higher Degree.

The research was carried out in the Physical Laboratory of St. Salvator's College, in the University of St. Andrews, under the supervision of Dr. F. A. Rushworth.

(Michael J. R. Hoch.)

CERTIFICATE

I certify that Michael J. R. Hoch, M.Sc., has spent nine terms at research work in the Physical Laboratory of St. Salvator's College, University of St. Andrews, under my direction, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and that he is qualified to submit the accompanying thesis in application for the Degree of Doctor of Philosophy.

Research Supervisor.

CAREER

Having graduated B.Sc. (Hons.) (1958) and M. Sc. (1960) in Physics (both with distinction) at the University of Natal, South Africa, I was awarded a Commonwealth Scholarship for research in experimental Physics for a higher Degree, tenable at the University of St. Andrews. I first matriculated in the University of St. Andrews in October 1960 and have subsequently been engaged in the research work reported in this thesis.

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1. INTRODUCTION

1. INTRODUCTION

Nuclear Magnetic Resonance has proved a powerful method for studying molecular reorientation processes in solids. By taking measurements over a wide range of temperatures it is in general possible to obtain information on both the rate and form of hindered molecular motion. It is also possible to estimate the magnitudes of the potential barriers hindering the various reorientation processes which may occur.

While solids consisting of small molecules may be expected to be of considerable interest in this connection, comparatively little or no information has been obtained for many of the smallest (Andrew, 1961). This may in some measure be ascribed to the fact that most of these substances are gaseous at room temperature which makes sample handling techniques slightly more difficult than for samples which are solids or liquids under similar conditions and also to the fact that, in many cases, the working temperature range needs to be extended to liquid hydrogen or liquid helium temperatures. This thesis is concerned with the investigation of some substances of this type.

The four substances which have been investigated are cyclopropane, cyclobutane, ethylene and n-butane. Considerable molecular reorientation has been found to occur well below the melting point in all of them. In cyclobutane and n-butane information has been obtained on motional changes associated with the solid state phase transitions which these substances exhibit. The importance of reorientation by quantum mechanical tunnelling through hindering potential barriers has been investigated for ethylene and n-butane.

2. THEORY

2. THEORY

2.1 Introduction

Since several excellent books and review articles have been published, e.g. Andrew (1955), Pake (1956), Abragam (1961), which treat the theory of nuclear magnetic resonance in bulk matter in detail, only the theory necessary for the interpretation of the experiments described in this thesis will be given. The reader is referred in particular to the recent comprehensive treatment of Abragam (1961), for further details.

In the experiments observations were made of the proton magnetic resonance in the samples, which were in polycrystalline form. The protons were effectively the only magnetic nuclei present. Both absorption spectra and spin-lattice relaxation time measurements were made using the continuous wave (C.W.) method.

2.2 Spectral Line-shapes and Line-widths

2.2.1 Rigid Lattice

In general the nuclear magnetic resonance absorption spectrum for a system of magnetic nuclei of spin I in a large external magnetic field H_0 has a finite line-width. If the nuclei have $I = \frac{1}{2}$ and are rigidly fixed in the lattice and provided H_0 is sufficiently homogeneous (and not extremely large) then the line-width is determined by the dipolar interactions between the nuclei. In certain cases the spectrum may be broadened and rendered asymmetrical by an anisotropic chemical shift due to the diamagnetic screening effects of the electronic environment.

(3)

This effect is unimportant for protons in fields of order 10^4 G. as used in these experiments (Andrew 1963).

For a system of spins in a magnetic field H_0 (along the z axis) the Hamiltonian may be written,

$$\mathcal{H} = -\gamma\hbar H_0 \sum_j I_{j,z} + \sum_{j>k} \left[\frac{\hbar^2 \gamma^2}{r_{jk}^3} \left[\bar{I}_j \cdot \bar{I}_k - 3(\bar{I}_j \cdot \bar{r}_{jk})(\bar{I}_k \cdot \bar{r}_{jk}) \right] \right] \quad (2.1)$$

where

γ is the gyromagnetic ratio

r_{jk} is the internuclear distance

and

\bar{r}_{jk} is the corresponding unit vector

The first term in \mathcal{H} represents the interaction of the nuclei with the external field and is usually termed the Zeeman Hamiltonian while the second term is the perturbing Hamiltonian due to the dipolar interaction.

It is only possible to obtain the perturbed energy eigenvalues in certain relatively simple cases when the nuclei occur in small fairly isolated groups. The two spin system was treated by Pake (1948). As is usual in two spin problems the unperturbed states of the Zeeman Hamiltonian may be divided into anti-symmetric singlet and symmetric triplet states. It is only necessary to consider the triplet states as transitions between singlet and triplet states are highly forbidden. The perturbed energy eigenstates may then be found in first order using the part of the expanded dipolar Hamiltonian which is diagonal in the Zeeman representation. For spin $\frac{1}{2}$ nuclei a pair of lines is predicted given by

(4)

$$h\nu = \gamma\hbar H_0 \pm \frac{3}{4} \frac{\gamma\hbar^2}{r^3} (1 - 3 \cos^2 \theta) \quad (2.2)$$

where θ is the angle the internuclear vector r makes with the applied field H_0 .

Pake (1948) verified this expression in a study of crystal hydrates in which the protons in the water molecules approximate to isolated pairs. For a polycrystalline sample of this type the absorption spectrum is given by the sum of a large number of doublets corresponding to different orientations of the internuclear vectors and is a double humped curve with the separation between the peaks approximately given by $\frac{3}{2} \cdot \frac{\gamma\hbar}{r^3}$. The broadening due to the small interactions between adjacent pairs may be allowed for in a semi-quantitative way.

It is not actually necessary that the two protons be rigidly fixed in the lattice as transitions are only considered between the symmetric triplet levels and thus an interchange of the protons will not affect the spectrum of isolated pairs. It is interesting that recent measurements by Holcomb and Pedersen (1962) on a single crystal of gypsum (one of the crystal species used by Pake in verifying equation (2.2)), have revealed that the proton pairs are actually executing 180° flip reorientations at a rate greater than 10^7 c/s, at room temperature. This type of behaviour is thought to be general in hydrated crystals. The only effect on the absorption spectrum is a reduction in the small interaction between adjacent pairs. The two spin problem has been discussed in some detail as it has important bearings on some of the experimental results to be described.

The perturbation problem has been solved for certain cases of three identical nuclei by Andrew and Bersohn (1950) and Andrew and Finch (1957) and also for certain cases of four identical nuclei by Itoh et.al. (1953) and Bersohn and Gutowsky (1954). It would be prohibitively tedious, and also less rewarding, to solve the problem for larger spin arrays as the groups are generally not in fact isolated and the detail of the theoretical spectrum is smeared out by the interactions between neighbouring groups.

Van Vleck (1948) has, however, obtained rigorous expressions for the mean square width or second moment and also for the fourth moment of the absorption spectrum in the general case, in a way which does not involve finding the eigenstates of the total Hamiltonian.

If the absorption spectrum is described by a normalized shape function $g(\nu - \nu_R)$ centred at ν_R then the n'th moment about the centre is defined as

$$M_n = \int_{-\infty}^{\infty} (\nu - \nu_R)^n g(\nu - \nu_R) d(\nu - \nu_R) \quad (2.3)$$

In terms of field strength rather than frequency this becomes

$$M_n = \int_{-\infty}^{\infty} h^n g(h) dh \quad (2.4)$$

where

$$\begin{aligned} h &= H_0 - H_R \\ &= \frac{2\pi}{\gamma} (\nu - \nu_R) \end{aligned}$$

The theoretical calculation makes use of a diagonal sum method. As mentioned in the two spin case only the secular (or diagonal) part of the perturbation Hamiltonian is retained as the non-secular part

gives rise to unobservably weak satellite lines at multiples of the Larmor frequency, which must be ignored.

In practice, the second moment is of most value in studying problems of structure and molecular motion. For a single crystal containing only one type of magnetic nucleus the result obtained in units of magnetic field squared is

$$M_2 = \frac{3}{2} I(I + 1) \gamma^2 \hbar^2 N^{-1} \sum_{j>k} (3 \cos^2 \theta_{jk} - 1)^2 r_{jk}^{-6} \quad (2.5)$$

where N is the number of nuclei over which the sum is taken. For a polycrystalline sample the angular factor must be averaged over all directions. This gives

$$M_2 = \frac{6}{5} I(I + 1) \gamma^2 \hbar^2 N^{-1} \sum_{j>k} r_{jk}^{-6} \quad (2.6)$$

These expressions have received ample experimental verification and have been of considerable use in structural determinations.

The evaluation of the theoretical mean square width for nuclei in a molecular crystal is conveniently split into two parts. The so-called intra-molecular contribution (denoted M_2') corresponds to interactions between nuclei within a single molecule while the inter-molecular contribution (M_2'') corresponds to interactions between nuclei in neighbouring molecules. In evaluating the inter-molecular contribution it is necessary to sum over all the nuclei in each unit cell and in neighbouring unit cells. Fortunately these sums converge fairly rapidly and symmetry within the unit cell often further reduces the computation involved.

A weakness of the method of moments is that a fairly large

contribution to the experimental value comes from the tails of the absorption spectra, where part of the signal may be lost in the noise. For this reason the signal to noise ratio should always be as high as possible.

2.2.2 Motion of the Spins in the Lattice

As mentioned in Section (1) it is often found that molecular motion occurs in solids. Before discussing how such motion affects the dipolar interactions, and hence the absorption spectrum, brief mention will be made of the types of motion which can occur.

If a molecule possesses an n-fold axis of symmetry its motion about this axis in the lattice will be restricted by an n-fold periodic potential barrier. Such molecules will execute torsional oscillations about the symmetry axis, either in the ground state or in various excited torsional states. These oscillations will be of high frequency ($>10^{12}$ c/s) and may be detected by Infra-red or Raman spectroscopy methods. The molecules may also reorient about the symmetry axis either by tunnelling through the potential barrier, or by being excited into torsional states above the barrier when classical rotation can occur. The latter process may clearly be expected to be temperature activated, and the reorientation rate may be expected to vary over a wide range of frequencies. If the molecules possess more than one symmetry axis then combinations of reorientation processes may occur, while if they possess no symmetry axis then only classical reorientation processes will be

important. Finally it is possible for self-diffusion of globular molecules through the lattice to take place (e.g. Andrew, 1961). This process is very often found when the molecules exhibit isotropic reorientation about their centres of mass.

Returning to the discussion of the Absorption Spectrum it is clear that when molecular motion is occurring in the lattice the internuclear vectors vary in direction and, in certain cases, in magnitude with time. For a rigid molecule which is reorienting, the intra-molecular internuclear vectors vary only in direction. As the angle θ_{jk} in equation (2.5) for the mean square width is a function of time it appears necessary to replace the term $(3 \cos^2 \theta_{jk} - 1)^2$ by its mean value over the motion. Following this line of reasoning Gutowsky and Pake (1950) have shown that provided the molecules are reorienting sufficiently rapidly about an axis of n -fold symmetry where $n \geq 3$, then for a polycrystalline specimen every term in the intra-molecular sum in equation (2.6) should be multiplied by a reduction factor

$$f_3 = \left[\frac{1}{2} (3 \cos^2 \gamma_{jk} - 1) \right]^2 \quad (2.7)$$

where γ_{jk} is the angle the internuclear vector makes with the axis of reorientation. This corresponds to ignoring the time dependent terms now involved in the factor $(3 \cos^2 \theta_{jk} - 1)^2$ for each nuclear pair, since their mean value is zero.

It can be shown on quite general grounds (e.g. Abragam, 1961, p 453) that the second moment should be invariant irrespective of any motion which may occur in the lattice while the higher moments should be

increased. The motion thus alters the shape of the absorption spectrum giving rise to a narrowed central portion and extended tails. Experimental evidence bearing on this point has been obtained by Andrew, Bradbury and Eades (1958, 1959) in which a single crystal of sodium chloride was macroscopically rotated at various uniform rates about a suitable axis. A narrowed central line flanked by sidebands was observed. When the contributions due to the sidebands were included, the second moment was found to be the same as for the stationary crystal. As the rate of rotation was increased the sidebands moved further away from the line centre and their intensity became correspondingly diminished. The uniform rotation makes the dipolar Hamiltonian periodic and this may be regarded as frequency-modulating the Larmor frequency.

For molecules reorienting in a crystal the rotation is of a random nature and the resultant sidebands are distributed over a range of frequencies. If the motion is sufficiently rapid the sidebands (tails) become unobservably weak and only the narrowed central portion of the line is recorded.

In such a case the reduction factor (2.7) may be used in the theoretical calculations of the second moment and this often enables the form of molecular motion to be elucidated. The neglect of the time-dependent terms in the dipolar Hamiltonian is similar in a sense to the truncation of the Hamiltonian employed in the deduction of the expression for the second moment. Both procedures eliminate from the

second moment expression, contributions which are experimentally unobservable (Abragam, 1961, p 453).

The criterion of the motion being sufficiently rapid to render only the narrow central portion of the line observable is that the rate of molecular reorientation must be much larger than the dipolar interaction expressed in frequency units. Typically for protons this means that the reorientation rate must be greater than about 10^4 to 10^5 c/s. When studying the second moment as a function of temperature in any substance, it is clearly only possible to make reliable deductions from values obtained well away from temperature regions in which any line-narrowing occurs.

This method does not distinguish between free rotation or discontinuous random motion about an axis of n -fold symmetry for $n \geq 3$. (Clearly, also, the reorientation energy must diffuse among the molecules at a rate much greater than the mean reorientation frequency so that all the molecules effectively participate in the process).

In the case of reorientation about a two-fold axis the reduction factor (2.7) does not apply (unless free classical rotation is occurring). For a polycrystalline sample the correct reduction factor in this case is, (Eades, 1952)

$$f_2 = (1 - 3 \sin^2 \gamma_{jk} \cos^2 \gamma_{jk}) \quad (2.8)$$

When γ_{jk} , the angle between the axis of reorientation and the inter-nuclear vector, is 0 or $\pi/2$ no reduction in the contribution to the intra-molecular second moment is predicted. The fact that no reduction

occurs in the latter case because of the symmetry properties of the two spin triplet state, was mentioned in Section 2.2.1.

The reduction factors (2.7) and (2.8) may only be used to calculate the reduction in the intra-molecular contribution to the second moment. In evaluating the motionally reduced inter-molecular contribution when both θ_{jk} and r_{jk} in equation (2.5) are time-dependent, it is necessary to use the more general expression deduced by Andrew and Eades (1953a) and quoted in Appendix (1). In applying this expression it is usually necessary to make certain approximations because of the amount of computation involved.

Finally in this section the effects of torsional oscillations on the second moment of the absorption spectrum will be mentioned. These effects may only be expected to be significant when the amplitude of the torsional oscillation is relatively large as in cases in which the moment of inertia of the oscillating molecule or group is small.

This problem has been treated by Andrew (1950) and Das (1957). It is necessary to average the angular factor in equation (2.5) over the torsional motion. Considering only the contribution due to dipolar interactions within the oscillating group and assuming that the axis of torsion is perpendicular to the internuclear vectors Das (1957) obtains the following expression for the reduction factor in a polycrystalline solid

$$f = 1 - \frac{112}{9} \frac{\langle V \rangle}{n^2 V_0} \quad (2.9)$$

where V_0 is the height of the n -fold potential barrier and $\langle V \rangle$ is the

average potential energy of the oscillating group.

It is possible to estimate $\langle V \rangle$ using an harmonic oscillator approximation. Further mention of the reduction in second moment due to this type of motion is given in Section (8) in the discussion of the results obtained with ethylene, the only case in the present work in which this correction was necessary.

2.3 Spin-Lattice Relaxation when motion of the spins is occurring

Spin-lattice relaxation is the term used to describe the process by which energy is exchanged between the nuclear spin system and the lattice, tending to bring them into thermal equilibrium. In this process it is necessary for a lattice mechanism to induce transitions between the nuclear magnetic energy levels. It can be readily shown (e.g. Andrew 1955) that the isolated spin system then exponentially approaches thermal equilibrium with the lattice with a time constant $\frac{1}{2W}$, where W is the average transition probability. This time constant is called the spin-lattice relaxation time T_1 .

In non-metallic fluids the fluctuating local fields caused by the Brownian motion of the molecules are found to be dominant in the relaxation mechanism. The theory of spin-lattice relaxation in fluids was developed by Bloembergen, Purcell and Pound (B.P.P.) (1948) who made use of the theory of random functions. It has been slightly modified by Kubo and Tomita (1954) and Solomon (1955). The theory has been found to be applicable in many solids in which molecular motion is

occurring, especially in cases in which the interactions responsible for the relaxation process may be considered to be confined to a pair or other small group of nuclei.

In the B.P.P. theory the Fourier intensities of the nuclear position functions are calculated in terms of a correlation time for the molecular motion. This correlation time τ_c may be regarded as the time required for the nuclear position coordinates to change significantly (and is of the order of time it takes for a molecule to turn through a radian). Hence the total probability of induced transitions in the spin system by this mechanism may be obtained and this gives the spin-lattice relaxation time directly, as mentioned above. In the treatment it is necessary to consider both single transitions at ω_0 , the nuclear Larmor frequency and double transitions at $2\omega_0$ which are made possible by the motion. It is the off-diagonal part of the dipolar Hamiltonian which is responsible for inducing the transitions.

The result obtained in terms of the correlation time τ_c is

$$\frac{1}{T_1} = C_1 \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \quad (2.10)$$

C_1 is a constant which, for the case of random rotational motion, was found by B.P.P. (1948) to be given by

$$C_1 = \frac{2}{5} \gamma^4 \hbar^2 I(I+1) \sum_j b_j^{-6} \quad (2.11)$$

where b_j is the distance between a typical nucleus and neighbouring nuclei in a molecule. The intermolecular contributions to the relaxation process are often much smaller than the intra-molecular contributions and

may be ignored except when molecular diffusion is occurring. It is not strictly correct to assume that a single correlation time applies to different nuclear pairs, but this is done for simplicity. That a single correlation time may be used to describe a large collection of molecules is in any case a simplifying assumption, but agreement with experiment has been satisfactory. For a proton pair executing random rotational motion (2.11) reduces to

$$C_1 = \frac{3}{10} \frac{\gamma^4 \hbar^2}{b^6} \quad (2.12)$$

where b is the interproton distance

Considering equation (2.10) two extremes may be distinguished.

When the correlation time of the motion is short and $\omega_0^2 \tau_c^2 \ll 1$ then (2.10) reduces to

$$\frac{1}{T_1} = 5 C_1 \tau_c \quad (2.13)$$

When the correlation time is long and $\omega_0^2 \tau_c^2 \gg 1$ (2.10) may be written

$$\frac{1}{T_1} = \frac{2 C_1}{\omega_0^2 \tau_c} \quad (2.14)$$

A minimum value for T_1 is predicted when $\omega_0 \tau_c \doteq 0.61$.

When deducing correlation times from measured relaxation times it is sometimes possible to use the value of C_1 given by (2.11), but it is preferable to estimate C_1 from the experimentally determined value of $(T_1)_{\min.}$, if a minimum is observed.

Finally it may be mentioned that when the lattice is effectively rigid T_1 is usually very long. The relaxation process in such a system has been shown to be primarily due to small traces of paramagnetic impurity (Bloembergen, 1949).

2.4 Saturation Effects

So far in this discussion the effect of the perturbing r.f. field at, or near, the nuclear Larmor frequency has not been considered beyond that it is the means by which information about the spin system may be obtained. In making measurements using the C.W. method it is desirable in general to keep the r.f. field fairly small so that the spin system is disturbed as little as possible.

A spin temperature may be defined in terms of the relative populations of the energy levels of the system. Taking a slightly simplified view of the situation the absorption of energy from the r.f. field results in a change in these populations and a consequent rise in the spin temperature. Equilibrium is reached, with the spin system at some temperature above the lattice temperature, when the rate of absorption of energy from the r.f. field is equal to the rate at which energy is dissipated to the lattice by the spin-lattice relaxation mechanism. Strictly the concept of spin temperature is only really valid in the absence of the r.f. field inducing transitions and when no transverse components of magnetization exist (Abragam, 1961, p 134). The simplified picture indicates that saturation effects will occur.

Statistically the spin system may be described by a density matrix. With no r.f. field present the diagonal elements correspond to the populations of the various energy levels. The r.f. field then has the effect of giving the magnetization transverse components at right angles to H_0 and there are correspondingly off-diagonal elements in the density

matrix. On switching off the r.f. field the off-diagonal elements decay with a characteristic time T_2 called the spin-spin relaxation time, about which a little more will be said later in this section. The diagonal elements assume the values given by the Boltzmann distribution with characteristic time T_1 .

For a system of effectively isolated spins each spin is an element of a statistical ensemble describable by a $(2I + 1) \times (2I + 1)$ density matrix. When the spins are all tightly coupled together as in a rigid solid it is necessary to treat the whole system of N spins collectively as an element of a statistical ensemble described by a $(2I + 1)^N \times (2I + 1)^N$ density matrix. As may be expected the latter case is considerably more difficult to deal with than the former. A useful concept in considering the effects of r.f. fields in a tightly coupled spin-system is that of spin temperature in the rotating frame introduced by Redfield (1955). It is outside the scope of the present discussion to pursue this topic however.

For simplicity the spin system will be regarded as approximating to a collection of individual spins with negligible interactions. If a magnetic field H_0 is applied along the z -direction then in the absence of an r.f. field the sample magnetization is

$$M_z = M_0 = \chi_0 H_0 \quad (2.15)$$

where χ_0 is the static nuclear susceptibility

$$M_x = M_y = 0$$

When an r.f. field of amplitude H_1 is applied perpendicular to H_0 at,

or very near, the Larmor frequency, then in the equilibrium state mentioned above M_z will have a value different from M_0 and transverse components of magnetization will exist.

By considering the energy level populations and the probability of induced transitions by the r.f. field and considering also the competing process of spin-lattice relaxation the following relationship may be deduced,

$$\frac{M_z}{M_0} = \frac{1}{1 + 2PT_1} \quad (2.16)$$

where P is the probability per unit time for r.f. induced transitions. From radiation theory the following expression is obtained for P ,

$$P = \frac{\pi}{2} \gamma^2 H_1^2 f(\omega) \quad (2.17)$$

where $f(\omega)$ is the normalized line shape function. Clearly for large H_1 the ratio $\frac{M_z}{M_0}$ will become quite small.

The term on the right of (2.16) is termed the saturation factor Z

$$Z = 1 + \gamma^2 H_1^2 T_1 \pi f(\omega) \quad (2.18)$$

The quantity $\pi f(\omega_0)$ is defined as the spin-spin interaction time T_2 and is a measure of the lifetime of a nuclear spin state.

This saturation effect affords a means of comparing spin-lattice relaxation times in a sample, at different temperatures. While there is no real justification for applying these relations to solids in which comparatively tight coupling of the spins exists, the results obtained experimentally using this method are usually in quite fair agreement with values obtained directly using transient methods, (Abragam, 1961; p 453, Powles, 1963).

3. EXPERIMENTAL APPARATUS AND TECHNIQUES

3. EXPERIMENTAL APPARATUS AND TECHNIQUES

3.1 The N.M.R. Spectrometer

The equipment used to study the proton magnetic resonance was of the conventional C.W. type using an r.f. bridge. A block diagram of this equipment is given in Figure 1.

The permanent magnet used was designed for broad line n.m.r. work in solids and has been described by Andrew and Rushworth (1955). The pole face diameter is eight inches and the gap two inches. The field for the experiments described in this thesis was 5,300 Gauss and at best the homogeneity was approximately 0.25 Gauss/cm^3 . The proton resonance frequency in this field is 22.6 Mc/s. In order to sweep the magnetic field by up to 40 Gauss, current from a bank of storage batteries was passed through the original magnetizing coils. This current could be slowly and continuously varied by a motor driven potentiometer. Modulation of the field by up to several gauss was accomplished by means of two coils, each consisting of 1,000 turns of 22 SWG copper wire wound on ebonite formers, which were clamped around the pole caps. The modulation current was supplied by a special 25 c/s audio-oscillator through a suitable power amplifier designed to give minimum distortion and which was capable of delivering 15 watts at 25 c/s into the modulation coils (Eades, 1952).

Two commercial electronic units apart from H.T. and L.T. power supplies were used in the equipment, namely the Signal Generator and the Receiver. The Signal Generator was an Airmec type 201 unit with an

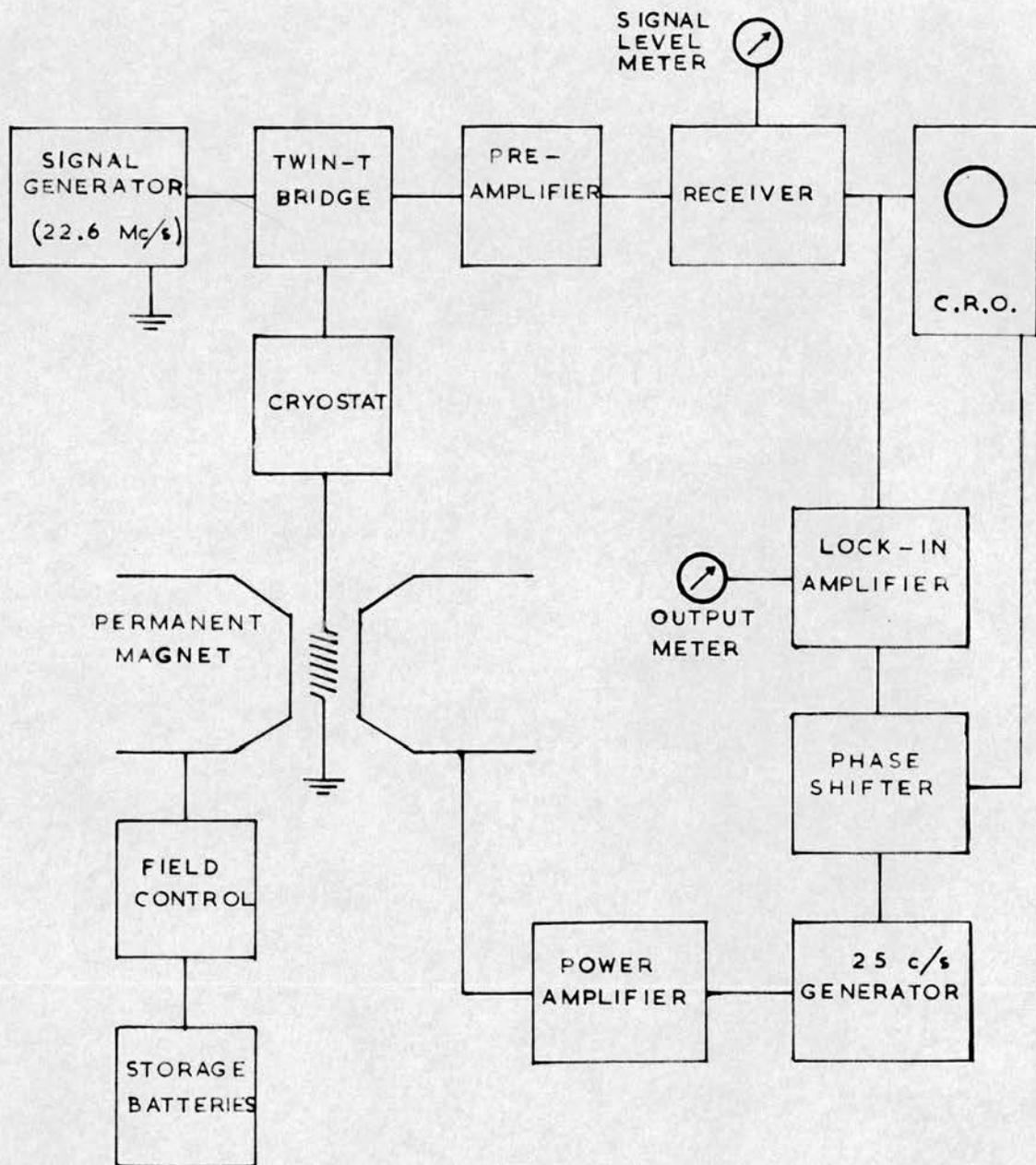


FIGURE 1.

output level continuously variable from 1 μ V to 1.1V R.M.S. and an output impedance of 75 ohms. (This instrument has internal frequency calibration facilities). The Receiver, an Eddystone "680" Communications model, was used to amplify and detect the signal. An external meter was used to monitor the second detector current and this gave an indication of the carrier level. The bandwidth used was 10 Kc/s (24 db down) which was sufficient for oscilloscope display. Well smoothed external H.T. and L.T. power supplies were used to run both these units to eliminate any spurious 50 c/s modulation effects. Solartron AS517 High stability H.T. power supplies and Advance (DC2) 6V D.C. supplies were used for this purpose.

The r.f. bridge was of the twin-T type (Anderson, 1949) and was housed in a rigid tinned copper box. The use of high quality components, internal shielding and overall rigidity of construction gave very satisfactory stability in operation. This type of bridge has the advantage of orthogonality of adjustment for resistive and reactive balance. In practice the bridge was adjusted for exact phase balance and roughly a 40 db down amplitude balance so that the absorption spectrum could be recorded. The coil containing the resonant nuclei in the magnet gap was connected to the rest of the bridge by a suitable co-axial lead (Section 3.2).

In order to improve the signal to noise ratio the Receiver was preceded by a low noise pre-amplifier. A cascode pre-amplifier employing a Mullard E88 cc special quality twin-triode was constructed

for this purpose. It was housed in a shielded section of the copper box containing the twin-T bridge.

The circuit was a modification of the original cascode circuit proposed by Wallman, MacNee, and Gadsen (1948) and employed a grounded cathode stage D.C. coupled to a grounded grid stage. Transformer coupling of input and output was used and tuning of these circuits to the centre frequency ensured a narrow bandwidth and high gain. The turns ratio of the input transformer was chosen to transform the source conductance to near the optimum value for low noise figure.

The E88 cc has a high mutual conductance and hence a low equivalent noise resistance R_{eq} . Under operating conditions R_{eq} was approximately 300 ohms and this ensured a good noise figure.

