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Proton Magnetic Resonance of the CH_3 Group. V. Temperature Dependence of T_1 in Several Molecular Crystals*

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The proton T_1 has been observed by rf pulse techniques in acetonitrile, neopentane, *t*-butyl chloride, 2,2-dichloropropane, and methyl chloroform from their melting points to temperatures about $-150°C$. Activation energies of 5 to 6 kcal/mole were obtained for self diffusion in the high-temperature solid phase of neopentane, *t*-butyl chloride, and 2,2-dichloropropane. Activation energies ranging from 1 to 4.5 kcal/mole were obtained for molecular tumbling and from 3 to 4 kcal/mole for CH_3 group reorientation in the series of tetrasubstituted methanes, neopentane to methyl chloroform. The effects of intermolecular forces on CH_3 group reorientation are shown by the activation energy of 2.1 kcal/mole found for acetonitrile, which has no internal barrier. The various results confirm that a tunneling mechanism is plausible for the CH_3 group reorientations.

Other results include: the Bloch decay after a 90° pulse in solid methyl chloroform has a "slow beat" which is the Fourier transform of the triplet line shape found in steady-state experiments. The dependence of T_1 upon resonance frequency in the low-temperature phase of methyl chloroform exhibits systematic effects attributable to