The noise figure of the pre-amplifier was measured using a Marconi type TF 987/1 Noise Generator. This instrument is calibrated directly in noise factor and the measurement was made using the Eddystone receiver second detector current as a means of comparing noise power after it had been verified, by varying the Noise Generator output, that this procedure was sufficiently linear for the purpose. The input tuned circuit was tuned to a slightly lower frequency than the frequency at which measurements were made, for minimum noise factor. The best value of noise factor obtained for the r.f. system was approximately 1.5 db which was very satisfactory.

It is important that matching between bridge output and pre-amplifier be as near optimum as possible. The input stage of the cascode

was designed to achieve this and empirical adjustment of the bridge component values was also carried out to give best results.

After the cascode stage another stage of r.f. amplification was employed before the signal was fed into the Eddystone receiver. This circuit used a Mullard EF 54 aligned grid pentode with tuned input and output circuits.

The output of the receiver was displayed on an oscilloscope and strong narrow absorption lines could be observed in this way using a modulation amplitude several times larger than the line-width.

For broad lines which were lost in the noise in the oscilloscope display the phase sensitive detector (or lock-in amplifier) was used. This method allows the use of bandwidths of a fraction of a cycle per second. The circuit employed was essentially the same as the one used by Bloembergen (1948) based on the design of Dicke (1946) and consisted of a narrow band amplifier, followed by a balanced mixer stage in which the signal was mixed with a reference signal derived from the 25 c/s modulation oscillator. The output stage was a balanced D.C. amplifier driving an Evershed recording microammeter. In recording spectra the field modulation amplitude was made much smaller than the absorption line-width while the field itself was slowly swept through resonance so that the first derivative of the absorption curve was obtained. The effective bandwidth B was determined by the time-constant τ of the circuits between the mixer stage and the output stage where $B \sim \frac{1}{\tau}$. By switching various R C circuits four values of τ were available and these

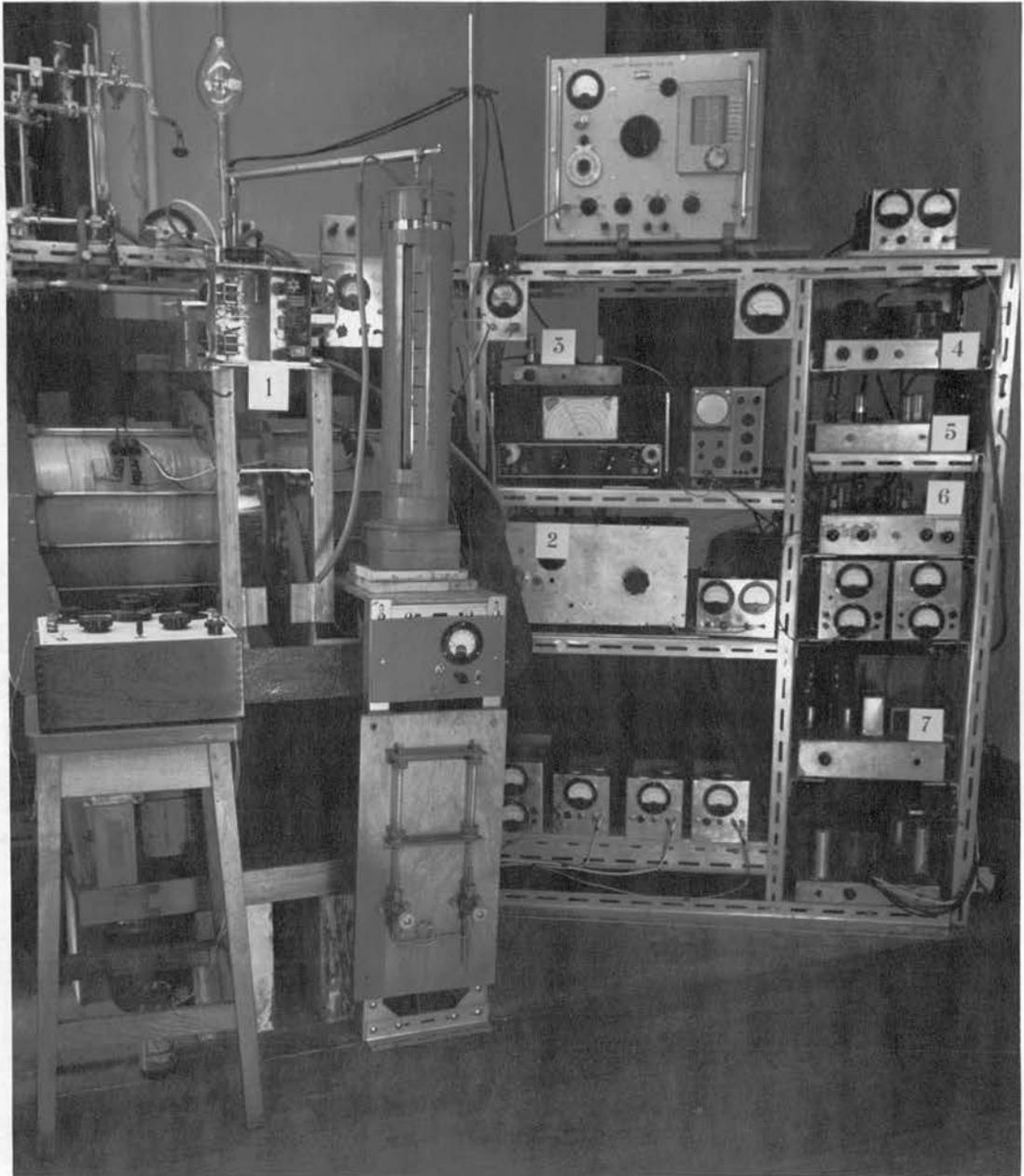


FIGURE 2.

were 0.5, 3, 5 and 8 seconds. A cathode follower stage for matching purposes was used between the Eddystone Receiver and the Lock-in amplifier input.

The field sweep current was measured using a millivoltmeter shunted by a 0.2 ohm resistance. Calibration of this meter in terms of field variation was accomplished by observing a strong proton signal on the oscilloscope screen and suitably altering the Signal Generator frequency as the field was varied in discrete steps so as to keep the position of the signal on the screen fixed. The frequency variation was measured with sufficient accuracy with a BC-221 frequency meter, which was lightly coupled into the r.f. system. Hence it was possible to obtain the field variation in gauss per scale division.

Calibration of the modulation current meter, in terms of modulation amplitude in gauss, was then possible using the field sweep calibration.

In Figures 2 and 3 photographs of the experimental arrangement are shown. In Figure 2 the numbered units are as follows

- (1) Twin-T bridge and cascode pre-amplifier unit.
- (2) EF 54 pre-amplifier.
- (3) A.F. cathode follower matching unit.
- (4) Phasing and transforming unit supplying X-sweep for C.R.O.
- (5) 25 c/s generator.
- (6) Lock-in amplifier.
- (7) Power amplifier for field modulation.

The other electronic units, with the exception of the Signal

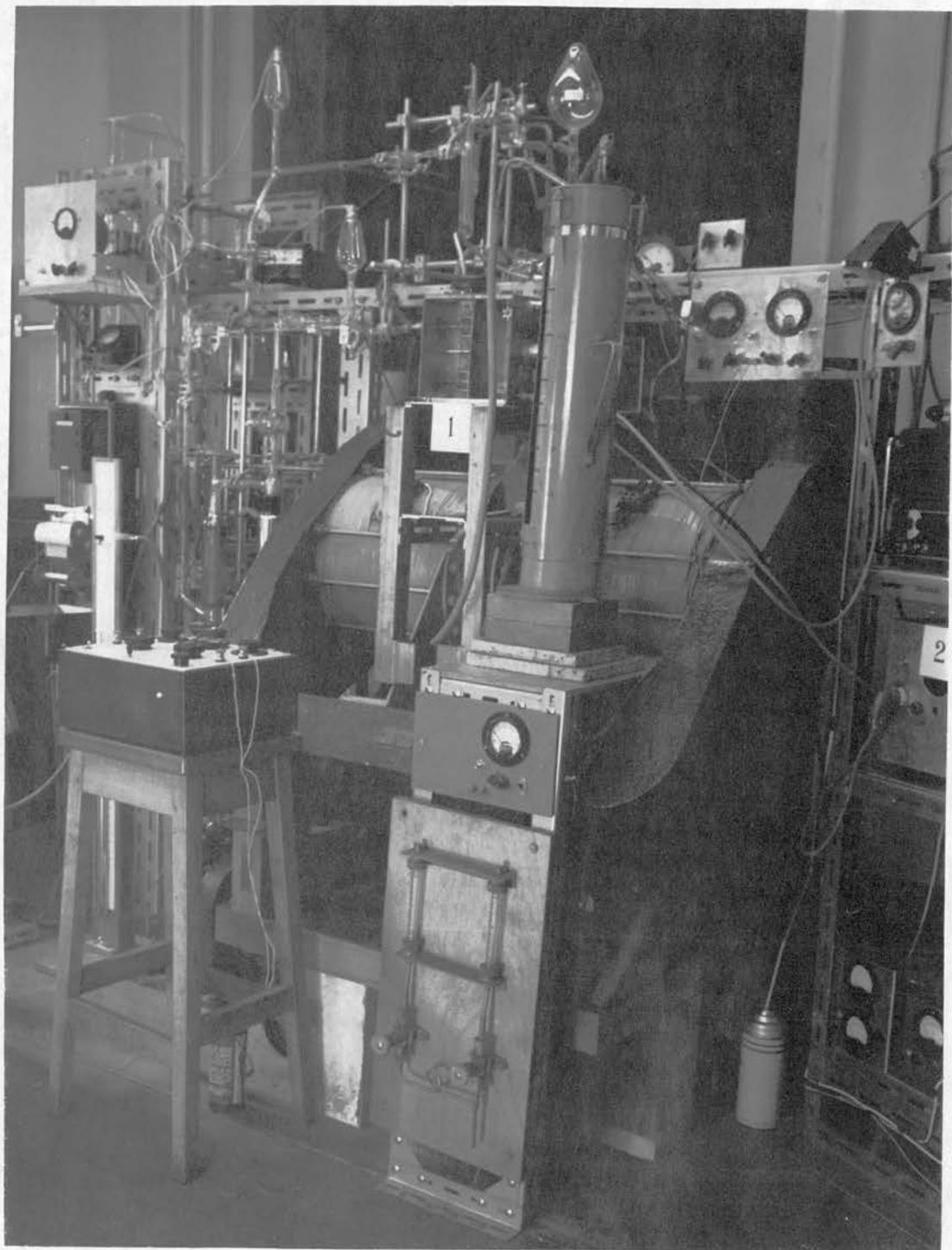


FIGURE 3.

Generator and Receiver, are the various power supplies. In Figure 3 the pen-recorder can be seen together with the vacuum system of which further mention will be made in Section (5.1). The cryostat and transfer vessel for liquid hydrogen, which can be seen in the photographs, are described in Section (3.2).

The overall performance of the spectrometer was satisfactory with adequate signal-to-noise ratio for all the samples investigated. A discussion of the theoretical signal-to-noise ratio with the aid of the Bloch equations (e.g. Abregam, 1961, p 82) will thus not be given. The usual precautions of using a resonance coil with as high a Q as possible and a reasonable sample filling factor (0.54) were taken. The fact that all the measurements were made at temperatures below 200°K was an advantage due to the enhanced population difference between energy levels.

3.2 Cryostat

The cryostat used in most of the work was designed to operate over the temperature interval 20°-200°K, using either liquid hydrogen or liquid nitrogen as coolant. Figure 4 is a diagram illustrating constructional details, while figure 5 is a photograph showing a sample (n-butane) in position in the cryostat.

Referring to figure 4 the resonance coil (1), which consisted of twelve turns of 18 Swg copper wire, was rigidly mounted inside a copper isothermal shield (2) with wall thickness 0.5 mm. (In figure 5 the

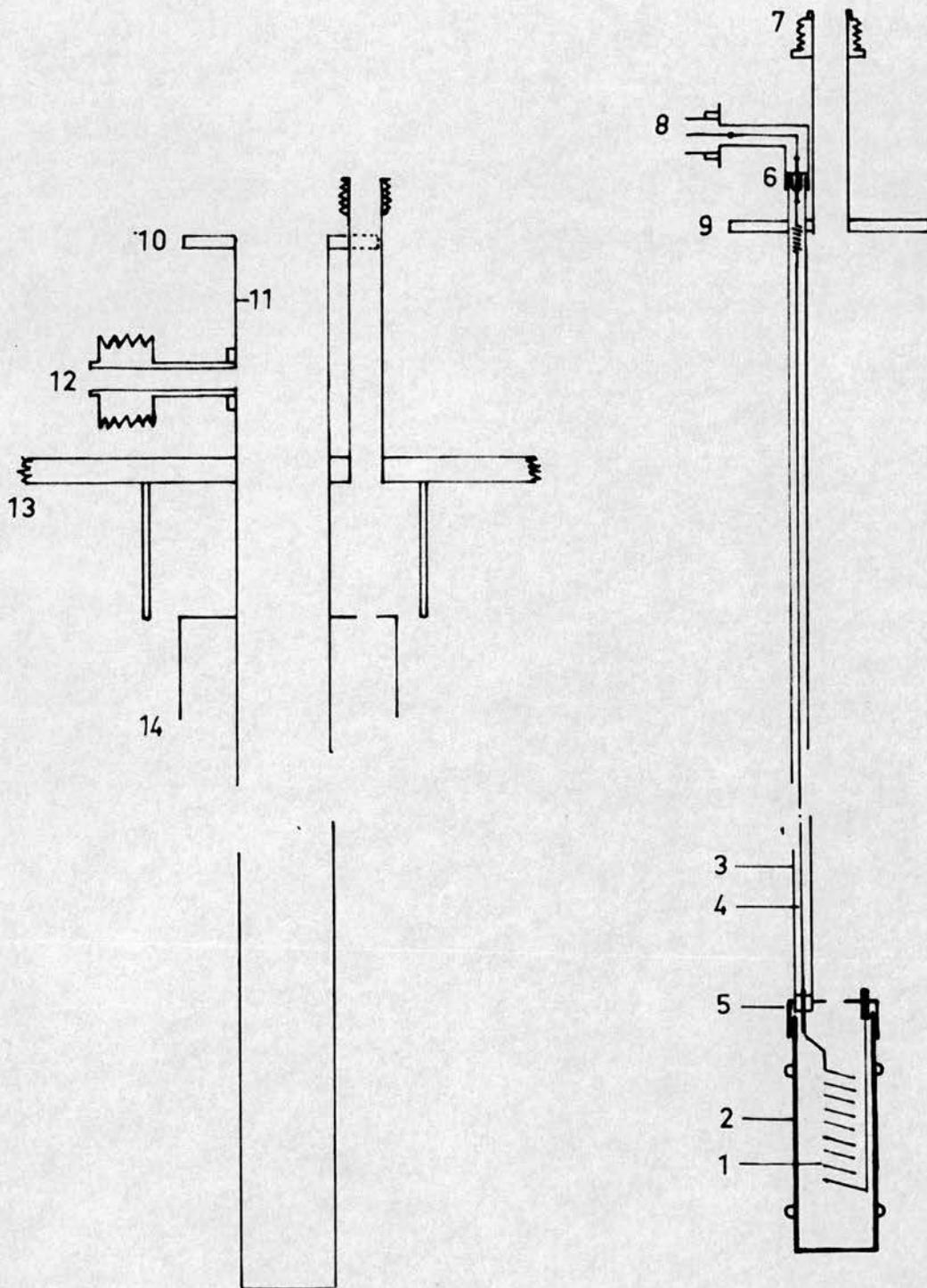


FIGURE 4.

lower part of this shield has been removed for clarity). A heater of 32 Swg Eureka was non-inductively wound to cover most of the exterior surface of the shield. R.f. power was fed to the resonance coil through a coaxial lead consisting of an outer conductor of 5 mm cupro-nickel tubing (3) and an inner conductor of 28 Swg copper wire (4), which was fixed to a Kovar to glass seal (6), at the upper end, and a teflon plug (5), at the lower end. The wire was kept under tension by a small phosphor bronze spring near the top.

Connection to the twin-T bridge was made by means of the coaxial socket (8) and a short length of 75 ohm coaxial cable.

The 5 mm cupro-nickel tube served as the main support for the shield and sample assembly. Short lengths of cupro-nickel wire were used to connect the resonance coil to the coaxial conductors, to improve the thermal isolation of the sample.

For samples which were gaseous at N.T.P. a pyrex flask above the top flange (9) served as the main storage space. From the flask a 10 mm pyrex tube led down into the cryostat through a vacuum tight O-ring coupling (7) and terminated in a tip which fitted the resonance coil and into which the sample could be condensed.

The assembly below the top flange (9) could be contained in the thin walled stainless steel jacket (11); the flanges (9) and (10) being coupled together with an O-ring. This enclosure could be evacuated through the pumping line (12) and surrounded by coolant.

To ensure rigidity and thermal insulation small nylon guides

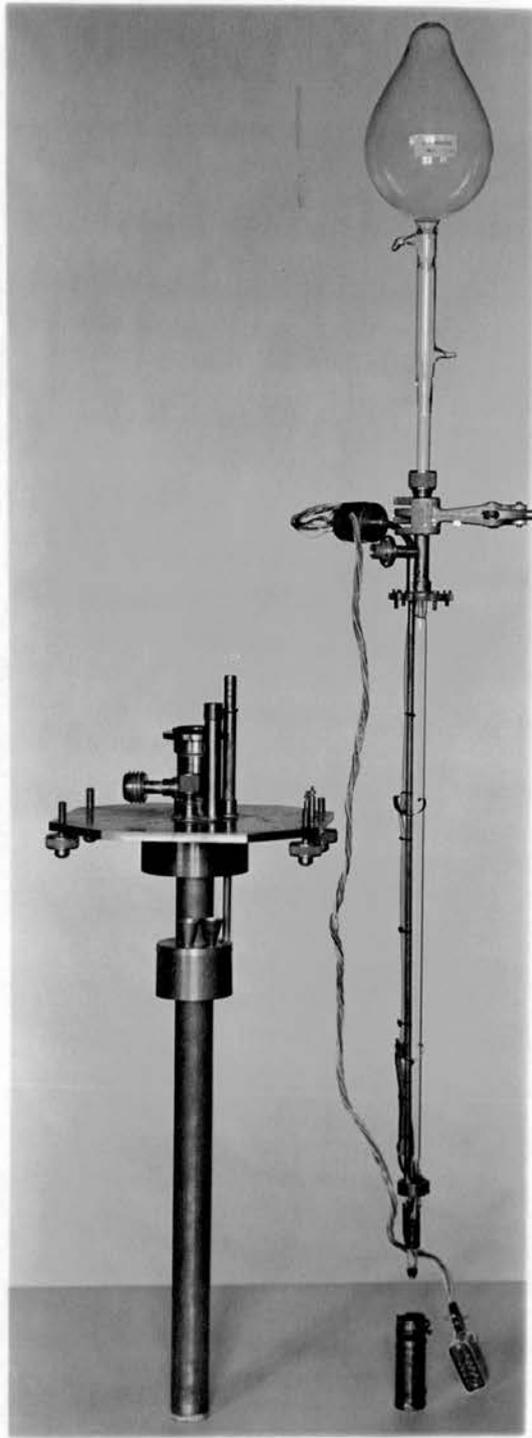


FIGURE 5.

located the isothermal shield inside the jacket. A stepped glass dewar of capacity 1 litre, which fitted into the magnet gap, was used to contain the coolant. The top plate of the cryostat (13) was supported by four levelling screws which facilitated adjustment of the sample position in the magnetic field. A radiation shield (14) was fitted around the stainless steel jacket, to reduce the heat leak.

Liquid nitrogen and liquid air were simply introduced into the dewar through a cupro-nickel funnel. Liquid hydrogen was transferred under slight pressure from a $2\frac{1}{2}$ litre storage vessel through a vacuum jacketed transfer tube which entered through the coupling (15).

By varying the coolant, the exchange gas pressure inside the stainless steel enclosure and the heater input, it was possible to maintain the sample temperature at any value over the required range. Using liquid nitrogen as coolant and an exchange gas pressure of less than 10^{-4} mm Hg, temperatures of 200°K could be achieved with heater inputs of less than $\frac{1}{2}$ watt. Using liquid hydrogen as coolant the average boil off rate was about 400 ml/hr which was quite reasonable.

Temperature measurements were made using two calibrated Copper-Constantan thermocouples one of which was fixed to the sample tube and the other to the top of the copper isothermal shield. Absolute accuracy was about $\pm 1^\circ\text{K}$ although it was usually quite easy to maintain temperatures with an accuracy greater than this. The temperature difference between shield and sample was always kept as small as possible to minimise temperature gradients. A small heater was also non-inductively

wound at the tip of the sample tube itself to expedite changing from one temperature to another. The thermocouple and heater leads were introduced into the cryostat enclosure through vacuum tight Kovar to glass seals which can be seen in figure 5.

In some of the early work on cyclopropane a gas flow cryostat, as described by Andrew and Eades (1953a), was used. In this method dry nitrogen, flowing at a controlled and measured rate, was cooled by passage through a metal spiral immersed in liquid air or liquid nitrogen. The cold gas was then caused to flow through a double ended dewar tube past the sample in the magnet gap. By varying the flow rate, temperatures between 90°K and 250°K could be maintained.

3.3 Measurements

3.3.1 Line width and Second Moment

In all cases the line widths of absorption spectra were for convenience taken as the interval in gauss between the points of maximum and minimum slope. This corresponds to the interval between the peaks of the derivative curves.

The second moments were computed directly from the derivative curves. From equation (2.4) the second moment is given by

$$M_2 = \frac{\int_{-\infty}^{\infty} h^2 g(h) dh}{\int_{-\infty}^{\infty} g(h) dh} \quad (3.1)$$

where the denominator is a normalizing factor. Integrating by parts this may be written

$$M_2 = \frac{1}{3} \frac{\int_{-\infty}^{\infty} h^3 \frac{dg(h)}{dh} dh}{\int_{-\infty}^{\infty} h \frac{dg(h)}{dh} dh} \quad (3.2)$$

The method used to obtain the second moment was numerical integration using the Trapezium rule. The quantity $\frac{dg(h)}{dh}$ is proportional to the output reading of the lock-in amplifier $F(h)$. Thus

$$M_2 = \frac{1}{3} \frac{\int h^3 F(h)}{\int h F(h)}$$

The second moment values were corrected for modulation broadening by deducting the quantity $\frac{1}{4} h_m^2$, where h_m is the modulation amplitude (Andrew, 1953). In all cases the modulation amplitude was made less than one-sixth of the line width to avoid distortion of the spectra. Unless otherwise stated the quoted experimental errors are simply the standard deviations of a set of data.

3.3.2 Spin-Lattice Relaxation Times

For values of the spin-lattice relaxation time greater than about thirty seconds it was possible to use the direct recovery method. (The time constant of the lock-in amplifier output circuit is the limiting factor). The signal was initially saturated with a large r.f. field, H_1 , and then the exponential recovery with time was monitored using a very small r.f. field. From a semi-logarithmic plot the value of T_1 could be obtained. Actually the time constant of the recovery is $T_1 Z$ where Z , the saturation parameter, is given by equation (2.18). It is thus necessary that Z be very close to unity. Andrew, Swanson and Williams, (1961) have described a method of measuring T_1 which can be used even if Z is not sufficiently close to unity. Apparent values of

T_1 are measured for a range of r.f. power levels used in monitoring the recovery and the true value of T_1 is obtained by extrapolating the data to zero power. This method was used in some of the experiments but the correction was generally negligible. When the absorption line is sufficiently strong and narrow for oscilloscope display, direct recovery methods may be used down to T_1 values of about one second, using a cine camera to monitor the recovery. Further details of this method are given in section (6.3.2).

When T_1 was less than thirty seconds the progressive saturation method, as described by Bloembergen (1948), generally had to be used. In this method the r.f. field H_1 , which is proportional to the signal generator output, is progressively increased and the maximum lock-in amplifier output meter reading, β_{Max} , noted. A plot of β_{Max} against the logarithm of the generator output yields a saturation curve and a family of such curves may be obtained by varying the sample temperature. From equation (2.18) it follows that corresponding points (usually the half-value points) on saturation curves at temperatures T_A and T_B are connected by the relationship

$$(\gamma^2 H_1 T_1 T_2)_A = (\gamma^2 H_1^2 T_1 T_2)_B$$

so that

$$\begin{aligned} \frac{T_{1A}}{T_{1B}} &= \left[\frac{H_{1B}}{H_{1A}} \right]^2 \frac{T_{2B}}{T_{2A}} \\ &= \left[\frac{V_B}{V_A} \right]^2 \frac{\Delta H_A}{\Delta H_B} \end{aligned} \quad (3.4)$$

where the value of T_2 is taken to be inversely proportional to the line-width ΔH . (This follows from the fact that the reciprocal of the shape-function gives a measure of the line-width). Provided the line-shape does not alter appreciably this proportionality will be sufficiently accurate.

V_B and V_A are the generator outputs corresponding to H_{1B} and H_{1A} .

Equation (3.4) only holds provided $\omega_m T_1 \ll 1$ (case 1) or $\omega_m T_1 \gg 1$ (case 2), where $\frac{\omega_m}{2\pi}$ is the magnetic field modulation frequency, and also provided the magnetic field inhomogeneity is negligible compared to the line-width.

Relative values of T_1 may be obtained in this way and these may be converted into absolute values if it is possible to make a direct measurement at some temperature. Values of T_1 obtained by the progressive saturation method are not as reliable as those obtained by the direct recovery method as explained in section (2.4).

4. THE EXPERIMENTAL PROGRAMME

4. THE EXPERIMENTAL PROGRAMME

As mentioned in Section 1 it was decided to investigate four organic solids, all consisting of fairly small molecules. The first two substances studied, cyclopropane and cyclobutane, were chosen as an extension of previous work in this laboratory on cyclohexane (Andrew and Eades, 1953a) and cyclopentane (Fushworth, 1954), which had provided interesting results. Cyclopropane was available in comparatively large quantities and was thus a suitable subject for developing the necessary techniques for condensing and studying samples which are gaseous at room temperature. Cyclobutane exhibits an important solid state thermal transition.

Ethylene was chosen since the molecules have the interesting feature of only possessing diad axes. Furthermore the moment of inertia of the molecules about their carbon bond diad axes is extremely small (comparable with that of a methyl group) and quantum mechanical tunnelling effects are possible.

The fourth substance studied was n-butane. In this case methyl group tunnelling effects were the main interest. This substance also exhibits a solid state phase transition.

5. CYCLOPROPANE (C_3H_6)

5. CYCLOPROPANE5.1 The Sample

Cyclopropane was the first substance studied and was obtained in a small steel cylinder (dated 4.10.61), under pressure, from the British Oxygen Company Ltd. It was manufactured by Imperial Chemical Industries Ltd., who supplied the following information regarding typical purity:-

Alcohol, acidity and water	0.15%
Unsaturated substances calculated as propylene	0.05%
Halogen containing substances calculated as propyl chloride	0.01%
Assay (absorption in H_2SO_4)	99.7 %

It was decided to further purify a sample drawn from the cylinder by fractional distillation and condensation using the usual methods (Sanderson 1948, p 89). Figure 6 shows the vacuum system used in performing the distillation. The system was first evacuated with stop-cocks 4, 6, 8, 9 and 10 closed and the others open. The needle valve was also kept closed. Pressure readings were taken on a sensitive Pirani gauge constructed for the purpose (Martin and Hill 1948, p 23) which was initially calibrated against a W. Edwards McLeod gauge. (This instrument is located immediately above the pen recorder in figure 3). When a satisfactory low pressure had been achieved, a suitable quantity of cyclopropane was introduced into the system. Several fractional distillation-condensation processes were carried out as follows. The sample was condensed in trap T_1 using liquid nitrogen and the system was thoroughly evacuated. Traps T_1 and T_2 were then

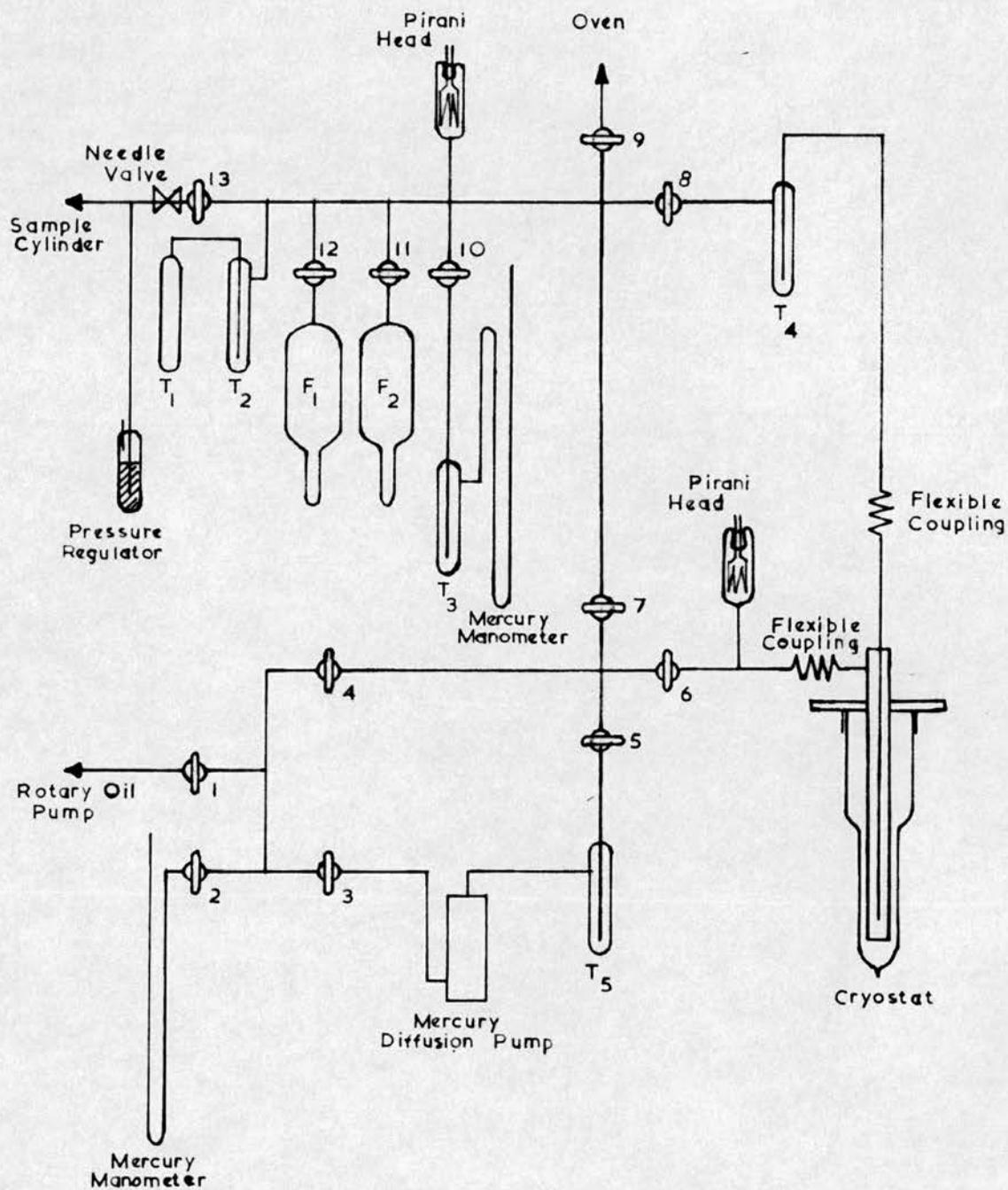


FIGURE 6.

surrounded with ethyl bromide slush baths. At this temperature ($\sim 155^\circ\text{K}$) cyclopropane has a vapour pressure of a few mm Hg. The top fraction of the distillate was discarded and the middle fraction condensed in storage flask F_1 or F_2 by surrounding the tail of the flask with liquid nitrogen. The tail fraction was discarded.

This procedure was repeated. Most of the impurities mentioned above should be removed in this way. The only means of checking the final sample purity was by vapour pressure measurement but this is not sufficiently accurate to indicate the presence of minute quantities of impurity. At the CO_2 point (194.7°K) agreement with published vapour pressure data was satisfactory.

Two methods were used for storing the sample during the n.m.r. investigation. These may be termed the Open and Closed system methods.

(a) Open System

In this method the purified sample was simply stored in flask F_1 or F_2 and could be introduced into the cryostat through stopcock 8 and T_4 (figure 6). A flexible coupling was used to connect the "condensation" tube, which extended down into the cryostat, to the rest of the vacuum system. This coupling consisted of two Sylphon brass bellows, joined to the otherwise all-glass system by Kovar to glass seals, which could be coupled together with an O-ring. Trap T_4 was surrounded by a CO_2 bath in an effort to prevent impurity vapours being condensed in the cryostat. With the relatively large quantity of sample used, (0.02 mole), the effect of any background impurity in the vacuum system at a

low partial pressure, such as water vapour or stopcock grease, may be expected to be of little consequence.

In the initial experiments using this method, marked differences in the absorption spectra obtained during different experimental runs were noted some 10° to 20° below the melting point. In particular the doublet fine structure varied a great deal in resolution, being very marked on some occasions and almost absent on later occasions. It was thought that this might be due to impurity gradually contaminating the sample and for this reason it was decided to adopt the Closed system method to see if the reproducibility could be improved. It should be mentioned at this stage that the Open system presents certain advantages over the Closed system in that it is simpler to change samples, and also that sample mixtures may be readily handled in this way. For these reasons it was the initial method tried.

(b) Closed System

A suitable pyrex flask to contain the sample volume at room temperature was constructed, with a long tail which could extend down into the cryostat. This flask was pumped and baked in a long cylindrical oven at 350°C for several hours. Freshly purified cyclopropane was introduced into the flask at room temperature, and was frozen in the tail. The flask was then sealed off. Two samples were bottled in this way and both gave quite reproducible spectra, but with barely any of the doublet fine structure which had previously been observed. One of these samples was used for the measurements which are reported.

The reasons for the variation in behaviour which were observed in the Open system experiments are uncertain, but the following possibilities may be mentioned. Firstly, gradual deterioration in purity of the sample may have been the cause. The deterioration may have been due to impurities from the system walls, or slight decomposition of the sample itself. This latter possibility may be considered to be quite unimportant at room temperature, unless some catalytic agent was present in the system, since the activation energy for the unimolecular isomerization to propylene is 65 k. cal./mole. (Chambers and Kistiakowsky, 1934). It was not possible to have an accurate mass spectrographic analysis of the sample carried out, as a high purity standard sample could not be obtained. The mechanism by which small quantities of impurity would markedly affect the n.m.r. absorption spectrum in this substance is not obvious.

Secondly, the frozen sample may have not been truly polycrystalline in some of the experiments. This could have been checked by rotating the sample in the magnetic field to see if any anisotropy of the second moment existed. This is clearly not feasible with the Open system method. The degree of polycrystallinity may be linked with sample purity and would also be affected by the rate at which the sample was cooled.

In any case, apart from the fine structure change, the overall behaviour of the samples in both Open and Closed system experiments, was very similar. Line narrowing was observed in the same temperature interval in all cases and the conclusions which could be drawn from the

second moment data were virtually unaltered. For these reasons no further time was devoted to this aspect.

5.2 Physical Data

5.2.1 Molecular Structure

The molecular structure of cyclopropane, C_3H_6 , has been of considerable interest because of its strained ring nature and both theoretical and experimental investigations have been carried out. It is generally accepted that the structure is a three membered ring with D_{3h} symmetry and with the C-C-C bond angles necessarily 60° . The other structural parameters are less certain.

Dunitz and Schomaker (1952) have summarized the early work on this problem. Both electron diffraction and spectroscopic experimental investigations have been carried out. The experimental and theoretical evidence indicates that the C-C bond lengths are shorter than in unstrained hydrocarbon molecules, in which the standard value is 1.54 Å, while the H-C-H angle is larger than tetrahedral. The following parameter values are likely on the basis of this early information,

$$C-C = 1.52 \text{ \AA}; C-H = 1.08 \text{ \AA}; H-C-H = 118^\circ.$$

More recently, further spectroscopic investigations have been performed by Baker and Lord (1955), Gunthard, Lord and McCubbin (1956) and Mathai, Shepherd and Welsh (1956). In the first two cases, the C-C bond length was unambiguously determined as 1.524 ± 0.014 Å. It was also suggested that if the C-H bond length is assumed to be 1.07 Å then the

H-C-H angle is just greater than 120° . The choice of 1.07 Å as the C-H distance was justified by analogy with early estimates of the C-H distance in ethylene. More recent work on ethylene (see Section 8.2.1) indicates that this distance is 1.08 Å and, if this value is assumed, then the results of Gunthard, Lord and McCubbin (1956) indicate an H-C-H angle appreciably larger than 120° .

Bastiansen and Skancke (1961) in a review article have referred to recent unpublished preliminary results which they have obtained by electron diffraction methods on gaseous cyclopropane. Bastiansen (1963, private communication) has supplied further details of these measurements prior to publication. The data derived from the radial distribution curve are

$$\text{C-C} = 1.509 \pm 0.003; \text{C-H} = 1.091 \pm 0.01; \text{H-C-H} = 113.8^\circ \pm 1$$

A least-squares method gives parameters in substantial agreement with these figures. The radial distribution method should give the most probable distance and these values have accordingly been used in the second moment calculations. Bastiansen has pointed out that the error limits (standard errors) do not allow for possible unknown scale errors.

Second moment calculations have been carried out for several sets of parameters because of the fairly wide discrepancies which are apparent.

5.2.2 Crystal Structure

The crystal structure has not been determined by X-ray methods. Brecher, Krikorian, Blanc and Halford (1961) have recently suggested, on

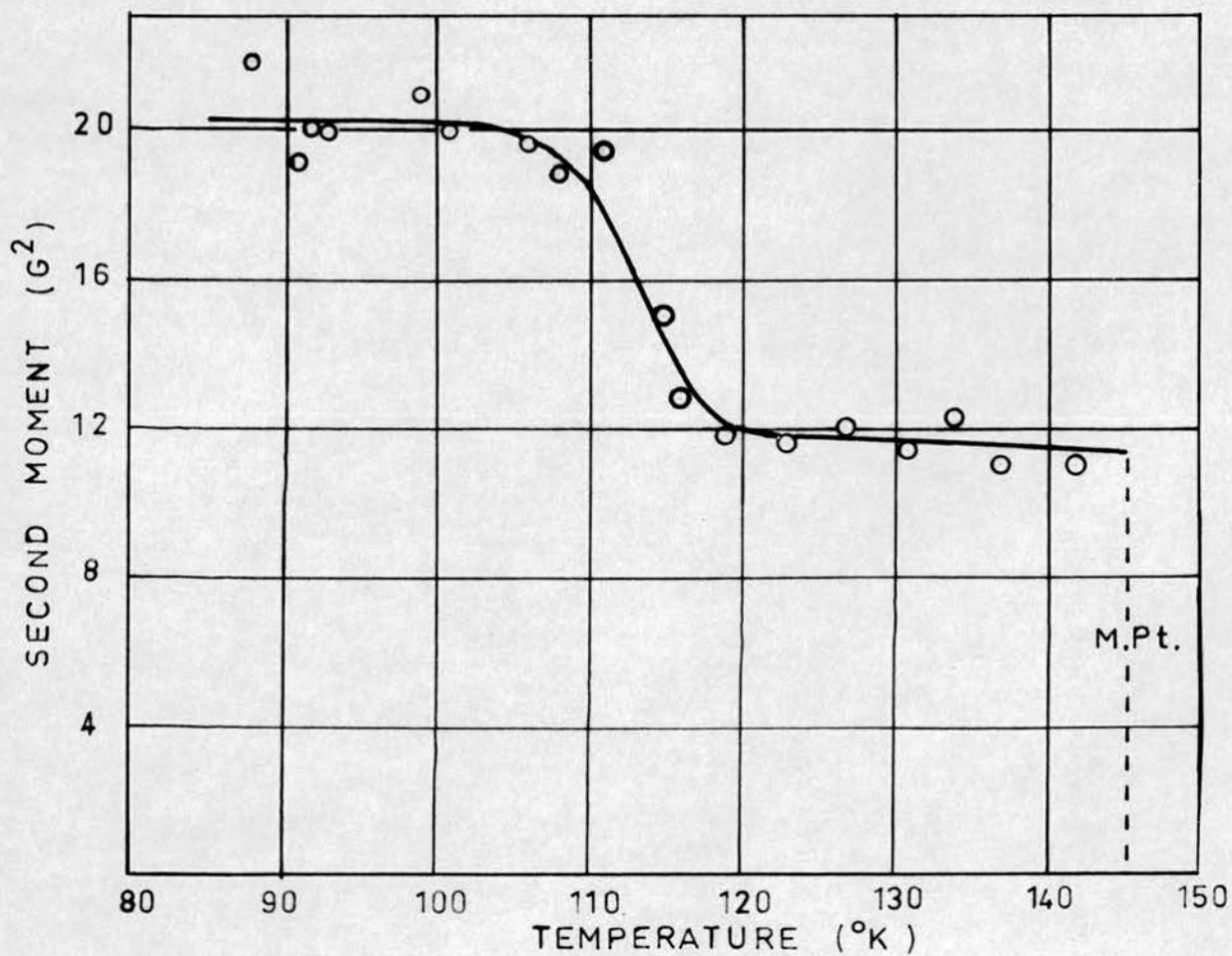
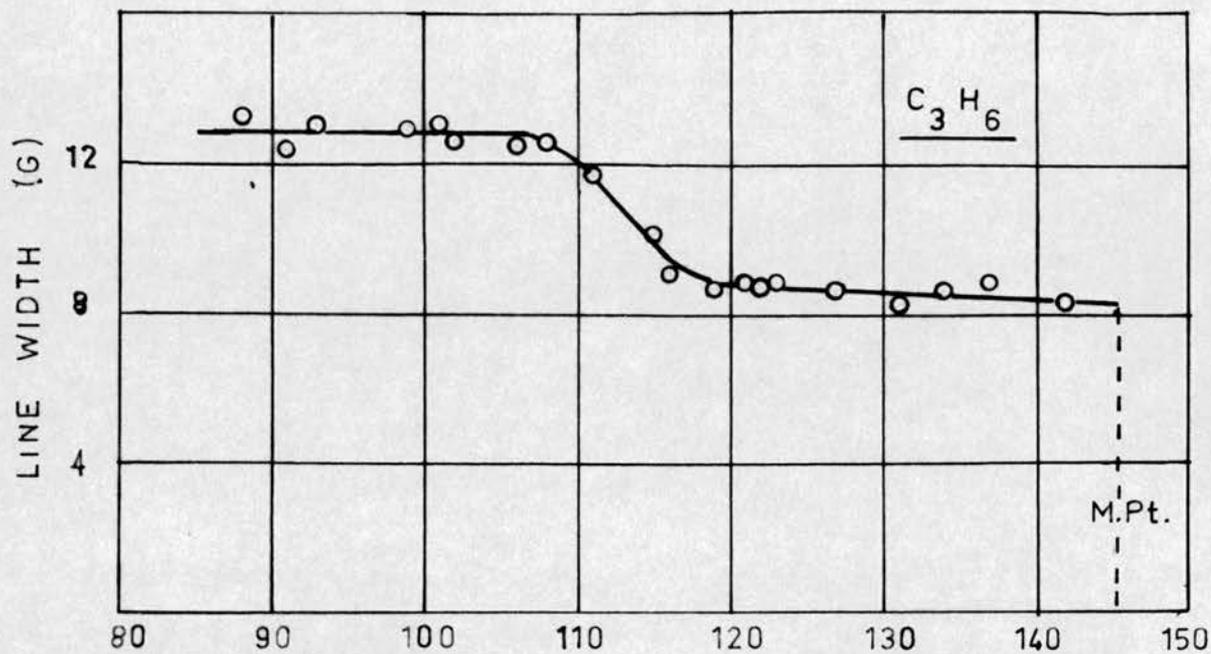


FIGURE 7.

the basis of infra-red studies of a cyclopropane single crystal, that the crystal structure probably belongs to the space group $C_{2v}^7 (P_{nm})$, with two molecules in an orthorhombic unit cell. No evidence confirming this structure by X-ray or neutron diffraction methods appears to have been published so far, and the unit cell dimensions are not known.

5.2.3 Thermal data

Ruehrwein and Powell (1946) have made heat capacity measurements on solid cyclopropane and found the melting point to be 145.54°K. No evidence of a solid state phase transition was obtained and the heats of fusion and vapourization were 1301 and 4793 cal./mole. respectively.

5.3 Results

5.3.1 Absorption Spectrum

The variation of the absorption spectrum line-width and second moment with temperature is shown in figure 7. Below 100°K both these quantities have effectively constant values, the average second moment being $20.2 \pm 0.9 \text{ G}^2$. Between 100°K and 120°K they both decrease and attain new steady values, which remain virtually unchanged to the melting point. The reduced second moment is approximately 11.9 G^2 . The spectrum did not exhibit fine structure at any point.

5.3.2 Spin-Lattice Relaxation Times

The spin-lattice relaxation time behaviour as a function of temperature is shown in figure 8. Below 100°K the direct recovery method was used, while the values at higher temperatures were obtained by progressive

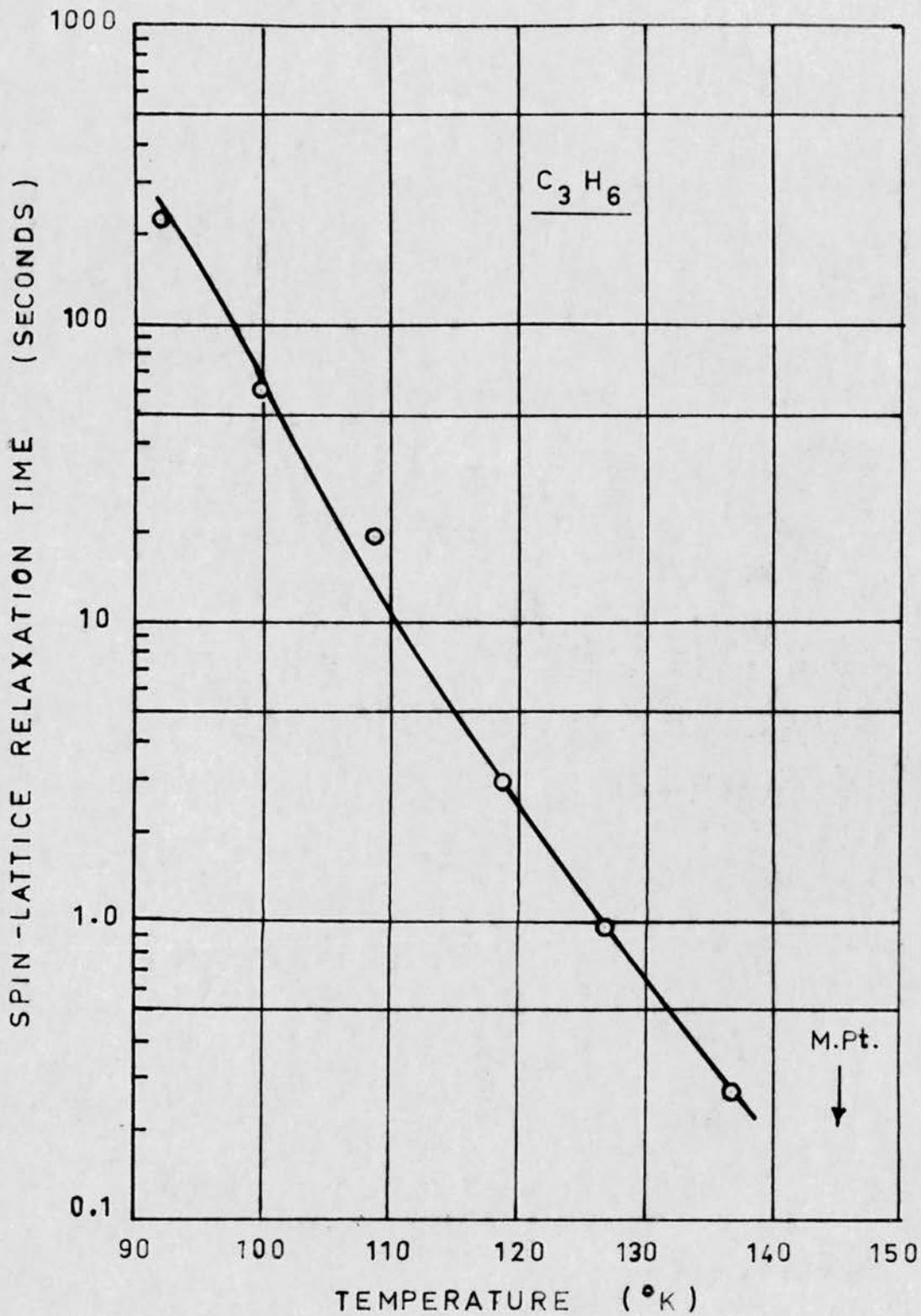


FIGURE 8.

saturation. The minimum value of $\omega_m T_1$ was approximately 30, so that the conditions of Case 2 (Section 3.3) were satisfied throughout.

5.4 Discussion

5.4.1 Absorption Spectrum

It is possible, with the aid of equation (2.6), to estimate the second moment of the absorption spectrum which may be expected when the lattice is rigid. The intra-molecular contribution, which is denoted M_2' , has been calculated for various values of the structural parameters and the results are shown in Table 5.1.

Table 5.1

Source	C-H A	C-C A	H-C-H	$M_2' \text{ G}^2$
Early Work	1.08	1.52	118°	12.8
Gunthard, Lord and McCubbin (1956)	1.07	1.52	120°	13.1
Bastiansen (1963)	1.09	1.51	113.8°	13.1

A value of $13.1 \pm 0.3 \text{ G}^2$ may reasonably be assumed for this contribution.

The intermolecular contribution cannot be evaluated in this way, since the crystal structure parameters have not been determined. A reasonable estimate can be made by comparison with other similar substances on which measurements have been carried out.

Nuclear magnetic resonance investigations of solid cyclohexane

(Andrew and Eades 1953a) and cyclopentane (Rushworth 1954) have yielded experimental values of $7.7 \pm 0.5 \text{ G}^2$ and $7.2 \pm 1.5 \text{ G}^2$ respectively for the rigid lattice intermolecular contributions M_2'' , at temperatures in the vicinity of 100°K . These values are obtained by deducting the reliable theoretical intra-molecular contributions from the experimentally measured second moments (corrected for modulation broadening) in the rigid lattice region.

It may be expected that the inter-molecular contribution for cyclopropane will be smaller than these two values because of the smaller number of protons per molecule. Andrew and Eades (1953a) have suggested that the lattice energy may serve as a semi-quantitative basis for comparison of inter-molecular contributions. With sufficient accuracy the lattice energy Q may be taken as the sum of the heats of transition, fusion, and vapourization. The following values are obtained from heat capacity data:

Cyclopropane (Ruehrwein and Powell 1946) $Q = 6.1 \text{ k. cal./mole.}$

Cyclopentane (Timmermans 1950) $Q = 8.4 \text{ k. cal./mole.}$

Cyclohexane (Timmermans 1950) $Q = 10.2 \text{ k. cal./mole.}$

Although the relationship between Q and M_2'' is clearly not a simple one for these three cases, a reasonable estimate for the intermolecular contribution for cyclopropane at 100°K is $6.5 \pm 1.0 \text{ G}^2$.

The total theoretical second moment for the rigid lattice at 100°K is thus $19.6 \pm 1.3 \text{ G}^2$. This is in quite fair agreement with the experimental value of $20.2 \pm 0.9 \text{ G}^2$ at 100°K and the lattice may be assumed to

be effectively rigid. It is clearly not possible to make any deductions concerning molecular structure from these results, because of the large uncertainties. It is to be hoped that further information on the crystal structure will soon be forthcoming so that a reliable value of the intermolecular contribution can be calculated.

Above 105°K molecular reorientation occurs at a rate sufficiently rapid to affect the absorption spectrum. The most likely process is reorientation of the molecules about their three fold axes. The reduction which this process produces in the intra-molecular contribution to the observable second moment is readily calculated using equation (2.7), and a value of 9.8 G^2 is obtained. Deducting this from the experimentally observed value of 11.9 G^2 , gives 2.1 G^2 as the reduced inter-molecular contribution. This is approximately one third of the rigid lattice value. In cyclohexane Andrew and Eades (1953a) found that reorientation of the molecules about their three fold axes also reduced the intermolecular contribution by a factor 3, from 7.7 G^2 to about 2.5 G^2 . On this evidence it seems probable that the cyclopropane molecules reorient about their three fold axes between 105°K and the melting point with a frequency greater than about $5 \times 10^4 \text{ c/s}$.

The only other form of restricted motion which might occur is molecular reorientation about a preferred diad axis. The reduction in the intra-molecular contribution produced by this process can be calculated with the aid of equation (2.8). This gives a value of 12.0 G^2 , which, even without the reduced intermolecular contribution, is as large as the

experimentally observed value of 11.9 G^2 . This process may therefore be considered to be unlikely as might be expected from steric considerations. Isotropic reorientation of the molecules about their centres of mass would reduce the intra-molecular contribution to zero leaving only the reduced inter-molecular contribution and this possibility may thus be definitely excluded.

The further slight reduction in second moment, which occurs between 120°K and 145°K , is probably due to an increase in the amplitude of molecular oscillations and to lattice expansion.

If the molecules reorient strictly about their three fold axes then the interactions between the protons in each methylene group are not affected since these interproton vectors are parallel to the axis of motion. All the other interactions are reduced by the motion. It is thus to be expected that the narrowed spectra should exhibit fine structure of the Pake doublet type. This was indeed observed to a varying extent with some of the samples used in the preliminary work, but not in the sample used for the reported results. Appreciable "rocking" of the molecules while they are reorienting would affect the resolution of the fine structure but it seems unlikely that sufficiently large variations in this behaviour would occur.

5.4.2 Spin-Lattice Relaxation

The steady decrease of the spin-lattice relaxation time with increasing temperature shown in figure 8, is consistent with the discussion of the reorientation process given above. The correlation time

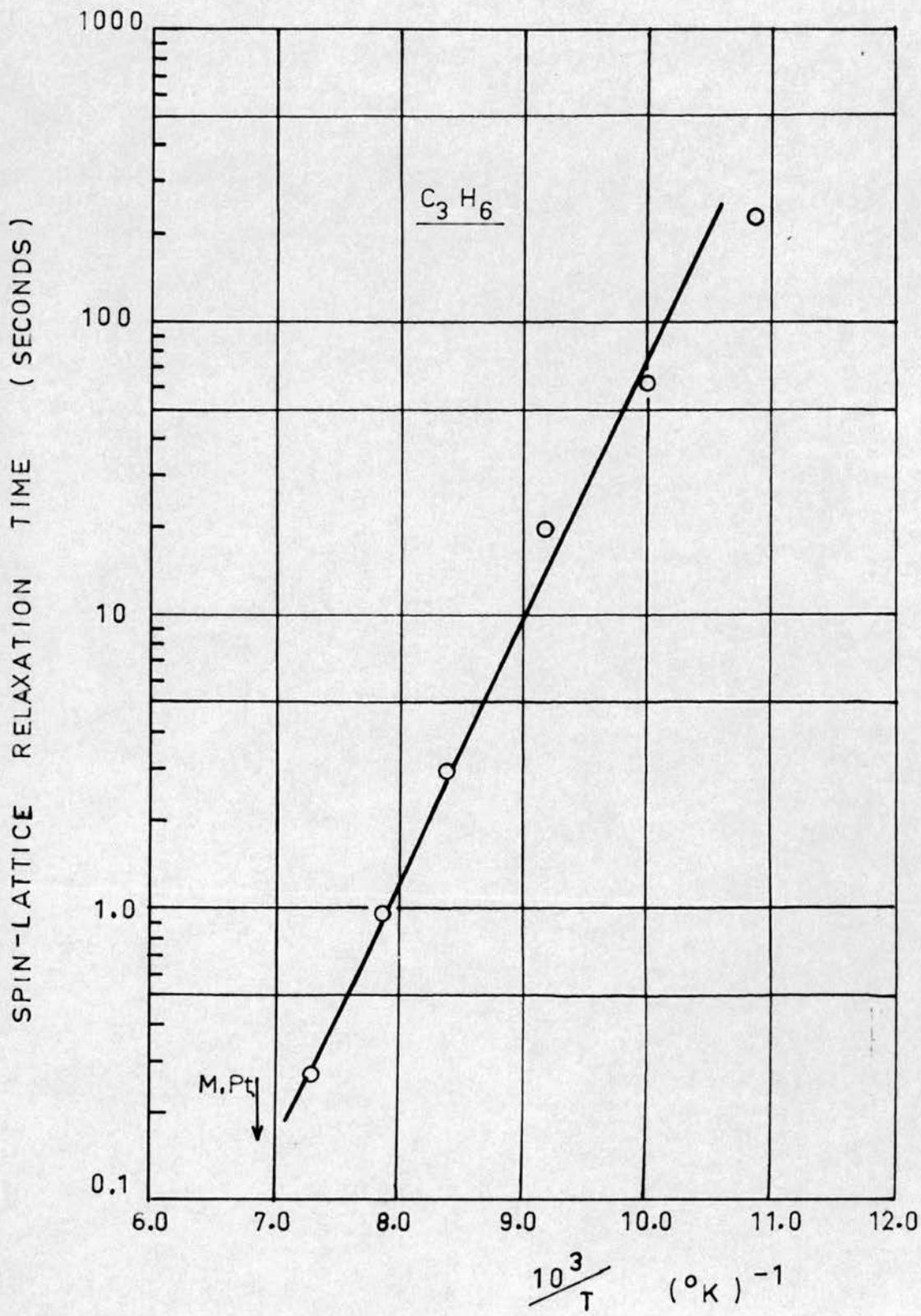


FIGURE 9.

(42)

τ_c (equation 2.10) for the reorientation process may be expected to vary with temperature according to the rate equation

$$\tau_c = \tau_0 \exp \frac{E_a}{RT} \quad (5.1)$$

where τ_0 is a constant, E_a is the activation energy for the process, and R is the gas constant.

It is clear from the T_1 data that the correlation time is on the long side of the minimum value and, as equation (2.14) shows,

$$T_1 \doteq \frac{\omega_0^2}{2C_1} \tau_c = \frac{\omega_0^2}{2C_1} \tau_0 \exp \frac{E_a}{RT} \quad (5.2)$$

Thus

$$\log T_1 = \frac{E_a}{RT} \log e + \log \frac{\omega_0^2 \tau_0}{2C_1} \quad (5.3)$$

$$\text{Provided } \omega_0^2 \tau_0^2 \gg 1.$$

A plot of $\log T_1$ against reciprocal temperature is shown in figure 9. From the slope of the straight line portion a value of 4.1 ± 0.5 k. cal./mole. is obtained for the activation energy. With the possible exception of the lowest T_1 value the use of equation (5.3) is well justified.

In cyclohexane the activation energy for molecular reorientation about the three fold axis was found to be 11 ± 1 k. cal./mole. (Andrew and Eades, 1953a). The large difference in values is understandable, since the hindering barriers are entirely intermolecular in origin in both cases. Because of the difference in molecular sizes and shapes, the molecules are likely to pack differently in their respective lattices. (The crystal structure of the low temperature phase of solid

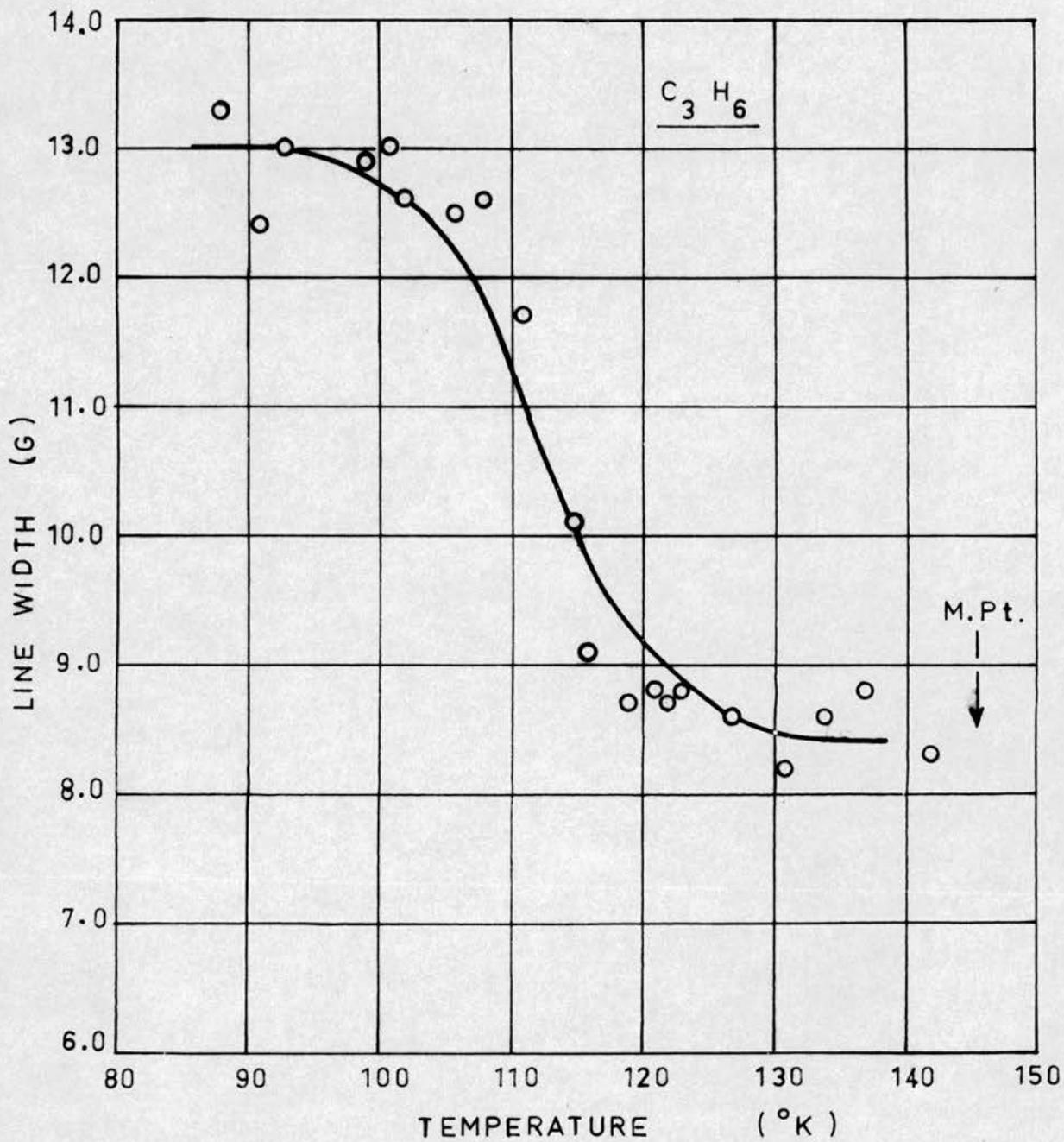


FIGURE 10.

cyclohexane is not known). The lattice energy values support this view. In the case of benzene, Andrew and Eades (1953b) found the activation energy for reorientation about the molecular six fold axis to be 3.7 ± 0.2 k. cal./mole.

It is possible to check the value of E_a obtained from the T_1 data by using this value to fit a curve to the line width transition in the manner suggested by Gutowsky and Pake (1950). They give the following expression relating line width and correlation frequency

$$(\delta H)^2 = B^2 + \frac{2}{\pi} C^2 \tan^{-1} \frac{\alpha \gamma \delta H}{2\pi \nu_c} \quad (5.4)$$

where δH is the line-width in the transition region,
 $(B^2 + C^2)^{\frac{1}{2}}$ is the line-width before narrowing occurs,
 B is the line-width after narrowing,
 ν_c is the correlation frequency defined as $\nu_c = \frac{1}{2\pi \tau_c}$,
 α is a constant with value approximately $\frac{1}{8 \ln 2}$

(Kubo and Tomita, 1954; Pake, 1956)

Following equation (5.1) it is assumed that

$$\nu_c = \nu_0 \exp - \frac{E_a}{RT} \quad (5.5)$$

By combining equations (5.4) and (5.5), and using the value of E_a obtained from the T_1 data, the curve shown in Figure 10 was obtained as a reasonable fit to the experimental data. The constant ν_0 was fixed by choosing the curve to pass through the experimental point at 115°K. The agreement between the theoretical curve and the observed line width transition gives rough confirmation of the value for E_a . It appears that

a slightly higher value of E_a would give a better fit. It has however been pointed out by Andrew and Jenks (1962) that the use of equation (5.4) tends to yield values for E_a which are too high.

An interesting point to note is that if the cyclopropane molecules are reorienting strictly about their three fold axes, then the interactions between the protons within each methylene group pair are not effective in the spin lattice relaxation mechanism. Since these interactions are not modulated by the motion (the angular coordinates specifying the orientation of these internuclear vectors with respect to the external magnetic field remain unchanged) it is the other neighbours in each molecule which are primarily responsible for the relaxation process.

Assuming equation (2.10) to apply it has been possible to obtain an experimental value for the constant C_1 by combining line width and T_1 data. With the aid of equation (5.3) a value of $1.72 \times 10^{22} \text{ sec}^{-3}$ is obtained for $\nu_0 C_1$ from the latter data. In synthesizing the line width transition curve ν_0 was found to be $2.70 \times 10^{13} \text{ sec}^{-1}$. Thus the experimental value for C_1 is approximately $6.4 \times 10^8 \text{ sec}^{-2}$, with a fairly large uncertainty.

Since the motion of the molecules is occurring about a single axis the B.P.P. value for C_1 given by equation (2.11) does not apply. Stejskal and Gutowsky (1958) have derived an expression for T_1 for the case of substances containing molecules in which methyl groups are reorienting about their three fold symmetry axes. (Their expression also allows for tumbling of the molecules about their centres of mass

(45)

and two correlation times are used to describe the composite motion). In the case in which only CH_3 group reorientations are occurring in a polycrystalline sample the expression takes the same functional form as equation (2.10) with the constant C_1 given by

$$C_1 = \frac{9\gamma^4 \hbar^2}{40r_0^6} \quad (5.6)$$

where r_0 is the interproton distance in each CH_3 group. Only interactions between the three protons in each CH_3 group are considered in deriving this expression.

Equation (5.6) may be used to estimate the value of C_1 in the case of cyclopropane considering only the interactions between the three next nearest neighbours in each molecule. A value of $4.9 \times 10^8 \text{ sec}^{-2}$ is predicted, which is slightly lower than the experimental value. This discrepancy is reasonable since the interactions of each proton with its two most distant neighbours in each molecule and with protons in neighbouring molecules have been ignored. The rough agreement does support the view that next nearest neighbours dominate in the relaxation process.

If isotropic reorientation of the molecules were occurring, so that nearest neighbour interactions were important, then equation (2.11) gives a value of $4.8 \times 10^9 \text{ sec}^{-2}$ for C_1 . This is about eight times higher than the experimental value. Using the experimental C_1 a minimum of 0.15 seconds is predicted for T_1 . The intervention of the melting point prevents the observation of the minimum and thus this value cannot be checked.

6. CYCLOBUTANE (C_4H_8)

6. CYCLOBUTANE6.1 The Sample

The Shell Thornton Research Centre kindly supplied the sample and stated that a mass spectrograph analysis revealed no detectable impurity. The ampoule in which it was supplied was opened under vacuo and the sample distilled into a small pyrex specimen tube which was then sealed off.

6.2 Physical Data6.2.1 Molecular Structure

Cyclobutane, C_4H_8 , like cyclopropane, is a strained ring compound. Dunitz and Schomaker (1952) have obtained the following values for the structural parameters using electron diffraction methods:-

$$C-C = 1.56 \pm 0.02 \text{ \AA}; C-H = 1.09 \pm 0.04 \text{ \AA}; H-C-H = 114 \pm 8^\circ$$

Furthermore their results indicate that on the average the ring is non-planar with dihedral angle 20° ($+10^\circ$, -20°) between opposite triads of carbon atoms. However they state that the equilibrium symmetry may be either D_{2d} (puckered ring) or D_{4h} (planar ring with low rigidity, leading to large amplitude out-of-plane bending). They postulated that the local C_{2v} symmetry of the CH_2 groups was retained.

Rathjens et.al. (1953) have carried out an infra-red spectroscopic investigation of gaseous cyclobutane. They suggest that the equilibrium symmetry is D_{2d} but that the barrier hindering inversion is sufficiently low that an appreciable number of molecules obey D_{4h} selection rules.

Octafluorocyclobutane has been studied by spectroscopic (Edgell and Weiblen, 1950) and electron diffraction methods (Lemair and Livingston, 1950) and the evidence indicates that some ring puckering is present. High resolution n.m.r. studies of liquid octafluorocyclobutane and 1, 1, 2, 2 - tetrafluorocyclobutane (Shoolery 1955, Phillips 1956), however, show only a single resonance line which indicates that the ring is effectively planar. This may be due to a high ring inversion frequency which would average the environments of the fluorine atoms. A single high resolution resonance line is also observed in gaseous cyclobutane (Petrakis and Sederholm, 1964).

While none of the quoted evidence is conclusive in determining whether the ring is planar or not, it seems likely that the molecules are performing rapid inversions between non-planar configurations in the gaseous and liquid phases and also, possibly, in the solid state.

6.2.2 Thermal data

Two heat capacity investigations of cyclobutane have been reported. In the first of these Kaarsemaker and Coops (1952) found evidence of a first order solid state transition at 146.4°K. The melting point was found to be 183.0°K. The entropy of transition was 9.43 e.u. (cal. deg⁻¹ mole⁻¹) while the entropy of fusion was 1.36 e.u.

Rathjens and Gwinn (1953) obtained values for the entropies of transition and fusion of 9.36 e.u. and 1.43 e.u., respectively. Their results gave evidence of a λ -type solid state transition with a region of very high heat capacity. The transition appeared to start at 120°K

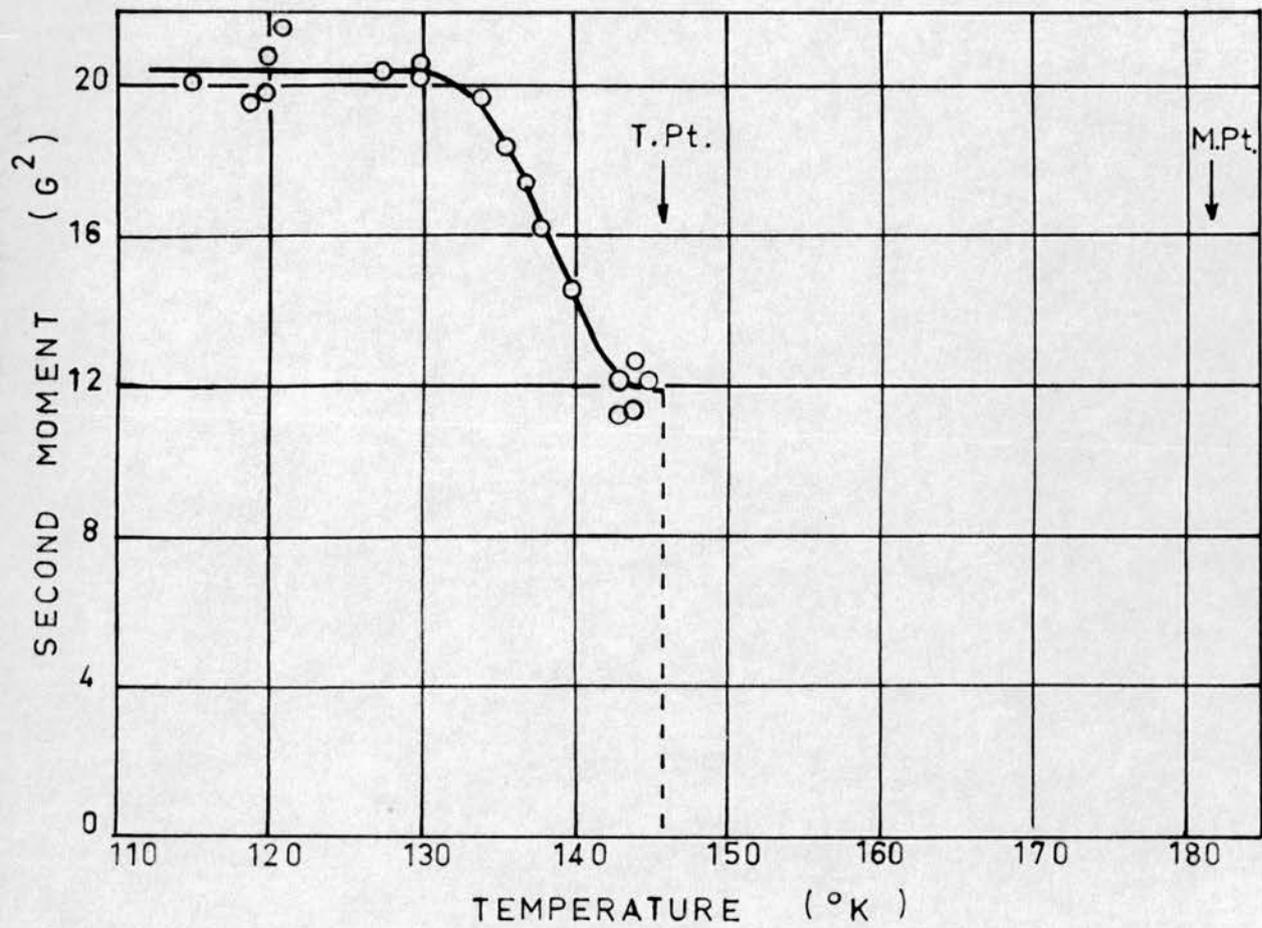
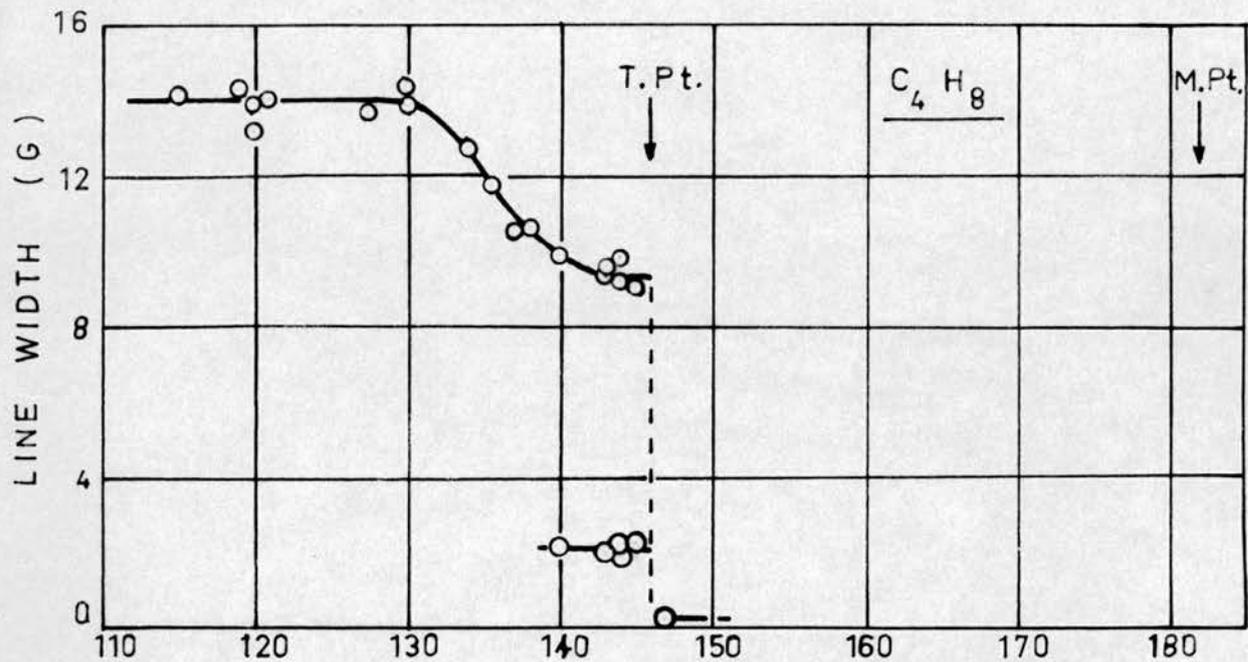


FIGURE 11.

and end abruptly at 145.7°K. The melting point was found to be 182.3°K.

The small entropy of melting indicates that considerable molecular freedom exists below the melting point (Timmermans, 1961; Andrew, 1961).

6.2.3 Crystal Structure

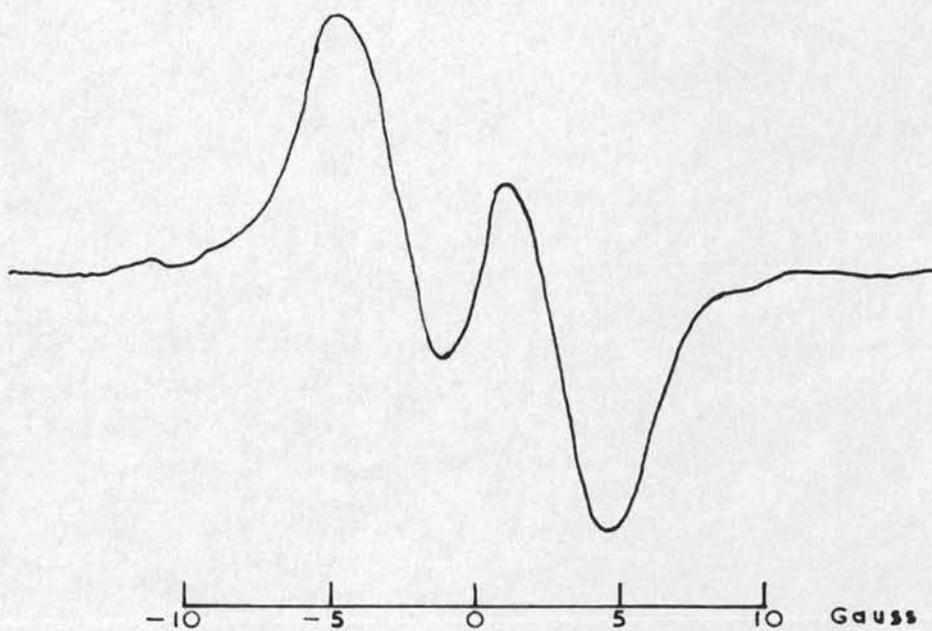
Carter and Templeton (1953) have determined the crystal structure of the high temperature solid form of cyclobutane using single crystal X-ray diffraction methods. The structure is body centred cubic with lattice constant $a = 6.06 \pm 0.03 \text{ \AA}$, at 173°K, and with two molecules per unit cell. They also obtained evidence that the molecules exhibit rotational disorder which approaches spherical symmetry in this phase. The crystal structure of the low temperature form is not cubic but could not be solved.

6.3 Results

6.3.1 Absorption Spectrum

Graphical plots of line width and second moment versus temperature are shown in figure 11. The spectrum exhibited fine structure of the Pake doublet type (Section 2.2.1) at temperatures just below the transition point, and two sets of line widths are plotted in this region. Figure 12 shows an absorption spectrum derivative curve at 143°K.

At the transition point the line width changed discontinuously and at temperatures above 146°K assumed the value governed by the magnetic field inhomogeneity over the sample (0.25 G). Consequently only an upper limit of 0.12 G^2 may be assigned to the second moment in this



CYCLOBUTANE 143° K

FIGURE 12.

region.

The temperature at which the discontinuity occurred was in good agreement with the quoted thermal data. The phase transition could be readily followed by observing the growth of the narrow line at the expense of the broad line at the transition point. Readings were generally taken during warming runs, to avoid supercooling effects, and no investigation of such possible supercooling was made.

6.3.2 Spin-Lattice Relaxation Time

Figure 13 shows the variation of T_1 with temperature. Below 130°K the direct recovery method was used but between 130°K and 146°K recourse had to be made to progressive saturation. The conditions of Case 2 (Section 3.3) were satisfied over the whole of this range. As the line shape changed somewhat in this temperature interval, notably in the appearance of fine structure, the assumption that T_2 was inversely proportional to the line width may have introduced a small systematic error.

Between 146°K and 190°K the line was strong and narrow and was observed on the oscilloscope. T_1 was sufficiently long (\sim one second) in this temperature region to enable measurements to be made by direct recovery. The signal was initially saturated and then, using a small r.f. power level, the recovery on the oscilloscope screen was recorded with a cine camera operating at a known frame speed. Frame by frame measurements were made from the film and T_1 was obtained by a least squares method from this data.

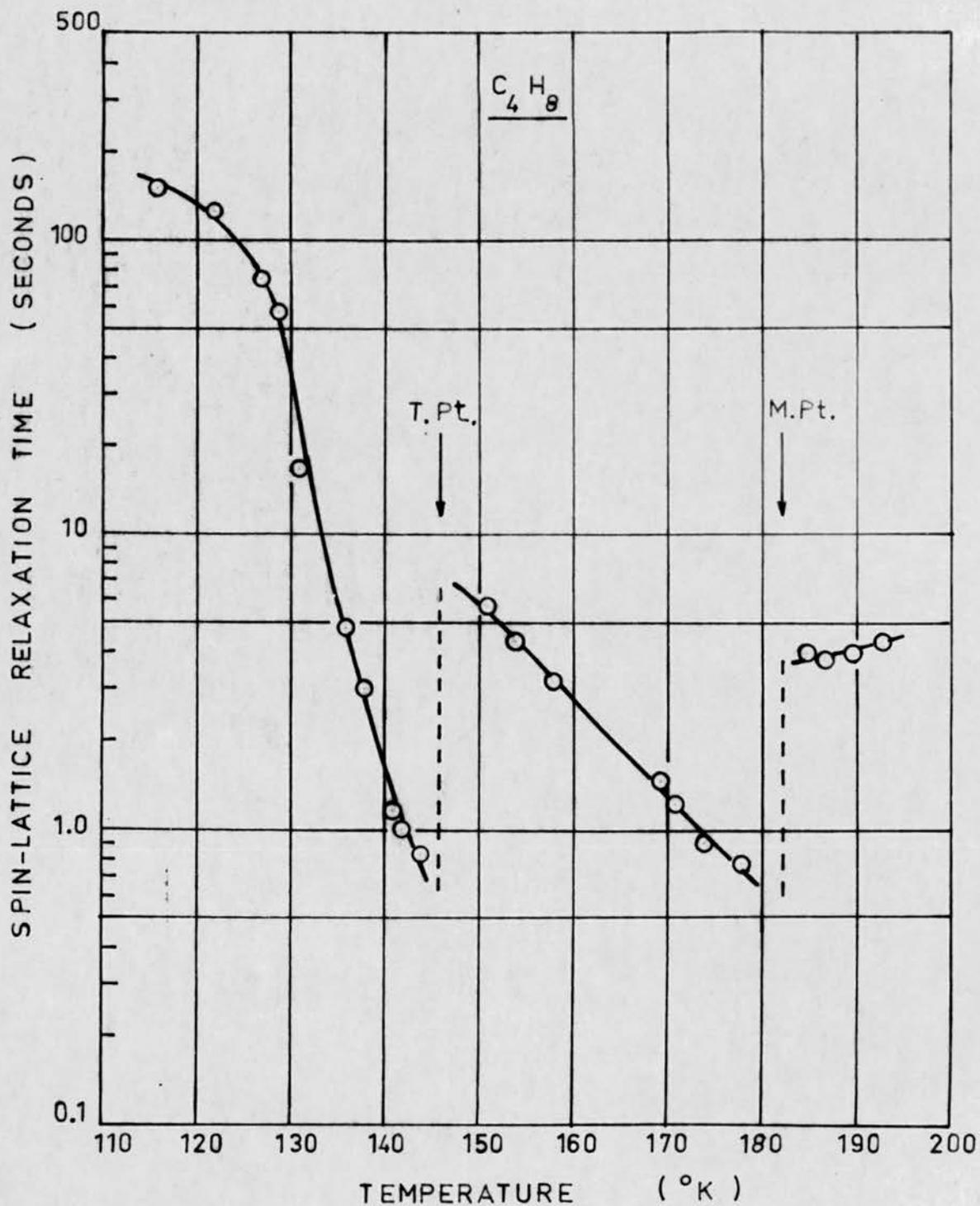


FIGURE 13

6.4 Discussion

6.4.1 Absorption Spectrum

The rigid lattice second moment has been estimated with the aid of equation (2.6). The structural data of Dunitz and Schomaker (1952) was used to calculate the intra-molecular contribution, M_2' , for both planar and non-planar molecular models. For the planar model M_2' is 13.90 G^2 , while for the non-planar model it is 13.93 G^2 . In the case of the non-planar model a dihedral angle of 20° was assumed and the C_{2v} symmetry of the methylene groups was retained.

The difference between the values for the two models is quite negligible and there is thus no possibility of deciding in favour of one or the other from the experimental results in the rigid lattice temperature region. The small difference is to be expected since the cosine of 20° (0.94) is close to unity, and furthermore approximately 65% of the contribution to M_2' in each case arises from the unaltered interactions between proton pairs in the methylene groups. Also, some of the changes which do occur in the various contributions are of opposite sign and thus partially cancel one another. It is clear that any "wagging" motion in the molecules, with a maximum dihedral angle amplitude of 20° , would have little effect on M_2' .

The fairly large uncertainties in the H-C-H angle and bond lengths quoted by Dunitz and Schomaker (1952) introduce a corresponding uncertainty into the value for M_2' . They state that from various considerations the error in the C-H bond distance is in fact probably not more

than 0.01 Å and this reduces the uncertainty in the H-C-H angle determination to $\pm 6^\circ$. This is still a large angular uncertainty, but using these extreme limits the possible error in M_2' may be quoted as $\pm 1.5 \text{ G}^2$. This seems unduly pessimistic, however, since several theoretical studies quoted by Dunitz and Schomaker tend to confirm the value of 114° for the H-C-H angle. It would probably be more realistic to quote M_2' as $13.9 \pm 0.3 \text{ G}^2$.

Since the crystal structure of the low temperature solid form of cyclobutane is not known, the intermolecular contribution to the second moment, M_2'' , has been estimated with the aid of data obtained on similar molecules, as was done in the case of cyclopropane. The lattice energy of cyclobutane may be taken as approximately 7.5 k. cal./mole. Using the figures for cyclohexane, cyclopentane and cyclopropane quoted in Section 5.4.1 a value of $6.9 \pm 1.0 \text{ G}^2$ is a reasonable estimate for M_2'' at temperatures near 100°K . In the case of cyclopentane, which has the same number of protons per molecule as cyclobutane, Lawrenson and Rushworth (1958) obtained a value of 6.6 G^2 for this contribution.

The total theoretical rigid lattice second moment may thus be taken as $20.8 \pm 1.3 \text{ G}^2$. This is in agreement with the experimental value of $20.4 \pm 0.6 \text{ G}^2$ obtained at temperatures below 130°K and the molecules must be effectively rigid in this temperature range.

Between 130°K and 146°K the line width and second moment values steadily decrease. The second moments are of qualitative significance only over most of this region as was mentioned in Section 2.2.2. Just

below the transition temperature the second moment attains a new steady value of about 11.9 G^2 which is probably meaningful.

The reduced values of the intramolecular contribution to the second moment of the observable spectrum, due to various possible reorientation processes, may be calculated with the aid of equations (2.7) and (2.8). For the planar molecular model reorientation about the four fold symmetry axis gives a value of 10.0 G^2 . There are two diad symmetry axes about which reorientation could conceivably occur for this model. Reorientation about the diagonal diad axis, passing through opposite carbon atoms in the ring, gives 10.6 G^2 , while for the diad axis passing through the mid-points of opposite C-C bonds the contribution would be 13.6 G^2 .

In the case of the non-planar model there is only a single diad symmetry axis about which reorientation could occur. For this process the reduced contribution would be 12.1 G^2 .

In the last two possibilities mentioned, the reduced intramolecular contributions are themselves larger than the experimentally observed second moment. The addition of the reduced intermolecular contributions would make the values appreciably larger and these reorientation processes may therefore be considered to be unlikely.

The reduced intermolecular contribution must be estimated by comparison with other similar cases. As was mentioned in Section 5.4.1, reorientation of the cyclohexane and cyclopropane molecules about their three fold axes reduces this contribution to about one third of the

rigid lattice value. In cyclopentene Lawrenson and Rushworth (1958) found that reorientation of the molecules about their pseudo five fold axes resulted in a reduction factor of roughly one quarter. For reorientation of the cyclobutane molecules about their four fold axes a reduction factor of one third seems a reasonable assumption and this gives a reduced intermolecular contribution of $2.3 G^2$, with a relatively large uncertainty. It will be shown later in this section that isotropic reorientation of the molecules on fixed lattice sites in the high temperature solid phase gives a value of $1.68 G^2$ for the intermolecular contribution. This is about one quarter of the rigid lattice value in the low temperature phase (in which closer molecular packing may be expected to occur).

In the case of reorientation of planar molecules about their diagonal diad symmetry axes the reduced intermolecular value may be expected to be slightly larger than for reorientation about their four fold axes. Only two of the four pairs of protons would change their positions in the lattice by a relatively large amount and also, because of the lower symmetry, the reduction produced by the motion may be expected to be smaller. However a value of $2.3 G^2$ with a large uncertainty will also be assumed for this case since no basis for a more reliable estimate is available.

The total reduced second moment for reorientation about the four fold axes is thus $12.3 G^2$ while for reorientation about the diagonal diad axes it is $12.9 G^2$. The experimental value of $11.9 G^2$ at 144°K is

in reasonable agreement with the first of these two figures but the evidence is not conclusive in deciding between the two possibilities. Steric considerations, however, favour reorientation about the four fold axes since in this case the molecules do not take up much more room in the lattice when reorienting than when stationary. It may be concluded that this is very probably the form of molecular motion which occurs. It must be mentioned that there is a possibility that the molecules may exist in a non-planar configuration for an appreciable time even though they appear to reorient in the planar configuration.

The doublet fine structure which occurs in the spectra at temperatures just below the transition point is undoubtedly due to the proton pairs in each methylene group. Since the interproton vector in each pair is parallel to the axis of reorientation no change in the interaction within the pair is produced by the motion, while the interactions with other proton neighbours are reduced. A partial decoupling of the proton pair from its magnetic neighbours occurs and the fine structure is enhanced.

As was mentioned in Section 2.2.1 the spectrum for proton pairs in polycrystalline material should consist of two peaks separated by approximately $\frac{3}{2} \cdot \frac{\gamma\hbar}{r^3}$, where r is the interproton distance. Using Dunitz and Schomakers (1952) data for cyclobutane the predicted separation is 6.7 G. The experimentally measured separation, which was obtained from spectra in which the modulation amplitude was made sufficiently small to avoid possible distortion of the fine structure, was about 4.8 G. The large difference is not easy to explain. Rocking of the molecules while

reorienting would reduce the peak separation somewhat. In the case of cyclopropane no fine structure at all was observed. It would be safer to confine deductions from fine structure measurements to the rigid lattice region for this type of molecule, but in many cases, including cyclobutane, the fine structure in the rigid lattice region is unfortunately insufficiently resolved to make this possible. (It may be mentioned that no reduction in the peak separation would be produced by reorientation of the molecules about their diagonal diad axes, except in the unlikely case of free rotation).

In the high temperature solid phase the absorption spectrum is narrow and the line-width is determined by the field inhomogeneity over the sample volume. As mentioned earlier only an upper limit of 0.12 G^2 may be assigned to the second moment.

Isotropic reorientation of the molecules about fixed centres of mass reduces the intramolecular contribution to zero. There is still a residual intermolecular contribution which can be evaluated using the results of Andrew and Eades (1953a). For the case of isotropic reorientation, these authors have shown that an approximate value for the intermolecular contribution may be obtained by considering all the protons in each molecule to be clustered together at the centre of mass. Smith (1962) has stated that this method gives exact results provided the reorientation is sufficiently rapid. The b.c.c. lattice sum obtained by Torrey (1954) is

$$\sum_k r_k^{-6} = 29.045 a^{-6} \quad (6.1)$$

where a is the lattice parameter.

Using this expression and the data of Carter and Templeton (1953) a value of 1.68 G^2 is predicted for the second moment in this case. (This value was also obtained by direct computation).

The observed second moment at temperatures above 146°K is more than an order of magnitude less than this and it is necessary to postulate that self-diffusion of the molecules occurs in the lattice at a rate sufficiently great to reduce the intermolecular contribution to a very small value. This phenomenon has been reported for a variety of molecular crystals in which the molecules exhibit isotropic reorientation (Andrew, 1961).

The magnet used in the present work did not provide a field of sufficient homogeneity to enable the true line width to be observed in the high temperature phase. It would be interesting to examine this substance using high resolution n.m.r. equipment, particularly at temperatures above and below the melting point. A change in molecular freedom must occur on melting since there is a small heat of melting and the spin lattice relaxation time exhibits a discontinuity at this point. Spin-echo measurements of the spin-spin relaxation time would also be interesting in this temperature range.

6.4.2 Spin Lattice Relaxation Times

(a) Low Temperature Solid Phase

As shown in figure 13, T_1 decreases from a value greater than 100 seconds at temperatures below 120°K to a value of approximately 0.7

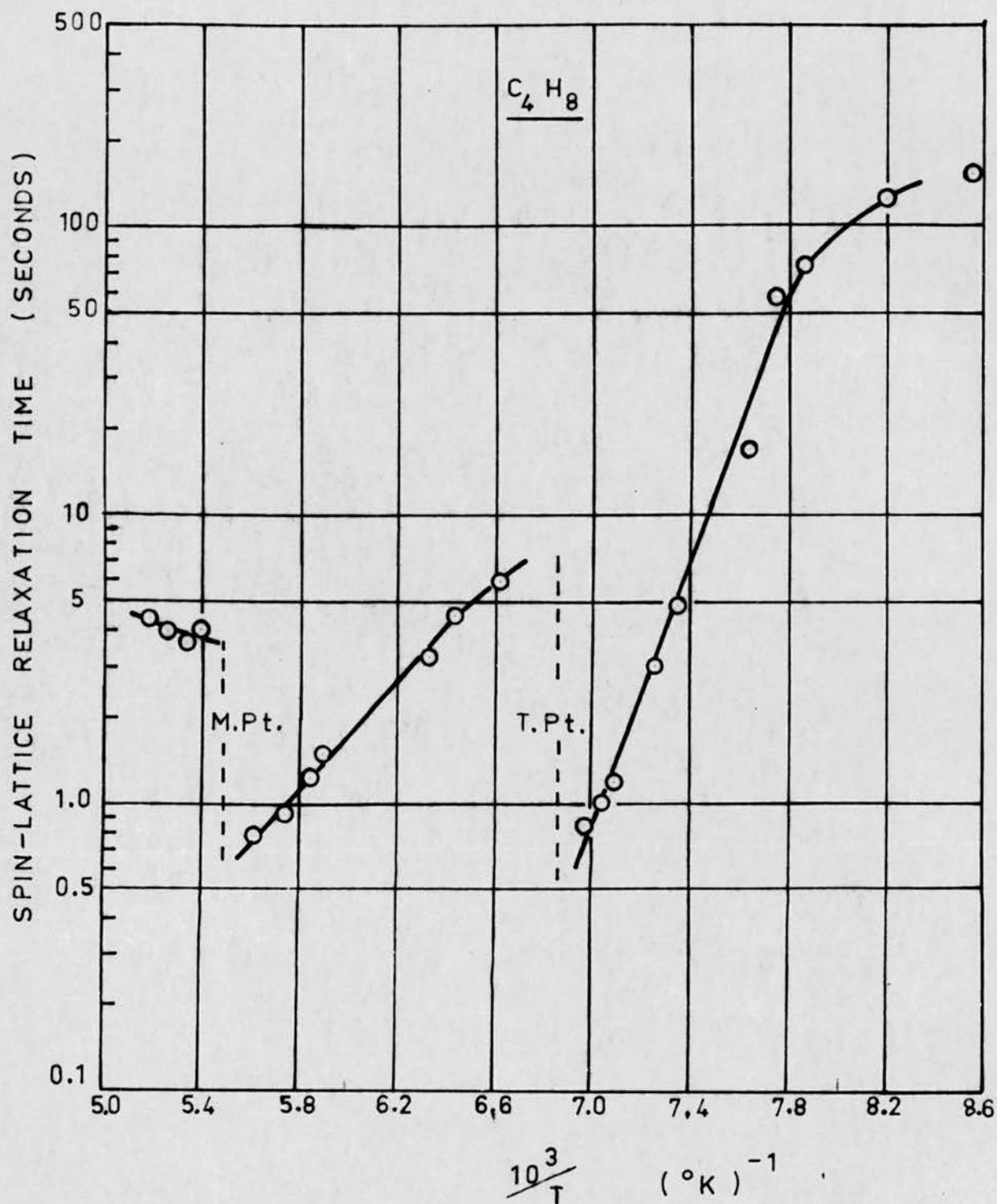


FIGURE 14.

seconds at the transition temperature, but does not reach a minimum value.

Figure 14 shows a plot of $\log T_1$ against reciprocal temperature. A least squares calculation of the slope of the straight line through the points, together with equation (5.3) yields a value of 10.5 ± 1.0 k. cal./mole. for the activation energy, E_a , of the reorientation process. This value is 2.5 times larger than the activation energy found for the reorientation process in cyclopropane and is approximately equal to the value obtained by Andrew and Eades (1953a) for reorientation of cyclohexane molecules about their three fold axes (11.0 ± 1.0 k. cal./mole.).

It would be possible to fit a curve to the line width transition using the Gutowsky and Pake (1950) expression (equation 5.4) together with the value of E_a determined from the T_1 measurements, just as was done for cyclopropane (Section 5.4.2). Instead the expression has been used to extract the values of the correlation frequency ν_c in the temperature region in which line narrowing occurs. From a plot of $\log \nu_c$ against $10^3/T$ ($^{\circ}\text{K}$) $^{-1}$ an independent value of 12 k. cal./mole. is obtained for E_a . The accuracy of this value is not high since the line narrowing occurs over a narrow temperature interval and only five line widths were measured in this region. Some change in line shape also occurred, but the calculation gives rough confirmation of the more reliable value deduced from the T_1 data.

Just as in cyclopropane in which it has been suggested (Section 5.4.2) that interactions between next nearest neighbours protons dominate

in the spin lattice relaxation process between 110°K and the melting point, it may be expected that interactions between next nearest neighbour protons in the cyclobutane molecules govern T_1 in the interval 120°K to the transition point. Since no T_1 minimum was experimentally observed an accurate check of this point cannot be made.

(b) High Temperature Region 146°K to 182.3°K (Melting Point)

A discontinuity in T_1 accompanies the phase transition, the value increasing by roughly an order of magnitude. Between the transition point and the melting point T_1 decreases steadily from about 8 seconds to 0.6 seconds. It is clear that a new process is dominant in the relaxation mechanism. From the line width observations it has been postulated that effectively isotropic reorientation accompanied by self-diffusion of the molecules is occurring. It is clearly self-diffusion which provides the important relaxation process in this temperature interval, the molecular reorientation having become too rapid.

In figure 14 a plot of $\log T_1$ against $10^3/T$ ($^{\circ}\text{K}$)⁻¹ is given. Since the points lie approximately on a straight line the activation energy, E_a' , for self-diffusion may be obtained. A least squares calculation gives a value of 4.1 ± 0.6 k. cal./mole. for E_a' .

It is possible that this value is somewhat low. Clearly over this temperature interval $\omega \tau_c < 1$ and $\omega \tau_D > 1$ where τ_c is the correlation time for molecular tumbling and τ_D is the corresponding correlation time for self-diffusion. While the importance of the one process in the relaxation mechanism decreases with increasing temperature, so the

importance of the other process increases. These overlapping effects may distort the T_1 curve so that a low value is obtained for E_a' . In favourable cases it is possible to separate the contributions from the two motions and thus obtain a more reliable value by making use of the fact that relaxation times may, with sufficient accuracy, be added as rates. This procedure has been used by Stejskal et.al. (1959) in the investigation of substituted methanes. It has not been possible in the present case but it is not expected that the error introduced is large.

Andrew (1954) has pointed out that the activation energy for self-diffusion by a vacancy mechanism, should be of the order of the lattice energy. In the high temperature solid phase the lattice energy of cyclobutane is roughly 6.0 k. cal./mole. which is somewhat larger than the experimental value for E_a' . An alternative approximate method of estimating E_a' is from the rate equation (Andrew, 1954),

$$\nu_R = f \exp \left(- \frac{E_a'}{RT} \right) \quad (6.2)$$

where ν_R is the frequency of jumping of a molecule into an adjacent vacancy and f is the vibrational frequency of the molecules in the crystal which may be taken as approximately 10^{12} c/s. In order to obtain values of ν_R the jumping frequency, a correlation time analysis of the results has been carried out.

Clearly

$$\nu_R = \frac{1}{\tau_R}$$

where τ_R is the time between random jumps.

For the case $\omega_0 \tau_R > 1$ it is necessary to use the theory developed by Torrey (1953, 1954) based on a random-walk model and which takes into

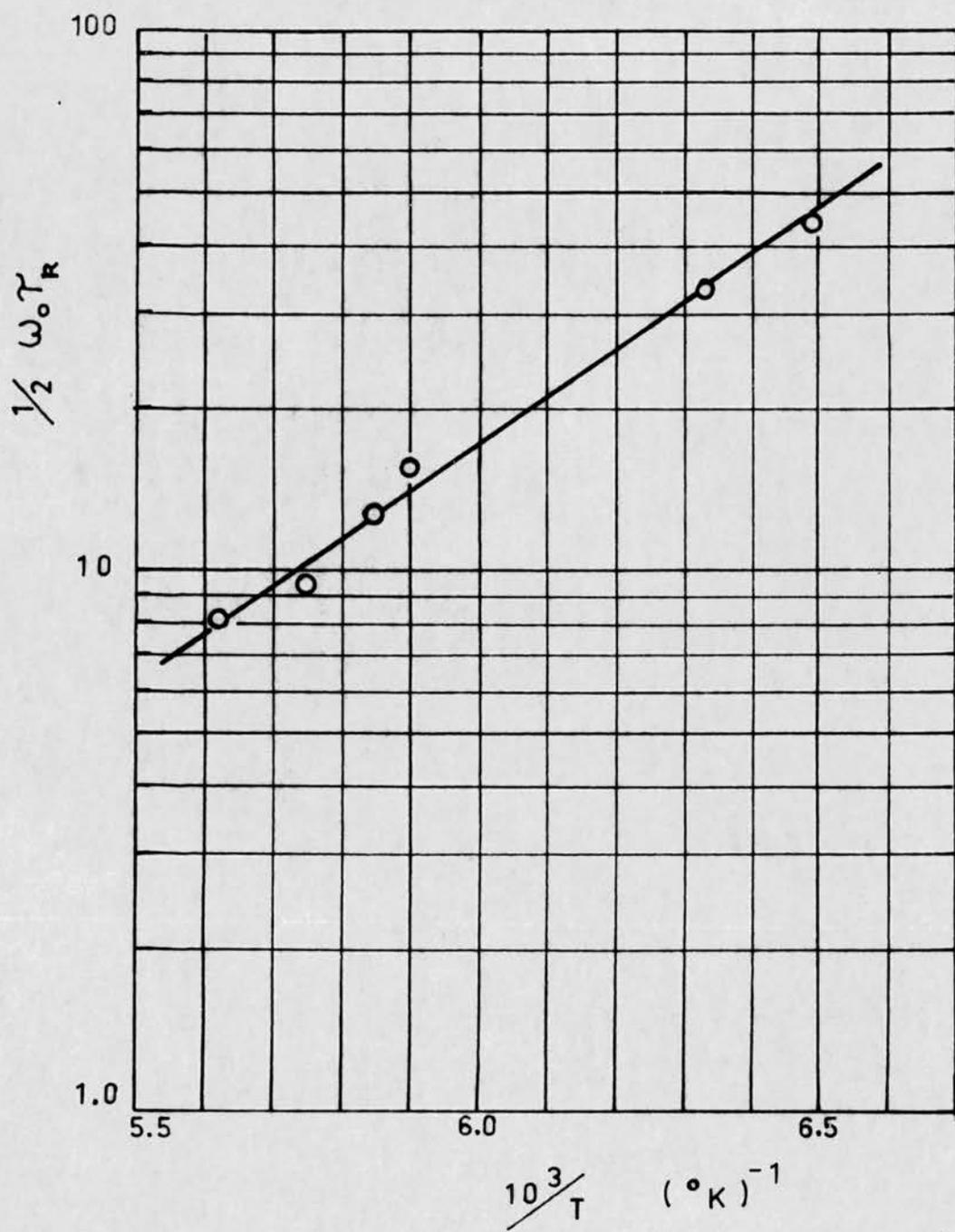


FIGURE 15.

(60)

account the microscopic features of the diffusion process (Abragam, 1961). For a b.c.c. lattice this theory yields the relationship

$$\left(\frac{1}{T_1}\right)_D = \frac{8\pi}{5} \gamma^4 \hbar^2 I(I+1) \frac{n}{kl^3\omega_0} \Phi(k, y) \quad (6.3)$$

where

$$y = \frac{1}{2} \omega_0 \gamma_R$$

$$n = 2 c a^{-3}$$

$$l = \frac{a\sqrt{3}}{2}$$

and

$$k = 0.763$$

a being the lattice spacing, c the ratio of the number of protons to lattice sites and l the distance between nearest neighbours. (The protons are considered to be clustered at the centres of mass of the molecules).

The function $\Phi(k, y)$ which depends on the spectral densities of the correlation functions has been tabulated for values of y by Torrey (1954). The values given have been corrected with sufficient accuracy over the required range using relationships derived by Torrey, since the incorrect dependence on the J_2 spectral density was originally used (Torrey, 1958).

Using the table and equation (6.3) the values of $\frac{\omega_0 \gamma_D}{2}$ corresponding to the measured values of T_1 have been determined. A semi-logarithmic plot of $\frac{\omega_0 \gamma_D}{2}$ against $10^3/T$ ($^{\circ}\text{K}$)⁻¹ is given in figure 15. The line drawn through the points has a slope corresponding to the activation energy of 4.1 k. cal./mole. found directly from figure 14. The fit is quite

acceptable.

Near the melting point the values of τ_R should be quite reliable. At 174°K the jumping frequency is approximately $7.1 \times 10^6 \text{ sec}^{-1}$. Substituting into equation (5.2) a value of 4.1 k. cal./mole. is obtained for E_a' . The good agreement with the value obtained directly from the T_1 data is to some extent fortuitous, because of the approximate value assumed for the factor f . However it does give increased confidence in the analysis.

The activation energy for self-diffusion varies fairly widely for different substances. For example in methane it is approximately 2.4 k. cal./mole., while in some substituted methanes it varies between 5 and 6 k. cal./mole. There is thus little point in seeking confirmation for the value found in cyclobutane by comparison with the limited amount of other data which is available.

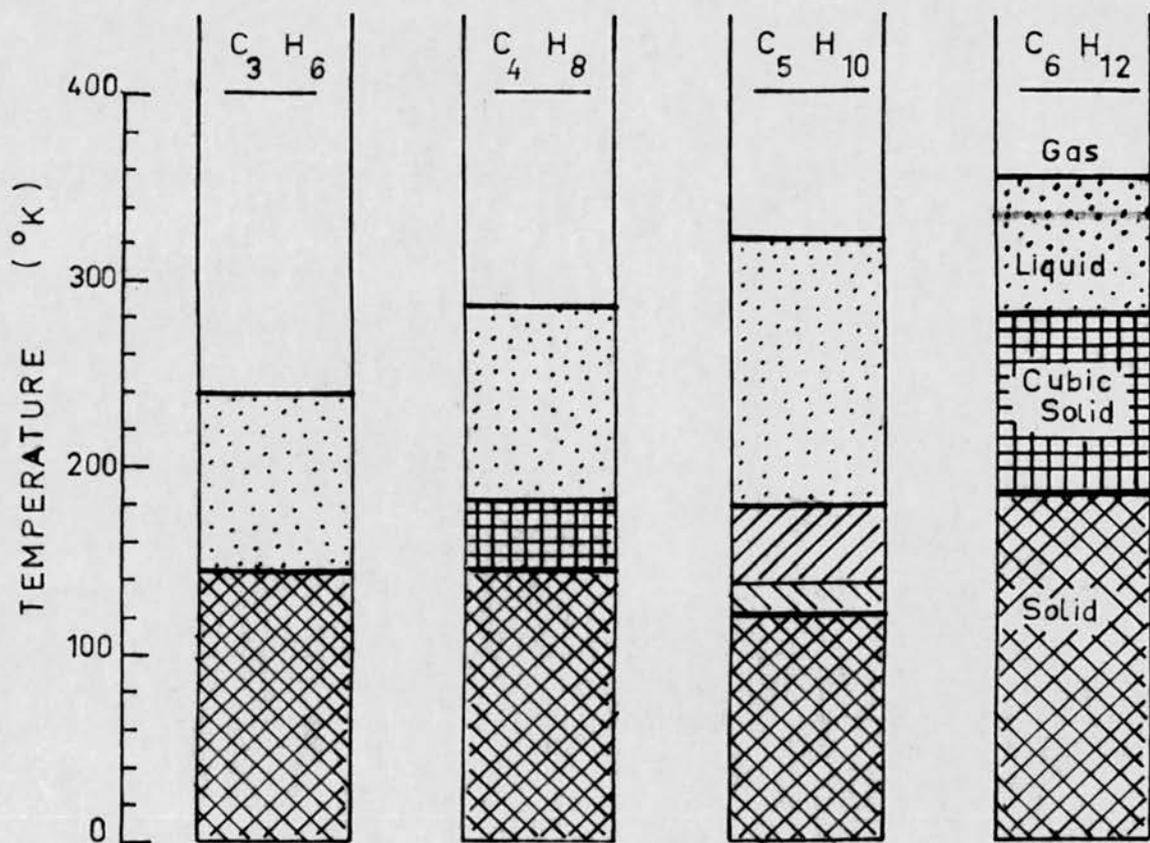
7. A BRIEF REVIEW OF THE RESULTS OBTAINED WITH
CYCLOPROPANE, CYCLOBUTANE, CYCLOPENTANE AND
CYCLOHEXANE

7. A BRIEF REVIEW OF THE RESULTS OBTAINED WITH CYCLOPROPANE, CYCLOBUTANE, CYCLOPENTANE AND CYCLOHEXANE

Four members of the homologous alicyclic hydrocarbon series, $(\text{CH}_2)_n$ ($n = 3, 4, 5, 6$), have now been studied in the solid state using n.m.r. methods. In this section a brief review of the reorientation processes will be given, with particular regard to the solid state transitions which three of these substances exhibit. Any discussion embracing these cases is necessarily mainly qualitative.

Figure 16 summarizes the data on all the phase transitions which occur in these materials. While all the molecules may be described as "globular", only the higher three exhibit rotational solid transitions. Between the transition point and the melting point C_4H_8 and C_6H_{12} crystallize in the cubic system while C_5H_{10} crystallizes in the close packed hexagonal system. These phases are generally referred to as plastic crystals because of the comparative ease with which they flow (Timmermans, 1961).

In cyclohexane and cyclobutane n.m.r. has revealed that just below the solid-solid transition points the molecules are reorienting sufficiently rapidly ($> 5 \times 10^4$ c/s) about their respective three and four fold axes, to narrow the absorption spectrum. Very similar activation energies of 11.0 and 10.5 k. cal./mole. respectively, are obtained for these processes. While the heat capacity curves are markedly different the general shape of the line width against temperature curves are very similar. (Cyclobutane exhibits a λ -transition with a region of very high heat capacity just below the transition point, while cyclohexane has a



	Transition Entropy (e.u.)	Melting Entropy (e.u.)
C_3H_6	—	8.9
C_4H_8	9.4	1.4
C_5H_{10}	9.5 0.6	0.8
C_6H_{12}	8.6	2.2

FIGURE 16.

normal first order transition). In cyclopentane the molecular motion occurs at too slow a rate ($< 5 \times 10^4$ c/s) to affect the line width although the T_1 measurements indicate that some motion does occur just below the transition temperature.

Above the solid state transitions effectively isotropic reorientation of the molecules occurs in all three cases, accompanied by self-diffusion which commences at a rate greater than 10^4 sec⁻¹ immediately for cyclobutane, very shortly for cyclopentane and at about 40° above the transition temperature for cyclohexane. The activation energies for these diffusion processes are mentioned later in this section.

In cyclopropane reorientation of the molecules about their three fold axes at a rate greater than 5×10^4 c/s occurs some 30° below the melting point. The barrier to this process is roughly 4.1 k. cal./mole. which is 2.5 times smaller than the equivalent barriers in cyclobutane and cyclohexane.

As can be seen from figure 16 the temperature range of the plastic crystal phase increases going up the series C_4H_8 to C_6H_{12} . The entropies of transition and melting are also summarized in figure 16. Leaving aside cyclopentane which exhibits two solid transitions, the proportionally larger entropy of melting in cyclohexane than in cyclobutane may be readily understood since n.m.r. has shown that there is a greater degree of molecular freedom below the melting point in the latter case than in the former. (There is also a larger increase of molecular freedom at the transition point in cyclobutane than in cyclohexane).

The n.m.r. results are clearly quite consistent with the thermodynamic data. As mentioned in Section 6.4.1 it should prove interesting to study the plastic crystal-liquid transitions using high resolution and spin echo methods.

It has been pointed out by Dunning (1961) that the van der Waals' diameters of cyclobutane, cyclopentane and cyclohexane are appreciably greater than the distances between molecular centres as measured by X-ray diffraction methods. In the case of cyclobutane for example the X-ray spacing is 5.25 \AA whereas the van der Waals' diameter of the molecule is about 6.2 \AA for both the planar and puckered forms, (the value of 5.1 \AA quoted by Dunning for the puckered form is incorrect (Dunning, 1962, private communication)). The "isotropic" reorientation process must therefore be some form of co-operative phenomenon in all cases since steric considerations preclude completely free rotation of individual molecules. Moreover if it is correct that self-diffusion occurs in these lattices, steric considerations again lead to the necessity for a comparatively large number of vacancies, in order to allow such a process to take place. (The molecular sizes and close-packing would appear to preclude the exchange or interstitial diffusion processes).

It is interesting that cyclopropane does not exhibit a solid rotational transition. It may be significant that this is the only member of this series which does not possess ring "flexibility", since this might inhibit co-operative effects. Ultimately however the problem of phase transitions is linked with the magnitude of the barriers

hindering molecular rotation and diffusion.

Pople and Karasz (1961 a, b) have suggested a theory of fusion of molecular crystals which includes the possibility of solid rotational transitions. The key parameter in this theory, ν , is a measure of the relative energy barriers for the rotation of a molecule and for its diffusion to an interstitial site. For values of ν less than a certain critical value the theory suggests that the rotational and melting transitions are separate but that when ν exceeds the critical value, the transitions coalesce.

While the model used in the theory is not physically realistic and it is not possible to estimate ν from available data, it is nevertheless interesting to consider the trends which occur in the series of substances under present consideration. In none of these cases has it been possible to estimate the activation energy for molecular tumbling from the T_g data. (Stejskal et.al. (1959) have obtained fairly reliable values for this quantity ranging between 1 and 2 k. cal./mole. for several substituted methanes in which rotational transitions occur, while the activation energies for self-diffusion in these substances were found to vary between 5 and 6 k. cal./mole.).

In cyclohexane Andrew (1954) has estimated from line width data that the activation energy for self-diffusion in the plastic crystal phase, is roughly 8.5 k. cal./mole; in cyclopentane it is between 5 and 6 k. cal./mole. while in cyclobutane a value of 4 k. cal./mole. has been obtained. It is at least plausible that in cyclopropane, which is

the most compact of all these molecules, that the activation energy for self-diffusion should be less than 4 k. cal./mole. Lattice energy considerations (Section 5.4.4) support this view. Thus if the barrier to rotation is not much less than the barrier to self-diffusion the critical value of a quantity corresponding to γ is exceeded and the rotational and melting transitions coincide.

It might prove interesting to make high pressure studies of cyclopropane. The activation energy for self-diffusion may be expected to be more pressure dependent than the activation energy for molecular tumbling, since it has been suggested that the former process involves a lattice vacancy mechanism. The rotational and melting transitions may separate at some point if the critical value mentioned above, is not greatly exceeded at zero pressure. Karasz and Pople (1961b) have tentatively suggested that a similar separation of transitions may occur in ethane at a pressure of 1900 atm.

8. ETHYLENE (C_2H_4)

8. ETHYLENE C_2H_4

8.1 The Sample

The sample was supplied by the National Chemical Laboratories, Teddington and had a stated purity of 99.9%, as determined by mass spectrograph methods, the most probable impurity being ethane. At N.T.P. the sample volume was 500 ml and it was supplied in a pyrex flask fitted with a break-tip seal.

Since the quantity of sample was convenient for the experiment, the following procedure was adopted. A suitable pyrex tube capable of extending down into the cryostat, and which terminated in a tip which fitted the resonance coil, was sealed on to the flask. A short length of pyrex capillary for use as the seal breaker was inserted in the tube and supported by a suitable constriction. The tube was pumped to a hard vacuum with occasional torching, and was sealed off. The breaker was then allowed to slide along the tube so that the seal on the flask was broken. This procedure ensured that the high purity of the sample was maintained.

8.2 Physical Data

8.2.1 Molecular Structure

It is well known that the ethylene molecule is planar with D_{2h} symmetry. The structural parameters have recently been accurately determined by electron diffraction (Bartell and Bonham, 1959) infra-red (Allen and Plyler, 1958) and Raman spectroscopic methods (Dowling and

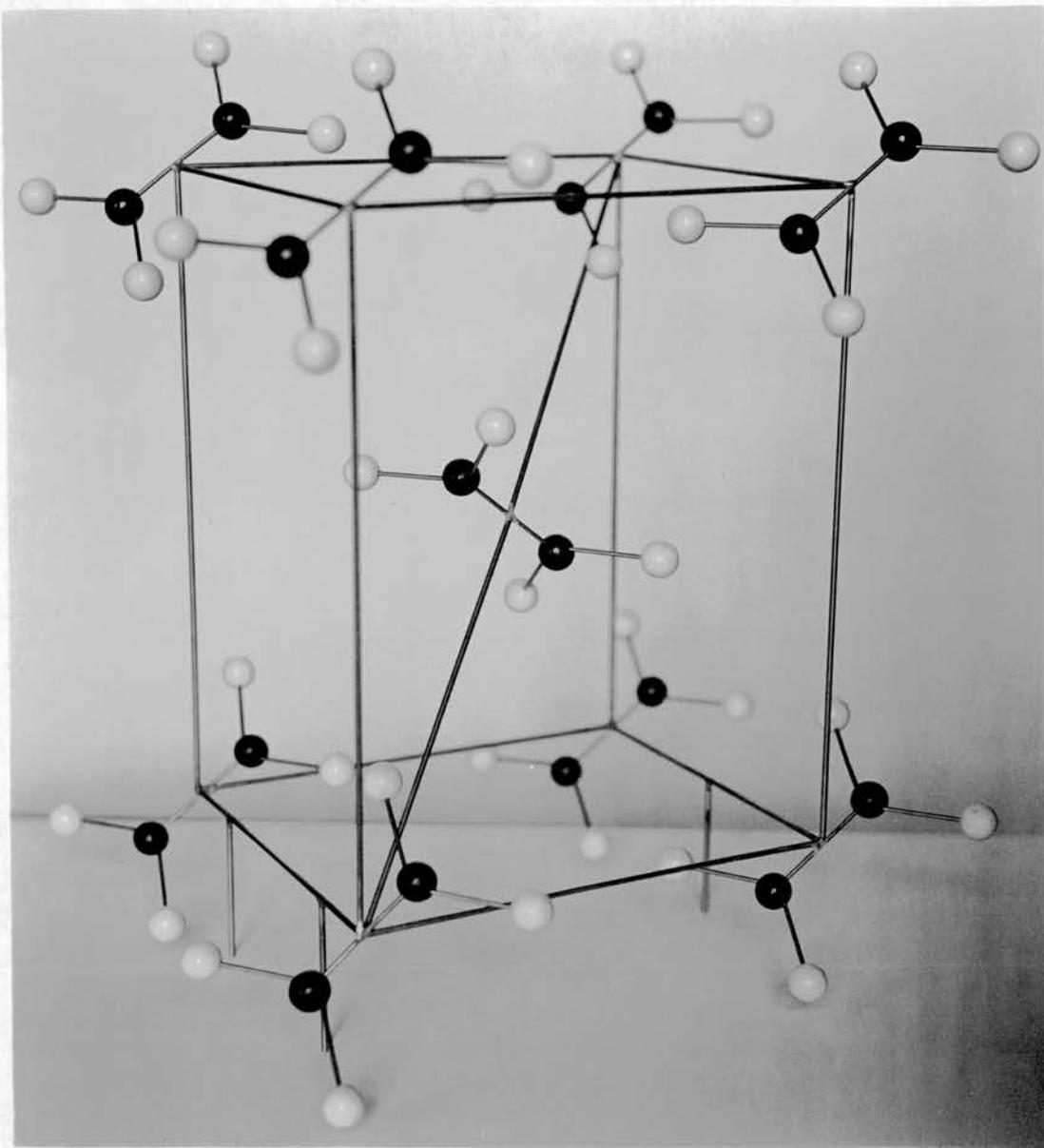


FIGURE 17.

Stoicheff, 1959). These results are summarized by Bartell and Bonham (1959).

There are slight discrepancies (greater than the estimated experimental errors) between the various values, which may in part be ascribed to the different operational definitions of the parameters. The electron diffraction results appear to involve fewer assumptions than the spectroscopic results and have accordingly been used in the calculations. The values are as follows,

$C = C$, $1.333 \pm 0.002 \text{ \AA}$; $C-H$, $1.084 \pm 0.003 \text{ \AA}$; $H-C-H$, $115.5 \pm 0.6^\circ$ (Bartell (1963, private communication) has however indicated that an electron diffraction redetermination of these parameters gives the C-H distance as much as 0.01 \AA higher than the value quoted above. No further details are yet available).

8.2.2 Crystal Structure

X-ray diffraction work (Keesom and Taconis, 1935; Bunn, 1944) has yielded information on the carbon atom lattice structure of solid ethylene. The structure is found to be orthorhombic with unit cell dimensions: $a = 4.87 \text{ \AA}$, $b = 6.46 \text{ \AA}$ and $c = 4.14 \text{ \AA}$, at $98^\circ K$. The $C = C$ bond (figure axis) in each molecule lies in the ab plane making an angle of 36° with the a axis. The two molecules in each unit cell tilt in opposite directions about the c axis. The positions of the protons could not be determined from these X-ray measurements.

An infra-red investigation of single crystals of ethylene by Brecher and Halford (1961) has yielded fresh information on this problem.

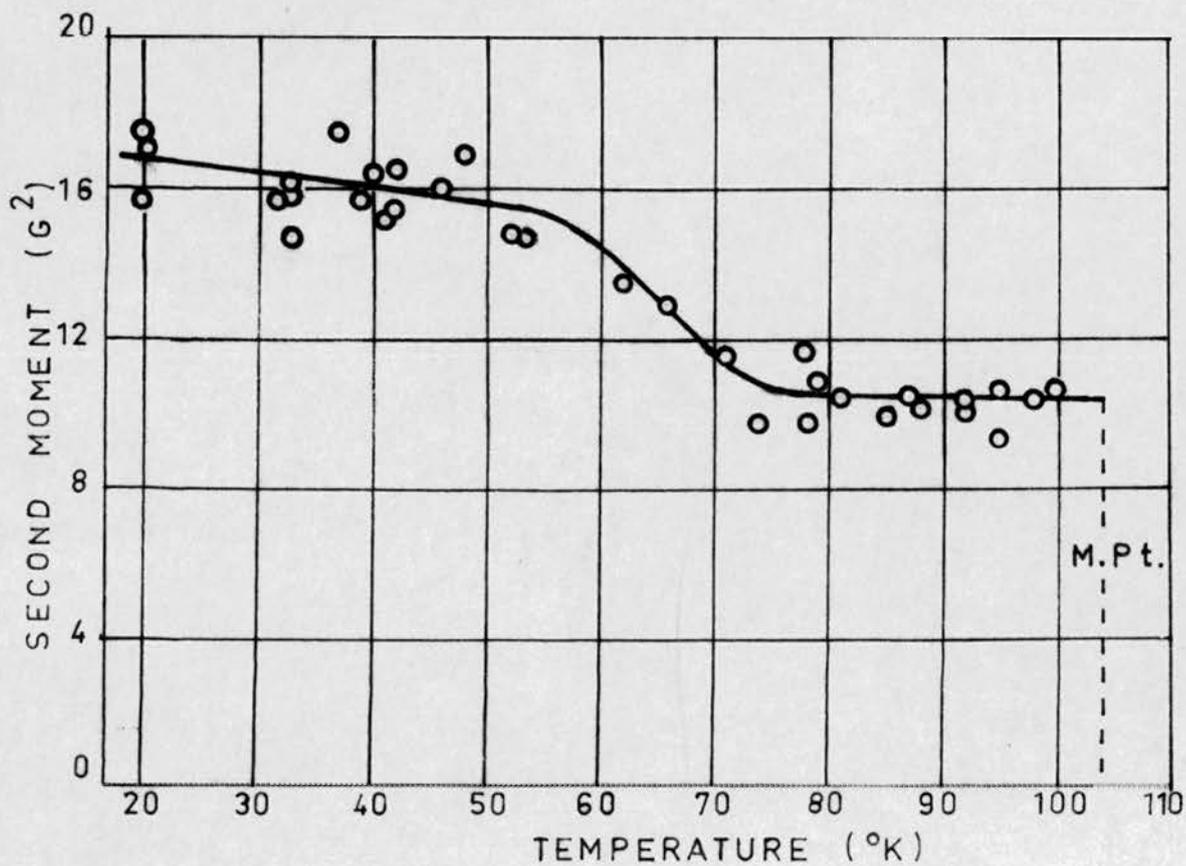
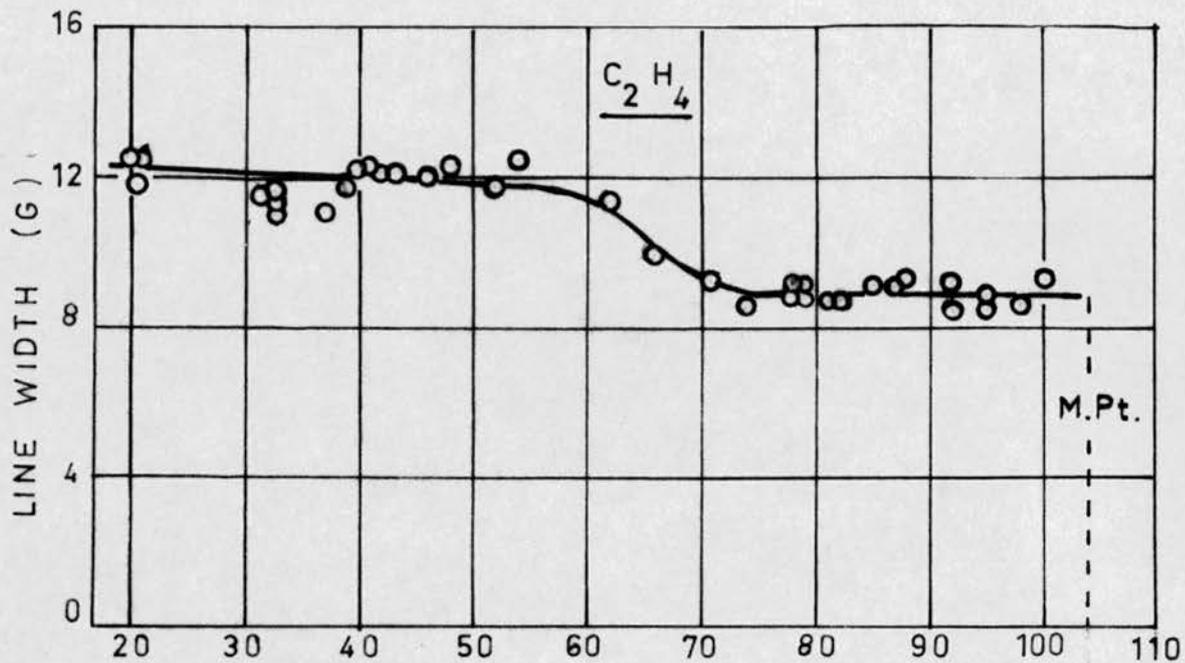


FIGURE 18.

These authors propose that the space group is $P2_1/n (C_{2h}^5)$ with the planes of the molecules perpendicular to the unit cell body diagonals. This structure is shown in figure 17. There appears to be no information concerning lattice contraction effects with decreasing temperature in this substance.

8.2.3 Thermal data

Heat capacity measurements on ethylene have been carried out by Egan and Kemp (1937) in the temperature range 15°K to the boiling point. No solid state transitions were found but there was a sharp rise in the heat capacity curve just below the melting point, which was found to be $103.95 \pm 0.05^\circ\text{K}$.

8.3 Results

8.3.1 The Absorption Spectrum

Line width and second moment values at temperatures between 20°K and the melting point are shown in figure 18. The spectra did not exhibit appreciable fine structure at any temperature.

In the temperature interval between 20°K and 70°K liquid hydrogen was used as coolant while from 70°K to the melting point liquid nitrogen was used. The experimental values above 70°K were obtained during a single experimental run while those at lower temperatures were obtained during several other runs.

8.3.2 Spin Lattice Relaxation Time

The variation of T_1 with temperature is shown in figure 19. A

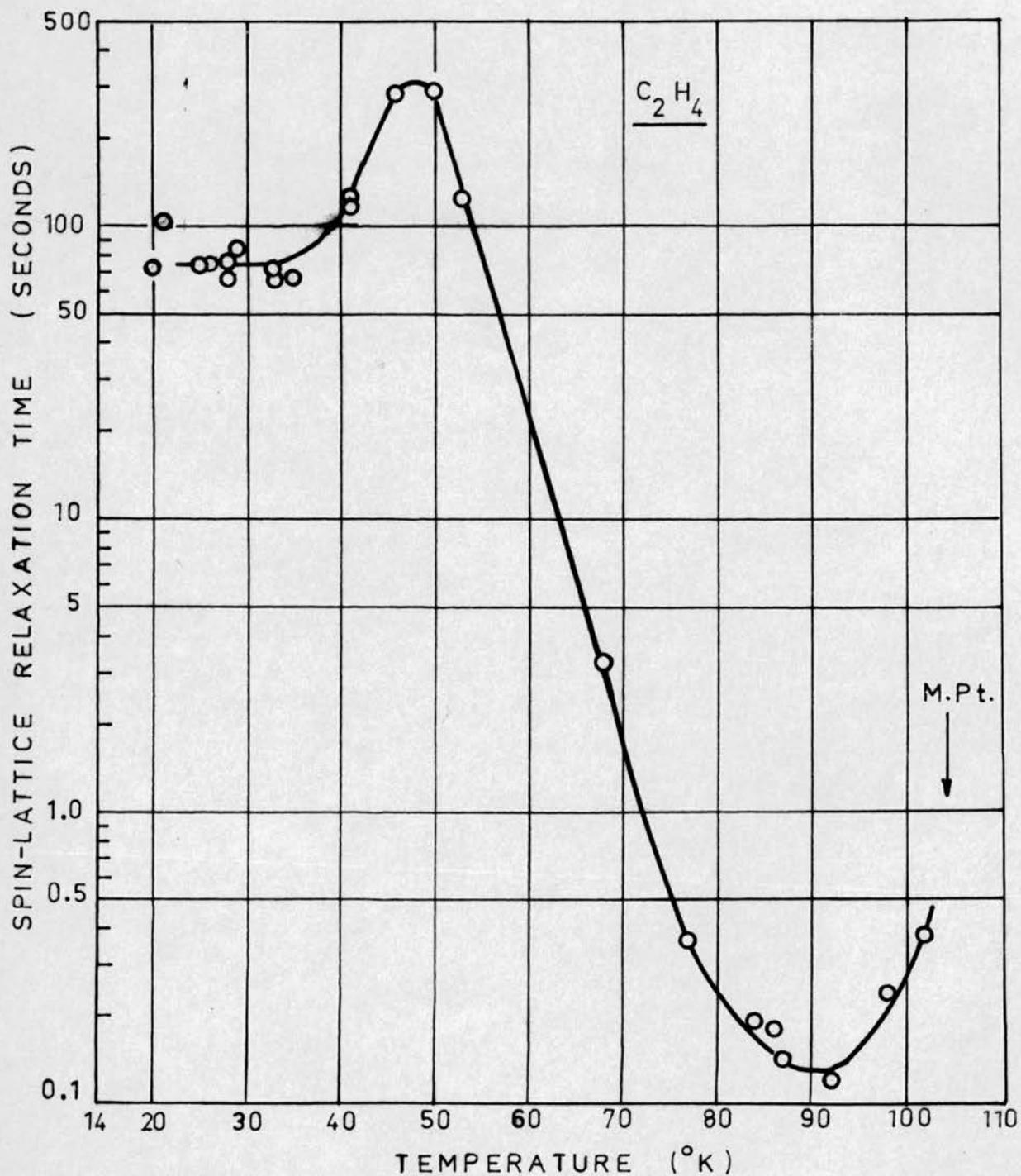


FIGURE 19.

minimum value was observed at about 90°K and also a curious anomaly below 50°K. Most of the experimental points were obtained during a single run using firstly liquid hydrogen and secondly liquid nitrogen as coolant, without allowing the sample to melt. The low temperature anomaly was checked in a separate run to ensure that it was a real effect. The minimum value for T_1 was also remeasured.

Below 60°K the direct recovery method was used while at temperatures higher than this it was necessary to use progressive saturation. In the latter case the minimum value of $\omega_m T_1$ was roughly 16 so that the conditions of Case 2 (Section 3.3) were reasonably well satisfied.

8.4 Discussion

8.4.1 The Absorption Spectrum

Using the structural parameters of Bartell and Bonham (1959) the rigid-lattice intramolecular contribution, M_2' , to the second moment is found to be 11.3 G^2 . The intermolecular contribution, M_2'' , can be reliably computed using the crystal structure data of Section (8.2.2). All inter-proton distances up to 7 \AA have been treated exactly and an integration, assuming a uniform density, has been performed for the remainder. A value of 6.2 G^2 is obtained for M_2'' at 98°K.

Two factors reduce the accuracy of the theoretical second moment value at temperatures below 40°K. Firstly the effects of lattice contraction cannot be reliably estimated. From the scant amount of evidence that is available on other crystals (e.g. cyclohexane and benzene,

Eades, 1952) a linear lattice contraction of the order of one percent may be expected for an 80° drop in temperature. This figure will be assumed as an approximate correction and this gives an intermolecular contribution of roughly 6.6 G^2 at temperatures in the region of 20° to 30°K. Secondly, large amplitude zero-point vibrations of the molecules in the lattice leads to a reduction in the intramolecular contribution by an appreciable amount, as mentioned in Section (2.2.2). This effect is particularly significant in ethylene because of the small moment of inertia of the ethylene molecule about the figure axis and the low barrier hindering reorientation of the molecules about this axis in the lattice. From the T_1 data (Section 8.4.2) it is estimated that this barrier is a little lower than 2.5 k. cal./mole.

Das (1957) has shown that the reduction in the contribution to the second moment due to a proton pair executing torsional oscillations about an axis perpendicular to the interproton vector is (equation (2.9) with $n = 2$)

$$f = \left[1 - \frac{3.1 \langle V \rangle}{V_0} \right] \quad (8.1)$$

where $\langle V \rangle$ is the average potential energy of the oscillating group and V_0 is the height of the hindering potential barrier. Assuming the molecules to be in the torsional ground state and that a harmonic oscillator approximation holds (e.g. Eyring, Walter and Kimball, 1948, p 360)

$$\langle V \rangle = \frac{1}{2} \langle E \rangle = \frac{\hbar}{2} \sqrt{\frac{V_0}{2I}} \quad (8.2)$$

where $\langle E \rangle$ is the ground state energy eigenvalue and I is the moment of

inertia of the molecule about the torsional axis.

Hence
$$f = [1 - 1.55 \frac{\hbar}{\sqrt{2IV_0}}] \quad (8.3)$$

This expression is slightly different from the expression given by Das (1957) which contained an error.

It is only necessary to consider oscillation of the whole molecule in the lattice potential in making the above correction. The barrier hindering torsion of the CH_2 groups with respect to one another is roughly 25 k. cal./mole. (Herzberg, 1945, p 277) and this process will thus produce much smaller effects.

Using equation (8.3) with the barrier height 2.5 k. cal./mole. mentioned earlier and the moment of inertia of the ethylene molecule about the figure axis, calculated with the aid of the structural data of Bartell and Bonham (1959), it is found that the intramolecular second moment is reduced to roughly 10.2 G^2 . While the torsional oscillations may be expected to affect some of the intermolecular second moment contributions as well, these reductions will be small and as an approximation will be neglected.

The total "rigid-lattice" theoretical second moment at temperatures in the region of 20° to 30°K may thus be quoted as 16.8 G^2 . It is difficult to estimate an uncertainty in this figure but taking all the factors into account safe limits are $\pm 1 \text{ G}^2$.

As can be seen from figure 18, the second moment values, while somewhat scattered, indicate a fairly marked temperature dependence in

the interval 20°K to 50°K. This is to be expected since an increasing number of molecules will be excited into torsional states higher than the ground state as the temperature is raised. An even larger reduction in second moment than is predicted by equation (8.3) will thus occur. Lattice expansion also plays a part in the temperature dependence.

The absorption spectra measurements were made before the T_1 measurements and, to ensure that no saturation was occurring, most of the spectra were run in the temperature interval 30-50°K. In fact evidence has been obtained that T_1 is considerably shorter at 20°K than at 40°K. It is desirable that further spectra be run at 20°K since at this temperature the reduction factor given by equation (8.3) should be fairly reliable. (Only 1 in 10^4 molecules are not in the vibrational ground state at 20°K while at 40°K this ratio has become 1 in 10^2).

From figure 18 it can however be seen that at 20°K the second moment has a value in the neighbourhood of 16.8 G^2 in good agreement with the "rigid-lattice" theoretical value. In view of the small amount of data at this temperature and the uncertainty in the theoretical intermolecular contribution, mentioned above, it is only possible to state that these measurements roughly confirm the molecular structure of Bartell and Bonham (1959).

Between 50°K and 70°K the spectrum appears to narrow indicating that some form of molecular reorientation is occurring at a rate greater than about 5×10^4 c/s. The steady value of the second moment attained between 70°K and the melting point is 10.6 G^2 .

There are three two fold axes in each molecule about which reorientation may occur. The moment of inertia of the molecule about the figure (C = C) axis is a factor six times smaller than the maximum moment of inertia. Motion about the figure axis only involves the hydrogen atoms and it may be considered the most likely possibility. Ultimately of course the form of motion depends on the relative magnitudes of the hindering potential barriers. (It seems unlikely that simultaneous reorientation about two axes would occur since this would approximate to isotropic reorientation).

Reorientation about any of the three diad axes produces a negligible reduction in the intramolecular contribution, M_2' . Using the two fold reduction factor (equation 2.8) it is found that for 180° flip reorientation about the figure axis (and allowing also for the effects of the rapid molecular oscillations about each mean position) M_2' has the reduced value of 9.9 G^2 . The reduction in the intermolecular contribution produced by this motion is more difficult to compute but an estimate of $4 \pm 1 \text{ G}^2$ at 98°K has been arrived at using the generalised reduction factor of Andrew and Eades (1953a). Details are given in Appendix 1. It is expected that motion about either of the other two diad axes would give a similar reduced intermolecular contribution, but these calculations have not been carried out. Free classical rotation of the molecules about their figure axes may be ruled out since at all temperatures the barrier height was more than an order of magnitude greater than RT. (This process would give a total reduced second moment

of less than 7.9 G^2).

The theoretical second moment for the case of 180° flip reorientation about the figure axis is thus $13.9 \pm 1 \text{ G}^2$ at 98°K . This is considerably higher than the experimental value of 10.6 G^2 . This discrepancy may in part be attributed to the fact that the effects of molecular vibrations have been under-estimated. Some doubt must however be expressed about the experimental values in this region. Gutowsky, Kistiakowsky, Pake and Purcell (1949) investigated the absorption spectrum of ethylene at a single temperature, 90°K , and obtained a value of 13.1 G^2 for the second moment. This is considerably closer to the theoretical estimate given above.

It is possible that in the present investigation the sample may not have been truly polycrystalline in the temperature interval 70°K to the melting point. As stated earlier, all the points in this interval were obtained during a single run. Cooling of the sample may have been carried out too slowly so that fairly large single crystals were formed. (Ethylene has a melting point only 27° above the liquid nitrogen boiling point and cooling of the sample was effected by means of exchange gas in the cryostat). In the readings taken using liquid hydrogen as coolant, the sample was cooled more rapidly and was thus probably more truly polycrystalline. Unfortunately the above possibilities only became apparent after the experimental readings had been completed.

It is desirable that the measurements between 70°K and the melting

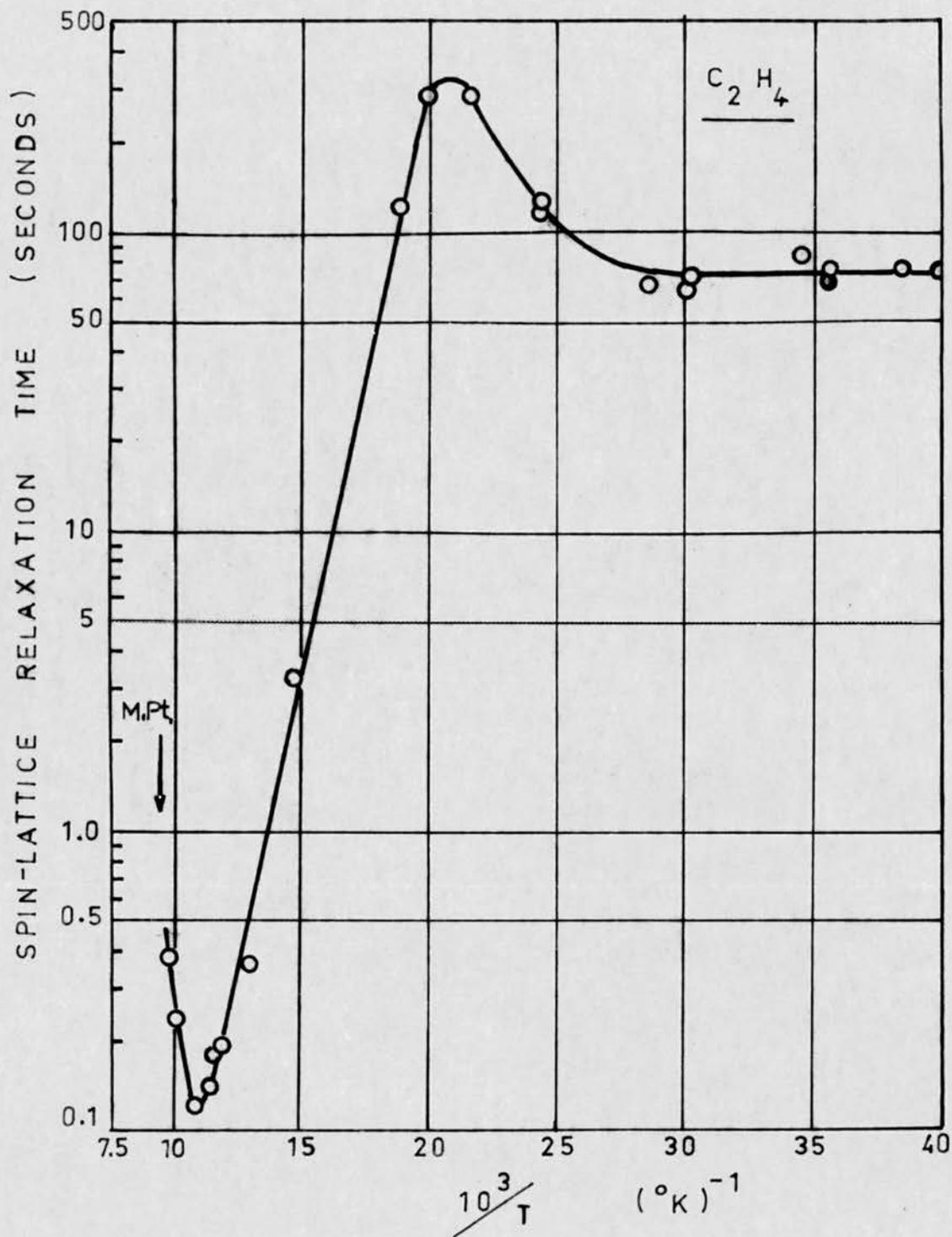


FIGURE 20.

point be repeated preferably after having frozen the sample using liquid hydrogen as coolant. A check on the polycrystallinity could be carried out by observing the spectra for various orientations of the sample in the magnetic field to ensure that there was no anisotropy.

No definite conclusions concerning the form of molecular motion near the melting point can be made at present. It seems, in any case, unlikely that the second moment data can ever provide unambiguous evidence on this point because of the relatively small overall reduction which is predicted. Nevertheless it can be stated that some form of motion does occur at a rate greater than about 5×10^4 c/s at temperatures above 60°K. It is clearly not isotropic reorientation of the molecules since this would reduce the second moment to $1.3 G^2$ in this case. The most likely form of reorientation consistent with the evidence is about the two fold molecular figure axis.

8.4.2 Spin Lattice Relaxation Time

As may be seen from figure 19 T_1 exhibits quite normal behaviour above 50°K and is consistent with the line width data. The minimum value of T_1 is 0.12 seconds at a temperature of 91°K. This minimum value is somewhat higher than has been observed in other solid hydrocarbons and the reasons for this will be discussed later in this section. Below 50°K an anomalous drop from 300 seconds to an apparently steady value of about 75 seconds was observed. This curious behaviour will also be discussed later.

In figure 20 a semi-logarithmic plot of T_1 against $10^3/T$ (°K)⁻¹

ETHYLENE

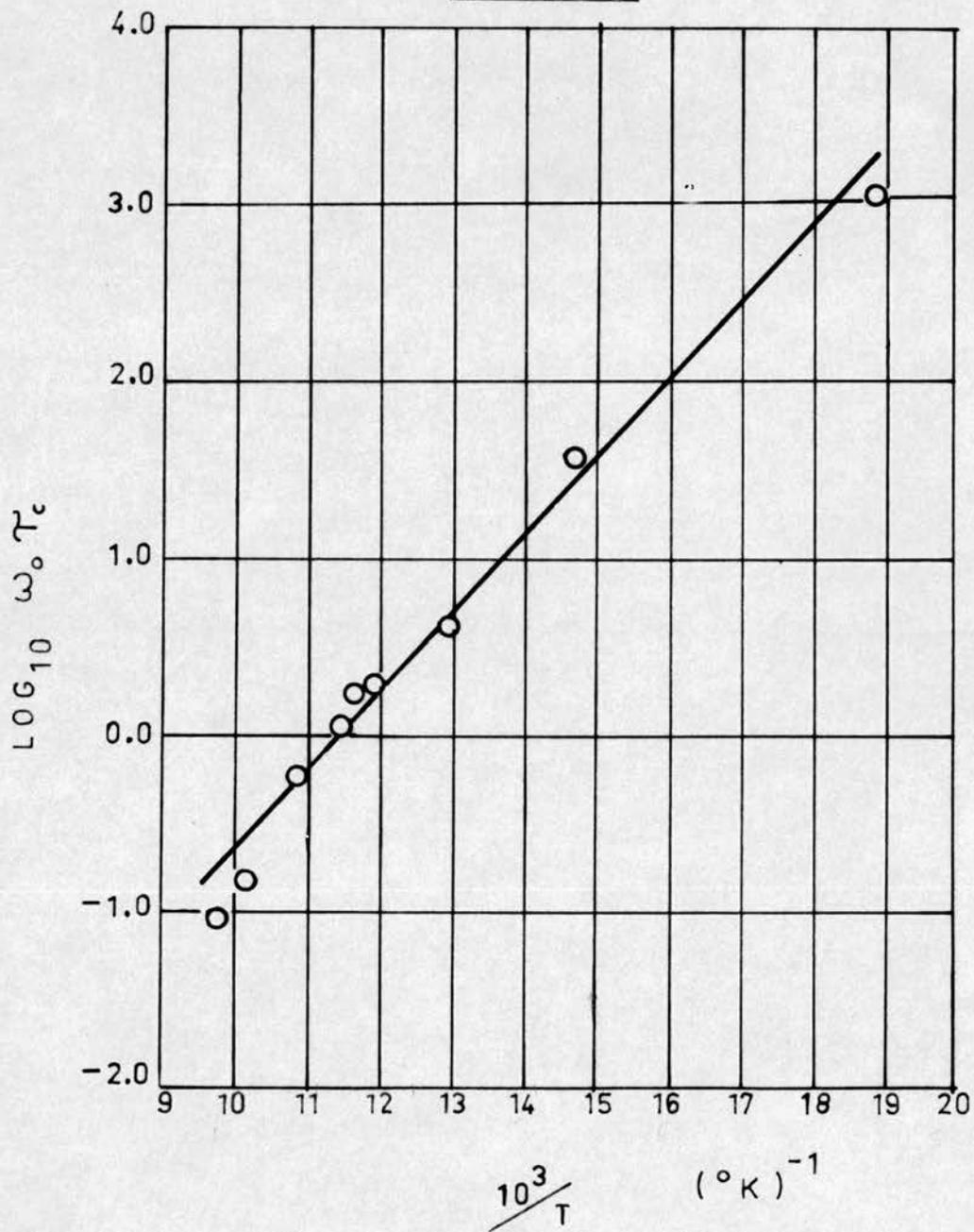


FIGURE 21.

is shown. From the limited number of points in the straight line region it is possible to obtain the activation energy, E_a , of the reorientation process. With the aid of equation (5.3) a value of about 1.9 k. cal./mole. is found.

Since a minimum was observed, and making the assumption that the reorientation process may be described by a single correlation time τ_c and that equation (2.10) applies, it is possible to obtain the value of the constant C_1 from the value of $(T_1)_{\text{Min}}$. The B.P.P. theory (equation 2.10) yields the relationship

$$\left(\frac{1}{T_1}\right)_{\text{Min}} = C_1 \times \frac{1.42}{\omega_0} \quad (8.4)$$

Using the value of C_1 thus obtained it is possible to deduce values of τ_c from the measured T_1 values. Figure 24 shows a plot of $\log_{10} \omega_0 \tau_c$ against $10^3/T$ ($^{\circ}\text{K}$)⁻¹ in the temperature interval 50 $^{\circ}\text{K}$ to the melting point. The slope of the straight line through the points gives a value of 2.0 ± 0.3 k. cal./mole. for E_a . The points do not lie on a good straight line and it seems likely that the simple expression for a thermally activated process (equation 5.1) does not strictly apply. In part this may be due to the effects of lattice expansion with rising temperature since this reduces the hindering potential barrier which is entirely intermolecular in origin. A more interesting possibility which must be considered is that of molecular reorientation by quantum mechanical tunnelling through the hindering potential barrier.

Tunnelling has been suggested as a possibility in several other substances (e.g. Sachs, 1949; Tomita, 1953; Powles and Gutowsky, 1955),

and must be considered whenever a system of protons is undergoing reorientation about a symmetry axis. Powles and Gutowsky (1955) have carried out a theoretical and experimental investigation of the importance of reorientation by tunnelling in the case of the methyl group. This work has been extended by Stejskal and Gutowsky (1958) and Stejskal, Woessner, Farrar and Gutowsky (1959). Das (1956, 1957) has given a generalised theoretical treatment of the tunnelling process in solids.

As is well known, the rate of barrier penetration by tunnelling depends on the area under the hindering potential barrier (i.e. it depends on the height and width of the barrier). For significant tunnelling effects to occur at low temperatures a low barrier, with an axis of as high a symmetry as possible, is advantageous. In favourable cases n.m.r. has shown that methyl group reorientation by tunnelling can persist down to very low temperatures ($< 20^{\circ}\text{K}$) at a rate sufficiently high to narrow the absorption spectrum (Lawrenson and Rushworth, 1959; Andrew, Eades, El Saffar and Llewellyn, 1960). While the relatively clear cut effect of tunnelling on the absorption spectrum may be readily understood, the relationship between the tunnelling frequencies and T_1 is probably more complex and this point has been discussed by Stejskal and Gutowsky (1958).

The problem of tunnelling in ethylene will be considered using the approach outlined by Powles and Gutowsky (1955), Stejskal and Gutowsky (1958) and Das (1957). The only possibility that need be consider is tunnelling of whole molecules, through the hindering lattice potential,

about their figure axes. The moment of inertia of the molecules about this axis is $5.64 \times 10^{-40} \text{ g cm}^2$ which is not much larger than that of the methyl group about its three fold axis ($5.34 \times 10^{-40} \text{ g cm}^2$).

The barrier hindering reorientation of the molecules in the lattice is assumed to be of the form

$$V = \frac{V_0}{2} (1 + \cos 2\phi) \quad (8.5)$$

where V_0 is the height of the barrier and ϕ is the angular coordinate referring to the molecular reorientation. As an approximation this barrier is assumed to be time and temperature independent. Neither of these assumptions is strictly valid and the barrier may not in fact be sinusoidal. Substituting the potential function given by equation (8.5) into the Schrodinger equation the two-nodal Mathieu equation is obtained

$$\frac{d^2 M(\phi)}{d^2 \phi} + \left[a - \frac{S}{2} \cos 2\phi \right] M(\phi) = 0 \quad (8.6)$$

where $M(\phi)$ is the wave function and

$$a = \frac{2I}{\hbar^2} \left[E - \frac{V_0}{2} \right]$$

$$S = \frac{2I}{\hbar^2} V_0$$

For $a \ll S$, (8.6) approximates to the harmonic oscillator equation while for $a \gg S$ it approximates to that of the rigid rotator. The general solution is not simple but fortunately very complete tables of solutions exist for the two-nodal equation viz: Tables Relating to Mathieu Functions (Columbia University Press, N.Y., 1951). These tables have been extended by Blanch and Rhodes (1955). In the tables the solutions

are given for the equation in the form

$$\frac{d^2 M(\phi)}{d^2 \phi} + (b - S \cos^2 \phi) M(\phi) = 0 \quad (8.7)$$

Equation (8.6) is obtained from (8.5) by making the substitution $\cos 2\phi = 2 \cos^2 \phi - 1$ and with $a = b - \frac{S}{2}$.

A set of pairs of torsional energy levels is obtained. The wave function of the lower energy level in each pair is antisymmetric with respect to inversion in the origin while the upper one is symmetric (Herzberg, 1945, p 225; Eyring, Walter and Kimball, 1944, p 310). It can be shown that the rate of barrier penetration by tunnelling is given by the splitting of each torsional pair (Eyring, Walter and Kimball, 1944, p 310). With the aid of the tables mentioned above the required splitting for the m 'th torsional state is

$$\frac{\hbar}{4\pi I} \Delta a_m = \frac{\hbar}{4\pi I} (b_{o_{m+1}} - b_{e_m}) \quad (8.8)$$

in frequency units. The tables are available for $m = 0$ to 15.

An average tunnelling frequency may be defined by the relationship

$$\bar{\nu}_t = \frac{\sum_{m=0}^{\infty} \nu_m \exp\left(-\frac{\bar{E}_m}{kT}\right)}{\sum_{m=0}^{\infty} \exp\left(-\frac{\bar{E}_m}{kT}\right)} \quad (8.9)$$

where ν_m is the tunnelling frequency for the m 'th pair of levels and \bar{E}_m is the mean energy of the pair. (Equation (8.9) corresponds to weighting the tunnelling frequency for each pair with the probability of a molecule being in this torsional state). Stejskal and Gutowsky (1958) have

pointed out that there are several objections to the use of equation (8.9), particularly when the higher torsional states become important. They remark that the best test of its validity is comparison with experiment.

Using equation (8.9) and the extended tables of Blanch and Rhodes (1955) the average tunnelling frequency has been calculated as a function of temperature for two barrier heights $V_0 = 2$ k. cal./mole. (700 cm^{-1}) and $V_0 = 2.5$ k. cal./mole. (825 cm^{-1}). In figure 22 $\log_{10} \nu_t$ is plotted against $10^3/T$ ($^{\circ}\text{K}$) $^{-1}$ for these two cases (full lines). Although the tables give the parameters to eight decimal places (nine or ten significant figures for the higher torsional states) they do not give the ground state splittings with sufficient accuracy in either case. Recourse has been made to the expression of Goldstein (1929) (quoted by Das, 1957). For the m 'th state the splitting is given by

$$\Delta b_m = \frac{2^{3m+4}}{\pi^{\frac{1}{2}} m!} S (2m+3)/4 \exp(-2S^{\frac{1}{2}}) \left(1 + \frac{C_1}{S^{\frac{1}{2}}} + \frac{C_2}{S} + \dots\right) \quad (8.10)$$

For the ground state ($m = 0$), $C_1 = -0.43$, and $C_2 = -0.19$. Using (8.10) accurate values of the ground state splittings were obtained which were consistent with the less accurate values obtained directly from the tables.

For the 2.0 k. cal./mole. barrier the ground state tunnelling frequency is found to be 2.4×10^3 c/s while for the 2.5 k. cal./mole. barrier it is 2.3×10^2 c/s. These frequencies are insufficient to narrow the absorption spectrum so that it attains its full width at very

low temperatures (apart from the zero point vibrational correction). The tunnelling frequency increases rapidly for the higher torsional states and thus this process may be expected to play an important role in the molecular reorientation at higher temperatures.

For the energy states above the barrier a classical expression may be used to describe the rotation. Das (1957) has given such an expression for the probability of transition from one well to another,

$$W = \frac{1}{2\pi} \left(\frac{V_0}{2I} \right) \exp \left(- \frac{V_0}{kT} \right) \quad (8.11)$$

The calculated reorientation frequencies at temperatures near the melting point have been checked with the aid of this expression, as has the infinite temperature limit, and good agreement obtained.

In order to compare the tunnelling theory predictions with experiment it is necessary to calculate reorientation frequencies from the T_1 data. Stejskal and Gutowsky (1958) have given a fairly lengthy discussion of this point. The simplest way of doing this is to assume that the motion may be described by a single correlation time, τ_c , and that an exponential form for the correlation function of the random motion may be used as is done in the B.P.P. theory. This leads to a Debye spectral density function which is the basis of equation (2.10). As will be mentioned later it is likely that the interactions between diagonally opposite protons in each molecule and the intermolecular interactions dominate in the spin lattice relaxation process. It will nevertheless be assumed that the B.P.P. theory may be applied and that the correlation time analysis carried out earlier in this section is

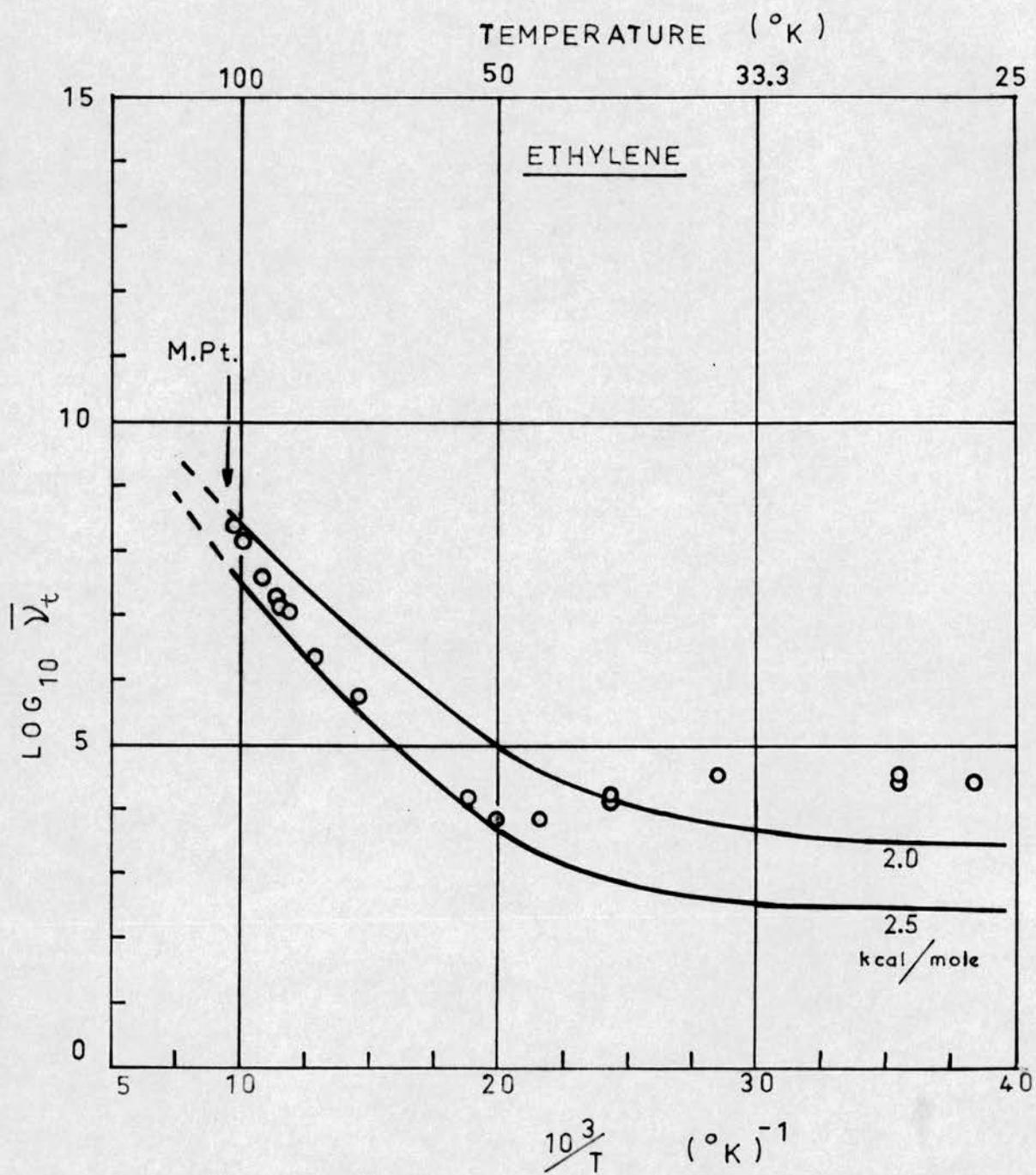


FIGURE 22.

valid. It will also be assumed that the relationship

$$\tau_c = \frac{1}{2\pi\nu_t} \quad (8.12)$$

may be used (unlike the three nodal case in which nearest neighbour interactions are most important and $\tau_c = \frac{1}{3\pi\nu_t}$ (Powles and Gutowsky, 1955)). This approach should be accurate enough for an order of magnitude comparison between theory and experiment.

Apparent tunnelling frequencies ν_t have been deduced from the relaxation times in this way and are plotted in figure 22. In the interval between 50°K and the melting point there is quite reasonable agreement with the theoretical predictions and a barrier height of about 2.4 k. cal./mole. is indicated. It is to be expected that the true barrier height should be higher than the apparent activation energy (even with the zero point energy of 0.2 k. cal./mole. included) when barrier penetration by tunnelling is occurring. The fact that the points curve more rapidly than the theory predicts may be partly explained by the temperature dependence of the barrier as a result of lattice expansion. Below 50°K the T_1 anomaly occurred and the points depart from the theoretical predictions.

In fact the relationship between T_1 and the tunnelling frequency may be rather complex especially at low temperatures when most of the molecules are in the lower torsional states. The Fourier spectral intensities of the position functions may not approximate to the Debye function and could quite conceivably possess structural features. Stejskal and Gutowsky (1958) have suggested that "tunnelling resonances"

may occur for certain values of the Larmor frequency. These authors furthermore point out that the mechanism by which energy is exchanged between spin system and lattice also needs careful consideration. Further mention of these points is made in Section (9.4.2) in the discussion of the results obtained on methyl group tunnelling in n-butane.

It must be stressed that the plotted points in figure 22 are only the apparent tunnelling frequencies. The values below 50°K clearly show that the simple theory is inadequate in this range.

Further experiments are required to investigate the anomaly in T_1 below 50°K. Firstly it is desirable that T_1 measurements be carried out on another sample of ethylene to ensure that it is a real phenomenon in this substance. It is difficult to see how any form of impurity could cause the effect. Smith (1962) has observed an anomalous minimum in the T_1 data of Hexamethylenetetramine at a temperature of 250°K. This was shown to be caused by a 0.1 percent impurity of water molecules which were diffusing rapidly through the host lattice. Heat treatment of the sample removed the water impurity and the sample then behaved normally.

At temperatures below 50°K it is most unlikely that self-diffusion of any proton bearing impurity through the ethylene lattice would occur. (The presence of H_2 impurity seems unlikely from the supplied purity data and in any case would not be condensed). The most probable impurity is 0.1 percent ethane. While methyl group reorientation in this molecule could persist down to these temperatures the reorientation rate

(and concentration) would appear to be too low to produce such a marked anomaly. Paramagnetic impurity would also not be expected to produce the anomalous behaviour.

Assuming for the moment that the effect is characteristic of pure ethylene then it is necessary that some form of molecular motion be responsible. It has been suggested that there are two forms of molecular motion occurring. Firstly there is the 180° flip reorientation about the molecular figure axis by tunnelling through the hindering barrier with an average frequency in the region of 10^3 c/s at 20°K . Secondly there are the associated relatively large amplitude torsional vibrations with a frequency of 5×10^{12} c/s in the ground state. It must be conjectured that one or other of these processes produces a greater Fourier spectral intensity in the neighbourhood of the Larmor frequency at 20°K than at 50°K . It is difficult to see how the tunnelling process could produce such an effect. As the temperature is lowered an increasing number of molecules occupy the torsional ground state so that a region of constant T_1 may be expected, but without the observed decrease. (It is unlikely that any drastic change in barrier shape could occur in this interval). It is conceivable that some combination of torsional and lattice vibrations could be responsible for the effect, becoming more important at low temperatures when most of the molecules are in the torsional ground state. There appears to be relatively little known about such processes and further experiments are clearly required over as wide a range of Larmor frequency as possible.

It would also be interesting to carry out an investigation of partially deuterated ethylene molecules such as $\text{CHD} = \text{CHD}$. High purity samples of this substance are commercially available. The weighting of the molecule would make tunnelling a much less important process.

Finally in this section it is necessary to consider the value of (T_1) min. The observed value was 0.12 seconds which is a factor five times higher than is predicted by the B.P.P. theory for the case of random molecular reorientation.

Holcomb and Pedersen (1962) have performed T_1 measurements on a single crystal of $\text{Ca SO}_4 \cdot 2\text{H}_2\text{O}$ and on $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ powder. They showed that 180° flip reorientations of the water molecules provided the relaxation mechanism. As mentioned in Section (2.2.1) for an isolated proton pair interchange of the two nuclei produces no change in the interaction because of the symmetry properties of the triplet state. Holcomb and Pedersen (1962) carried out theoretical calculations for a four spin system consisting of two pairs undergoing 180° reorientations (approximating to a favourable orientation of the $\text{Ca SO}_4 \cdot 2\text{H}_2\text{O}$ crystal). While the singlet-triplet representation is no longer a good one they showed that the relaxation was due to interpair rather than intrapair dipolar interactions. (Correspondingly the only effect on the absorption spectrum is a slight narrowing due to the decrease in the interpair interactions produced by the motion).

For ethylene molecules performing 180° reorientations (about their $\text{C} = \text{C}$ axes) it can be seen by performing classical averages over the

various position functions that only the interactions between diagonally opposite protons in each molecule and the intermolecular interactions, will be responsible for the relaxation process. Interactions between nearest neighbours in each molecule only become effective when random motion is occurring. The high value of the T_1 minimum is thus consistent with the proposed form of molecular reorientation. Quantitative calculations for relaxation in single reorienting ethylene molecules are under consideration.

9. n-BUTANE ($n\text{-C}_4\text{H}_{10}$)

9. n-BUTANE $n\text{-C}_4\text{H}_{10}$ 9.1 The Sample

As in the case of ethylene the sample was supplied by the National Chemical Laboratories, Teddington. The stated purity was 99.97% as determined by mass-spectrograph and gas chromatography methods. The only detectable impurity was 0.03% iso-butane.

Since n-butane is gaseous at room temperature it was supplied at atmospheric pressure in a 500 ml pyrex flask with break-tip seal. Exactly the same procedure was followed as was used in adapting the ethylene sample for investigation (Section 8.1).

9.2 Physical Data9.2.1 Molecular Structure

n-butane is a saturated normal hydrocarbon and the bond lengths and bond angles may be expected to conform to the usual values found for this type of molecule. Reference to Tables of Interatomic Distances (Chemical Society Special Publication No. 11, 1958) gives the following values

$$\text{C} - \text{C} = 1.54 \text{ \AA}; \text{C} - \text{H} = 1.10 \text{ \AA},$$

with all the angles tetrahedral.

9.2.2 Thermal Data

Heat capacity measurements on n-butane have been made by Aston and Messerly (1940). A first order solid state phase transition was observed at $107.56 \pm 0.10^\circ\text{K}$ while the melting point was found to be $134.87 \pm 0.05^\circ\text{K}$. The data gives:-

Entropy of Transition = 4.6 e.u.

Entropy of Fusion = 8.25 e.u.

The entropy values indicate that the high temperature solid phase does not belong to the plastic crystal classification. Timmermans (1961) has given a rough upper limit of 5 e.u. for the entropy of fusion of plastic crystals and it is often considerably lower than this (c.f. cyclobutane).

9.2.3 Crystal Structure

The crystal structure of n-butane does not appear to have been studied directly in either of the two solid phases. X-ray crystallographic studies have been carried out on other members of the n-paraffin series, $n\text{-C}_N\text{H}_{2N+2}$, for various N values between 5 and 36, notably by Miller (1928, 1930, 1932), Miller and Lonsdale (1948), Mazee (1948) and Smith (1953). All the evidence relating to the structures, including geometrical close packing arrangements, is given by Kitaigorodskii (1961, pp. 187-207). It appears that there are four crystalline modifications. In all of them the molecular axes are aligned parallel and the carbon atoms form a planar zigzag structure in the crystal.

For N even and between 8 and 24 the structure is triclinic. (For odd N the structure is orthorhombic). The reasons for the differences in structure are readily explained by the differences in molecular symmetry and a recent discussion of this point has been given by Mnyukh (1963).

For odd $N \geq 9$ a solid rotational transition is exhibited near the

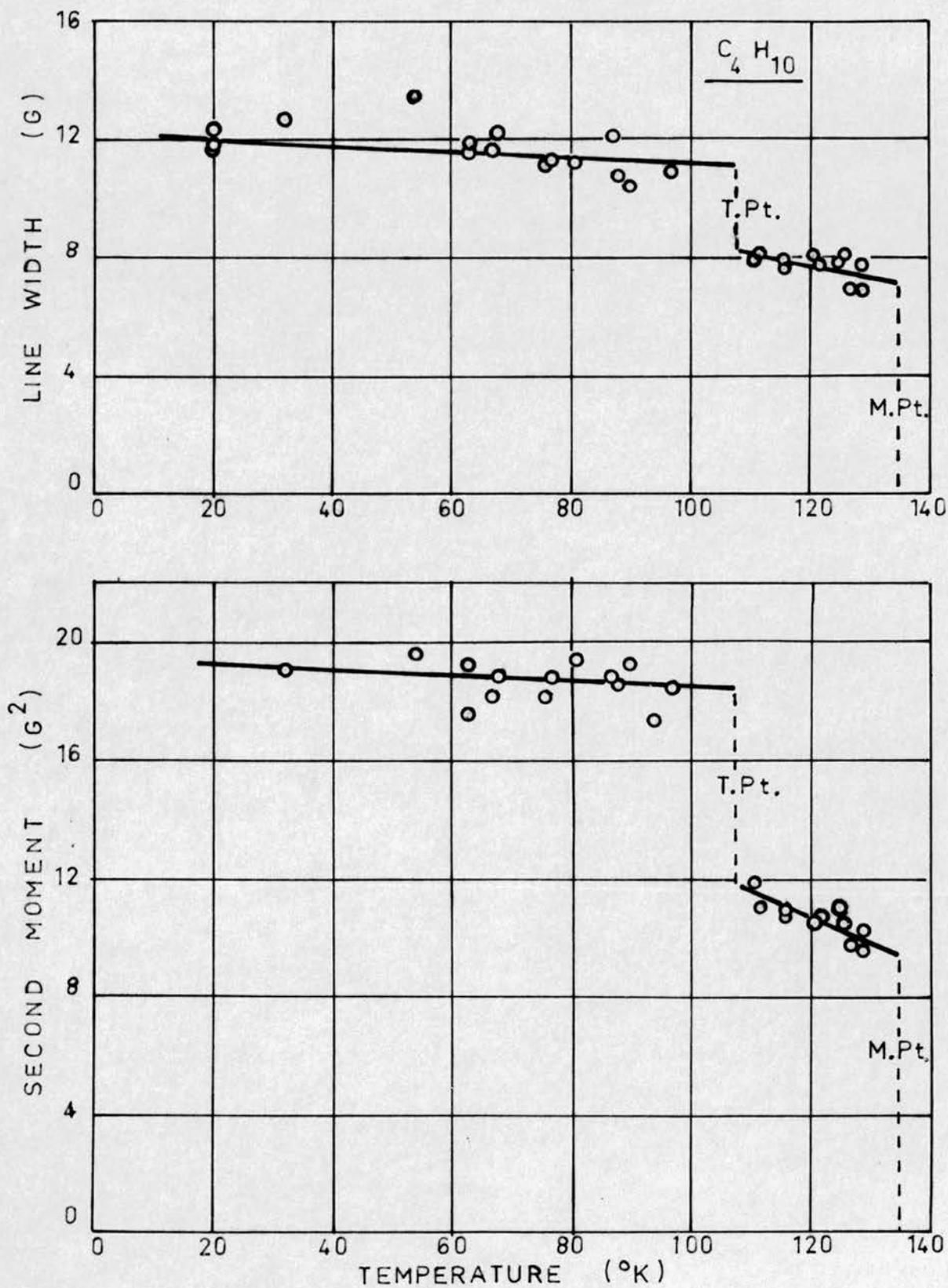


FIGURE 23.

melting points, the molecules starting to rotate about their long axes. For $N \geq 21$ all the homologues (up to $N = 36$, the highest member studied) exhibit such transitions. The crystal structure of the high temperature solid phase approximates to close packed hexagonal in all cases. The thermal data for these cases is summarized by Schaerer, Bayle and Mazee (1956) and is further discussed by Mnyukh (1963).

9.3 Results

9.3.1 Line width and Second Moment

These parameters are shown plotted versus temperature in figure 23. Observations were made over the temperature range 20°K to the melting point. Below the solid state transition temperature both line width and second moment have effectively constant values. An excessively long spin lattice relaxation time prevented reliable measurement of the second moment at the lowest temperatures. Even with very small r.f. power levels the second moment values were smaller at 20°K than at higher temperatures which indicated that slight saturation was occurring. At 90°K the measured second moment was $18.5 \pm 0.7 \text{ G}^2$.

The transition at 107.6°K was accompanied by an abrupt change in line width and second moment. Between this point and the melting point these quantities exhibited a fairly marked, and reproducible, temperature dependence. It is thus not possible to assign a specific value to the second moment in this region and the significance of the values is somewhat reduced as mentioned in Section (2.2.2).

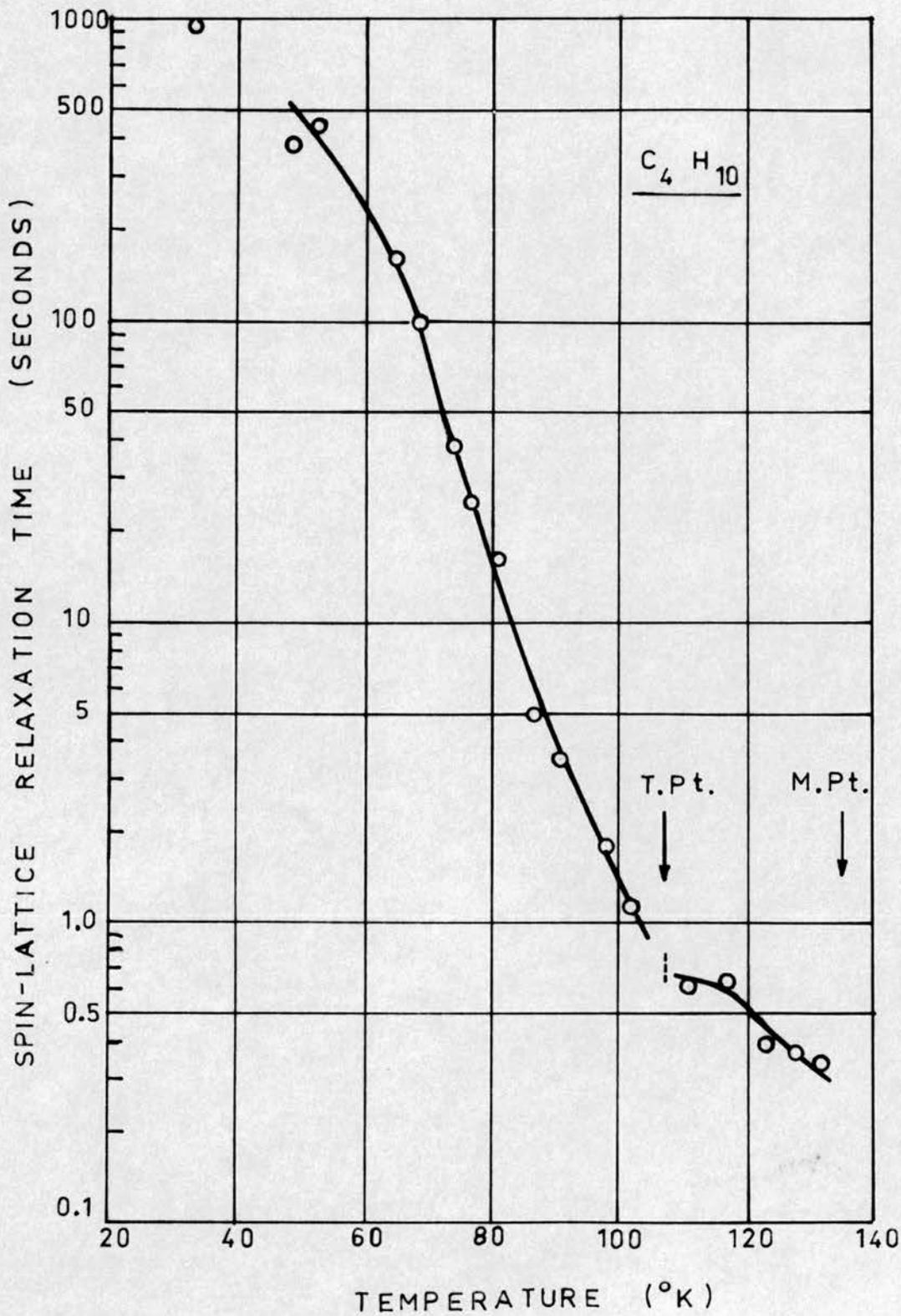


FIGURE 24.

9.3.2 Spin Lattice Relaxation

Figure 24 shows the variation of T_1 with temperature. Below 75°K direct recovery was used while at higher temperatures progressive saturation was necessary. The conditions of Case 2 (Section 3.3) were well satisfied in the latter case since the minimum value of $\omega_m T_1$ was roughly 47.

Most of the readings were taken in a run in which the sample was kept frozen for several days. Two attempts were made to measure T_1 at 20°K, without success. The limiting factor was the lack of long term stability of the equipment at this temperature (mainly because of the hydrogen boil off rate). It must be concluded that T_1 at temperatures near 20°K is somewhat longer than 10^3 seconds.

At the solid state transition point a discontinuity in slope and, to a small extent, in magnitude of T_1 occurred.

9.4 Discussion

9.4.1 The Absorption Spectrum

(a) Low Temperature Solid Phase 20°-107.6°K

The intramolecular contribution M_2' to the rigid lattice second moment may be calculated using the structural parameters of Section 9.2.1. From the Van Vleck (1948) expression (equation 2.6) a value of 22.1 G^2 is obtained. (Andrew (1950) has given an expression for the intra contribution for the general member of the $C_n H_{2n+2}$ series, which for $n=C_{10}H_{22}$ yields the value 22.3 G^2).

It is necessary to estimate the reduction produced in this value by torsional oscillations of the two CH_3 groups. For the case of a group of three nuclei oscillating about the three fold symmetry axis the general second moment reduction factor of Das (1957) takes the form (equation 2.9 with $n = 3$)

$$f = 1 - \frac{112}{81} \frac{\langle V \rangle}{V_0} \quad (9.1)$$

where $\langle V \rangle$ is the mean potential energy of the group and V_0 is the height of the hindering potential barrier. Using the harmonic oscillator approximation to the three nodal Mathieu equation (Byring, Walter and Kimball, 1944, p 360) and considering only ground state vibrations (quite a good approximation at 20°K) the reduction factor for each CH_3 group oscillating about its three fold axis is

$$f = \left[1 - 1.04 \frac{\hbar}{\sqrt{21V_0}} \right] \quad (9.2)$$

Using this expression and assuming a value of 2.5 k. cal./mole. for V_0 (Section 9.4.2) it is found that the intra contribution is reduced by roughly 5 percent to 21.1 G^2 .

Even without the intermolecular contribution the above value is considerably larger than the observed second moment at all temperatures at which measurements were made. This indicates that some form of molecular reorientation was occurring. From previous n.m.r. work on this type of molecule by Rushworth (1954) and Lawrenson and Rushworth (1959) it is highly likely that methyl group reorientation is the cause of the line narrowing in the low temperature solid phase.

The rigid lattice intermolecular contribution to the second moment, M_2'' , which is appreciably smaller than the intra contribution, may be estimated from the crystal structure data available for the higher members of the series. Andrew and Eades (1953a) have calculated M_2'' for n-hexane at 120°K. Assuming an orthorhombic unit cell on the basis of the work of Müller (1930) they considered the interactions of a typical methylene group pair in one molecule with protons in neighbouring molecules. Distances up to 5^oÅ were treated exactly and an integration, assuming a uniform proton density, performed for the remainder. Allowing for lattice contraction a value of 9.6 G² was obtained at 120°K. This value will be more accurate the longer the carbon chain length assuming that the molecular packing remains the same. Actually the crystal structure of n-hexane is probably triclinic from the more recent evidence quoted in Section (9.2.3). However, because of the general similarity in packing in the two structures, the above value should be reasonably reliable.

With sufficient accuracy for determining qualitative motional information which is clearly all that can be obtained, this same value will be assumed for M_2'' in n-butane. Allowing a large uncertainty, the total "rigid-lattice" second moment may be quoted as 30.7 ± 1.5 G² at temperatures near 100°K.

As mentioned above, CH₃ group reorientation about the three fold symmetry axis is the probable form of motion below the solid state transition temperature. The reduction in M_2' produced by this motion has

been calculated as follows. Firstly the contributions due to the protons in each CH_3 group are reduced by a factor 4 as may be seen from equation (2.7). In considering the reduction in the contributions due to interactions between protons in each CH_3 group with the other protons in the molecule, it is necessary to use the general expression of Andrew and Eades (1953a) since both the interproton distances and directions are time varying. (The general reduction factor is quoted in Appendix 1). These calculations yield a value of 11.0 G^2 for the reduced intramolecular contribution. It should be noted that it is not necessary to consider the effects of torsional vibrations when CH_3 group reorientation is occurring since n.m.r. does not distinguish between continuous and discontinuous motion about an axis of three fold or higher symmetry (c.f. ethylene).

Deducting the reduced value of M_2' from the experimental value of $18.5 \pm 0.7 \text{ G}^2$ (at 90°K) leaves $7.5 \pm 0.7 \text{ G}^2$ as the reduced intermolecular contribution. This is 22 percent smaller than the suggested rigid lattice value. A fairly small reduction due to CH_3 group reorientation is to be expected since only six out of the ten protons in each molecule are moving. Taking into account the persistence of motion at a rate sufficiently rapid to narrow the spectrum even at 20°K (and which will be accounted for by the CH_3 group tunnelling theory) it may be concluded that CH_3 group reorientation is the actual form of motion at temperatures below 107.6°K .

(b) High Temperature Solid Phase 107.6°-134.9°K (Melting Point)

The abrupt change in line width and second moment which accompanies the solid state transition indicates the onset of a new form of molecular motion. The most probable form of motion, consistent with the thermal data, is reorientation of the molecules about their long axes (passing through the mid-points of the C - C bonds).

The effect of such motion on M_2' has been estimated as follows. Firstly it is necessary to consider the composite motion of the CH_3 groups about two axes. Powles and Gutowsky (1953a, b) have treated this case. They have shown that for a CH_3 group reorienting about its three fold axis and also executing free rotation about some other axis making an angle ψ with the first, the second moment reduction factor is given by

$$f_3^* = \frac{1}{16} (3 \cos^2 \psi - 1)^2 \quad (9.3)$$

(For $\psi = 0$ this reduces to the value 0.25 obtained from equation (2.7)). Using equation (9.3) the reduced contribution due to the interaction between the protons in each CH_3 group may be calculated. The reduction in the second moment contribution due to the interactions between the four methylene group protons may also be readily calculated using equation (2.7). As an approximation the remaining contributions due to interactions between the CH_3 protons and the other protons in the molecule have been assumed to be the same for the composite motion as when CH_3 group reorientation alone is occurring. This gives an upper limit value for the reduced intra contribution (to quite a good approximation).

The value obtained is 3.1 G^2 .

The reduced intermolecular contribution cannot be estimated as reliably. Andrew (1950) has given a theoretical treatment for the case of uncorrelated rotation of long chain n-hydrocarbons about their long axes (assumed parallel). It was shown that the intermolecular contribution to the second moment is reduced to about one third of the rigid lattice value by this process. While this factor will be less accurate the shorter the carbon chain length, it nevertheless gives a reasonable indication of the reduction to be expected.

Some change in crystal structure must accompany the transition in n-butane. If the molecules start to reorient about their long axes then the structure will approximate to that of close packed cylinders giving the hexagonal type lattice which is found in the long chain n-hydrocarbons near their melting points (Section 9.2.3).

With sufficient accuracy however a value of $3 \pm 1.5 \text{ G}^2$ will be assumed for the reduced M_2'' in n-butane for the case of uncorrelated long axis rotation. The total theoretical second moment for this type of motion is thus $6.1 \pm 1.5 \text{ G}^2$. The observed second moment decreases from a value of roughly 11.5 G^2 at 108°K to 9.5 G^2 at the melting point. This slow regular (and reproducible) decrease is quite different from the normal line width transition behaviour (c.f. cyclopropane).

The discrepancy between theory and experiment indicates that in this phase the molecules are not in fact rotating freely about their long axes. A possible explanation is that some correlation of the

motion of neighbouring molecules is present. Andrew (1950) has suggested that this may occur in dicetyl, $n\text{-C}_{32}\text{H}_{66}$, near the melting point.

Correlated motion of the molecules may be expected to give a higher reduced intermolecular contribution than for uncorrelated motion. If only a certain fraction of the molecules effectively rotate at any specific temperature, because of the correlation, then both intra and inter contributions will be proportionally higher. The marked temperature dependence of the second moment between the transition point and the melting point may then be explained by assuming that the motion becomes increasingly uncorrelated as the temperature is raised. Associated with such motional changes a marked increase in the volume of the unit cell may be expected to occur. X-ray studies in this phase would be interesting. It is possible that other effects, such as torsional oscillations and "flexing" of the molecules, may also be important.

9.4.2 Spin-Lattice Relaxation

Although T_1 measurements were made in both solid phases, as can be seen from figure 24, it is only possible to obtain quantitative information from the measurements in the low temperature region. Above the transition T_1 appears to decrease rather slowly. It has been suggested in the preceding section that there are two forms of molecular motion in this phase; CH_3 group reorientation and also reorientation of whole molecules about their long axes. There are correspondingly two correla-

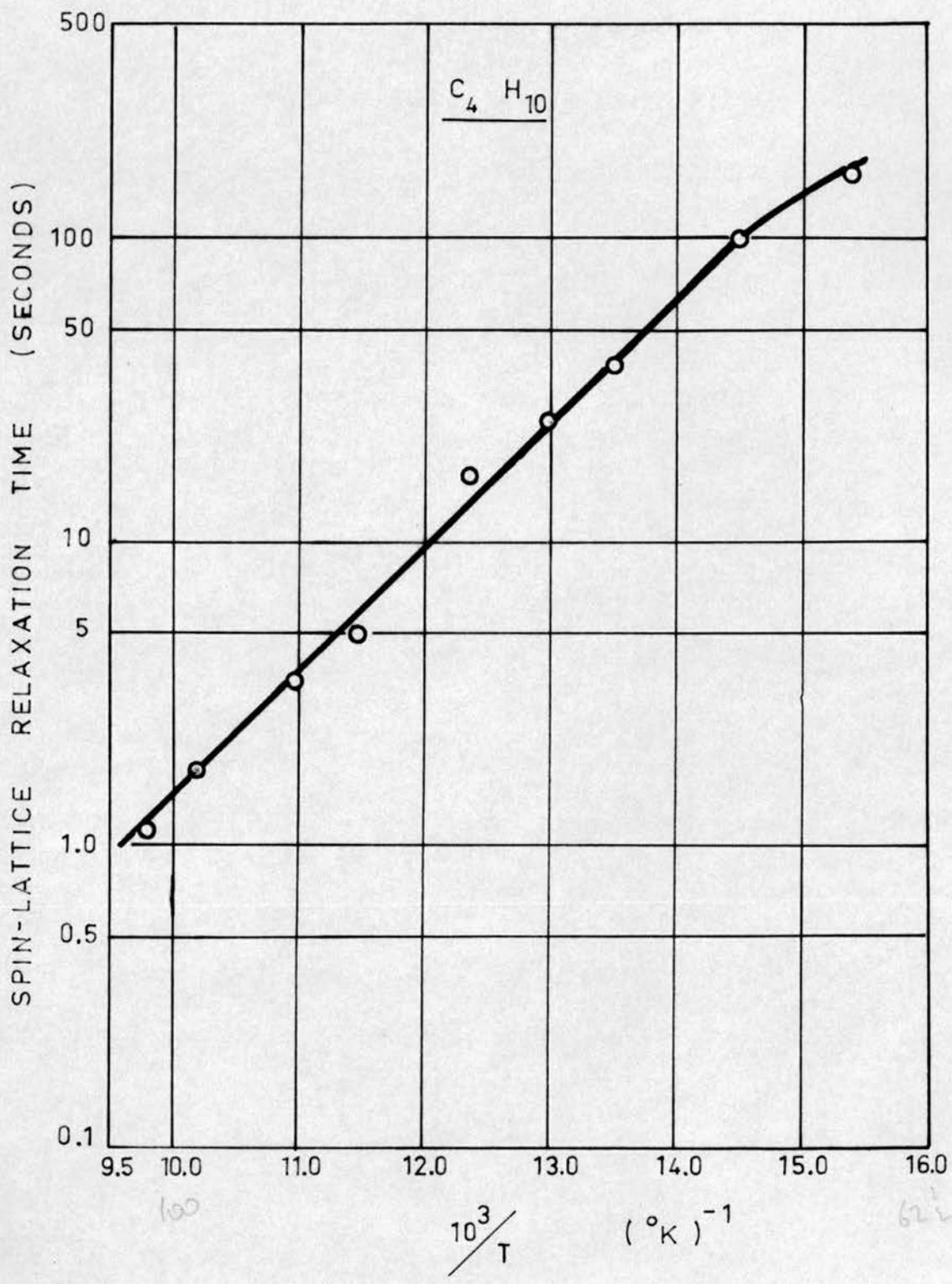


FIGURE 25.

tion times to describe this composite motion. It would appear that the correlation time for the CH_3 group motion is on the short side of the value corresponding to the T_1 minimum (the rate of this motion having discontinuously increased at the transition point) while the correlation time for the more general motion is on the long side of the value corresponding to the minimum. The overlapping of these two effects leads to the relatively constant value of T_1 between 108°K and 135°K .

Figure 25 shows a semi-logarithmic plot of T_1 against $10^3/T$ ($^\circ\text{K}$)⁻¹ for the low temperature solid phase. A least squares calculation yields a value of 1.9 k. cal./mole. for the activation energy of the CH_3 group reorientation process. Rushworth (1954) has obtained values for the equivalent activation energies in n-hexane and n-pentane. These were 2.9 and 2.7 k. cal./mole. respectively. The activation energy in n-butane thus appears to be appreciably lower than in either of these two cases. (The zero point energy is about 0.3 k. cal./mole. for all these cases).

Since the absorption spectrum has not broadened to the rigid lattice value at temperatures below 40°K it is necessary to assume that CH_3 group reorientation is occurring at a rate greater than 5×10^4 c/s at these temperatures. Stejskal and Gutowsky (1958) have, as mentioned in Section (8.4.2), treated in detail the problem of CH_3 group tunneling through hindering potential barriers in solids. They have solved (with the aid of a computer) the three nodal Mathieu equation which is applicable to the torsional oscillations in this case. From the splittings

of the torsional energy levels they have calculated tunnelling frequencies for each torsional state in a manner analogous to that used in the case of ethylene (Section 8.4.2). Average tunnelling frequencies were calculated from these values, as a function of temperature, using the definition given by equation (8.9). They have given their results as a family of curves showing the average CH_3 group tunnelling frequencies for various barrier heights plotted against reciprocal temperature.

For barrier heights of 2.5 k. cal./mole. or less the ground state tunnelling frequency is greater than 10^6 c/s. It is clear that in such cases the absorption spectrum will still be narrowed by this process even at very low temperatures ($\sim 1^\circ\text{K}$). The absorption spectrum observations in n-butane are consistent with tunnelling theory predictions.

As mentioned in Section 8.4.2 the relationship between the tunnelling frequencies and T_1 may be rather complex. Just as in the case of ethylene the predicted tunnelling frequencies have been compared with the reorientation frequencies calculated from the T_1 data using the B.P.P. theory.

Stejskal and Gutowsky (1958) have adapted the B.P.P. theory to the problem of spin lattice relaxation in a polycrystalline substance in which CH_3 group reorientation is occurring. For this case they obtain the expression

$$\frac{1}{T_1} = \frac{9}{40} \frac{\gamma^4 \hbar^2}{r^6} \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \quad (9.4)$$

where r is the interproton distance in each CH_3 group and τ_c is the correlation time. This expression is of the same functional form as equation (2.10). Only the interactions between the CH_3 group protons were considered in the derivation.

While it is possible to use the theoretical constant $C_1' = (9/40)(\gamma^4 h^2 / r^6)$ in equation (9.4) in extracting correlation times from the T_1 data, it is preferable to estimate C_1' from the T_1 minimum value using equation (8.4). No minimum was observed in n-butane but Rushworth (1954) has found that the minimum values in n-hexane and n-pentane are roughly 0.01 seconds. In n-butane approximately the same minimum value may be expected (a small error here will not greatly affect the conclusions). Hence C_1' is found to be $1.00 \times 10^{10} \text{ sec}^{-2}$. This is to be compared with the theoretical value of $3.81 \times 10^9 \text{ sec}^{-2}$. The discrepancy, by a factor 2.5, is in the right direction since interactions between the CH_3 group protons and other protons in the molecule and in adjacent molecules have been ignored in the theoretical treatment. Using the experimental value for C_1' the correlation times τ_c have been calculated from the measured T_1 values.

For the case of random tunnelling of a methyl group between its three equivalent positions Powles and Gutowsky (1955) have shown that the tunnelling frequency ν_t and the correlation time are connected by the relationship

$$\tau_c = \frac{1}{3\pi\nu_t} \quad (9.5)$$

Values of the apparent tunnelling frequencies have been obtained from

n - BUTANE
METHYL GROUP TUNNELLING FREQUENCIES

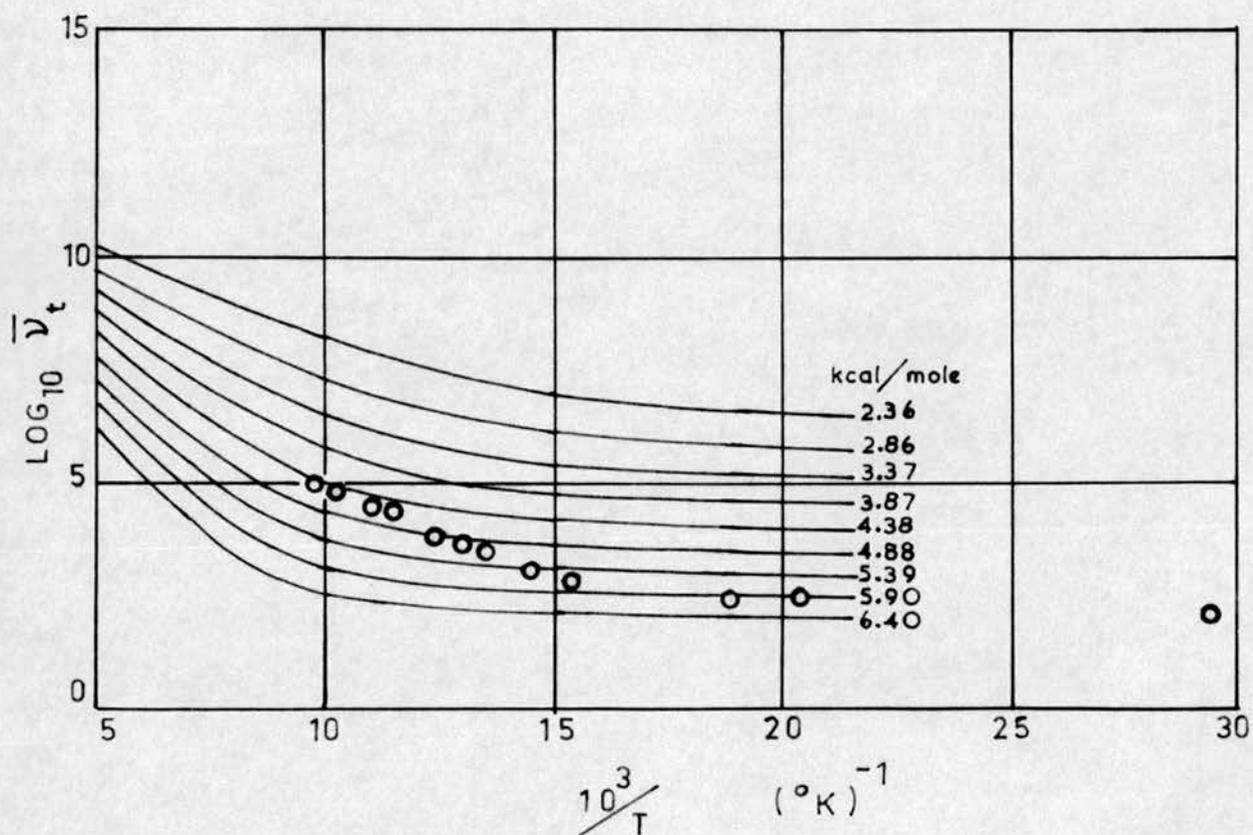


FIGURE 26.

the T_1 data in this way and are plotted versus $10^3/T$ ($^{\circ}\text{K}$)⁻¹ in figure 26. The theoretical curves shown are the predicted tunnelling frequencies for various barrier heights as calculated by Stejskal and Gutowsky (1958).

While a definite departure from linearity of the apparent experimental tunnelling frequencies occurs at the lowest temperatures, as predicted by the theory, there are marked discrepancies which must be considered. At the lowest temperatures the plotted points indicate a barrier height of approximately 6 k. cal./mole. with a corresponding ground state tunnelling frequency of less than 10^3 c/s. This is in disagreement with the second moment results from which it was concluded that ν_t was somewhat greater than 5×10^4 c/s. At higher temperatures the experimental tunnelling frequencies increase more rapidly than is predicted for a 5 to 6 k. cal./mole. barrier. In fact the experimental points lie along a curve roughly parallel to that for a barrier in the neighbourhood of 2.5 k. cal./mole. It appears likely that the apparent tunnelling frequencies, derived from the T_1 data, are displaced with respect to the actual values.

The reason for this displacement probably lies in the use of the B.P.F. theory in extracting the tunnelling frequencies from the T_1 values. The B.P.F. theory assumes an exponential form for the correlation function of the "random motion". This leads to a Debye spectral density function for the Fourier intensities of the nuclear position coordinates. In the case of tunnelling at low temperatures, when most of the CH_3 groups are in

the ground torsional state, the quantized motion may be expected to give rise to a spectral density function with maximum intensity at the tunnelling frequency. A sharper cut-off in the intensity at higher frequencies than is given by the Debye spectral density function may also be expected. These simple arguments indicate that the use of the B.P.P. theory for tunnelling frequency calculations could produce misleading results of the type observed.

It is important to remember that the absorption spectrum and T_1 are sensitive to very different motional frequencies. The extremely long T_1 values near 20°K are thus not incompatible with the fact that the spectrum is still narrowed by the CH_3 group tunnelling.

Stejskal and Gutowsky (1958) have suggested ways of obtaining a modified spectral density function applicable to the case of tunnelling reorientation. Considering the various tunnelling frequencies, and allowing for lifetime broadening of the torsional energy levels, an expression for the spectral density function, which exhibits structural features, may be obtained. In deriving this expression it is necessary to introduce a number of uncertain constants which are likely to vary with temperature. It is to be expected that as the rotational states become more important at higher temperatures the spectral density function will tend towards the B.P.P. approximation.

It appears worthwhile to carry out T_1 measurements at low temperatures (20°-40°K) as a function of Larmor frequency. At lower frequencies than that used in the present investigation (22.6 Mc/s),

particularly at frequencies lower than 10 Mc/s, an anomalous decrease in T_1 may occur. (Unfortunately the permanent magnet used in the present investigation only permits operation at 22.6 Mc/s).

Finally it should be mentioned that there may well be other factors which need to be considered in the relaxation process. For example, Stejskal and Gutowsky (1958) have pointed out that, because of the symmetry requirements of the total wave function of the CH_3 group, no exchange of torsional and nuclear magnetic energy within a pair of torsional levels is allowed. (For an effectively isolated molecule no relaxation would occur even in a torsional state in which tunnelling occurred at the Larmor frequency). Perturbing intermolecular effects thus play an important part in the relaxation process.

Tunnelling effects appear to differ from case to case. In an investigation of the dimethylbutanes and trimethylbenzenes Andrew, Eades, El Saffar and Llewellyn (1960) have obtained reasonable agreement between the T_1 data and the simple tunnelling theory predictions of Stejskal and Gutowsky (1958). Further theoretical and experimental work on this problem is clearly necessary.

10. SUMMARY OF RESULTS OBTAINED WITH
ETHYLENE AND n-BUTANE

10. SUMMARY OF RESULTS OBTAINED WITH ETHYLENE AND n-BUTANE

Molecular reorientation has been shown to occur in the solid state in both these substances. In both cases it has been suggested that tunnelling plays an important part in the reorientation process.

In ethylene it is probable that the molecules reorient about their two fold C = C symmetry axes. At 20°K the tunnelling frequency for this process is insufficiently rapid to average out the dipolar interaction and the full absorption line width is observed apart from the reduction produced by zero point torsional oscillations. Over the temperature range 50°K to the melting point, 104°K, the spin lattice relaxation time data may be satisfactorily accounted for by the simple tunnelling theory (which includes the effects of classical reorientation at the higher temperatures). A barrier of about 2.4 k. cal./mole. is indicated. Below 50°K an unexplained anomaly in the spin lattice relaxation time behaviour occurred. Further experiments to investigate this effect are suggested.

In n-butane CH₃ group reorientation occurs below the solid state transition temperature. This process persists down to 20°K at a rate sufficiently rapid to narrow the absorption spectrum, in agreement with tunnelling theory predictions for a barrier height of less than 3 k. cal./mole. The apparent activation energy for this process given directly by the spin lattice relaxation time data is 2 k. cal./mole. The reorientation rates deduced from the spin lattice time data are, however, not in good agreement with the tunnelling theory predictions. Various

possible reasons for this are discussed. Above the solid state transition temperature it is suggested that correlated motion of the molecules about their long axes occurs; the degree of correlation decreasing as the melting point is approached.

APPENDIX

APPENDIX 1Ethylene: Reduced intermolecular contribution to the Second Moment when hindered reorientation is occurring about the two fold figure axis

Andrew and Eades (1953a) have derived the following results for the reduced intermolecular contribution in the case of discontinuous reorientation of the molecules about an n-fold axis in the lattice.

In this case (in the notation of equation 2.5)

$$M_2'' = \frac{3}{2} I(I+1) \gamma^2 h^2 N^{-1} \sum_{j > k} \bar{Q}_{jk}$$

where for a polycrystalline specimen

$$\begin{aligned} \bar{Q}_{jk} = & \frac{1}{5} (A^2 + D^2 + F^2 + 5G^2) + \frac{4}{15} (B^2 + C^2 + E^2) \\ & + \frac{2}{15} (AD + AF + DF) - \frac{2}{3} G (A + D + F) \end{aligned}$$

with

$$\begin{aligned} A &= \frac{3}{n^2} \sum_{j,k}^{n^2} r_{jk}^{-3} \cos^2 \psi_{jk} \\ B &= \frac{3}{2n^2} \sum_{j,k}^{n^2} r_{jk}^{-3} \sin 2\psi_{jk} \cos \phi_{jk} \\ C &= \frac{3}{2n^2} \sum_{j,k}^{n^2} r_{jk}^{-3} \sin 2\psi_{jk} \sin \phi_{jk} \\ D &= \frac{3}{n^2} \sum_{j,k}^{n^2} r_{jk}^{-3} \sin^2 \psi_{jk} \cos^2 \phi_{jk} \\ E &= \frac{3}{2n^2} \sum_{j,k}^{n^2} r_{jk}^{-3} \sin^2 \psi_{jk} \sin 2\phi_{jk} \end{aligned}$$

$$F = \frac{3}{n^2} \sum_{j,k}^{n^2} r_{jk}^{-3} \sin^2 \psi_{jk} \sin^2 \phi_{jk}$$

$$G = \frac{1}{n^2} \sum_{j,k}^{n^2} r_{jk}^{-3}$$

and where ϕ_{jk} and ψ_{jk} are the azimuth and polar angles respectively of the internuclear vector r_{jk} with respect to the Z-axis of the crystal.

For ethylene each sum contains four terms. Because of the large amount of computation involved only the twelve shortest distances (less than 3 \AA) have been treated exactly and an estimate has been made for the remainder.

(a) $r_{jk} = 3 \text{ \AA}$

These 12 inter-proton distances were treated exactly and the contribution due to this group was found to be reduced by a factor of 5.1, compared to the rigid lattice contribution. In the rigid lattice case this group provides 46 percent of the intermolecular second moment.

(b) $r_{jk} = 3 - 4 \text{ \AA}$

In this interval 10 proton pairs out of a total of 36 were incidentally considered in the calculations for group (a). A reduction by a factor of 1.5 was found for these 10 which appear to be fairly representative of this group. As an approximation this reduction factor will be applied to the whole group.

(c) $r_{jk} = 4 - 5 \text{ \AA}$

Again 12 proton pairs out of a total of 62 were considered in the calculations for group (a). For all 12 the contributions were increased

by an average factor of 2.6. These 12 pairs are not however typical since they were at times brought quite close together ($< 3 \text{ \AA}$) by the motion. Out of the remaining 50 in this group the motion produced relatively small changes in spacing for about half of them. Most of the remainder were at times brought somewhat closer together by the motion but a few moved further apart. A nett increased contribution from this group is likely and a factor of 1.5 will be assumed.

(d) $r_{jk} = 5 - 7 \text{ \AA}$

In the rigid lattice case this group of 124 protons contributes roughly 6 percent of the total intermolecular contribution. It is difficult to estimate the effect of the motion on this contribution but a nett increase is likely. A factor 2 will be assumed.

(e) $r_{jk} > 7 \text{ \AA}$

The effect of motion on the contribution due to proton pairs more than 7 \AA apart will be treated as negligible though this is not strictly true. The contribution due to this group is obtained by integration assuming a uniform proton density.

By using the above approximations a value of $4 \pm 1 \text{ G}^2$ at 98°K may be quoted for the reduced intermolecular contribution.

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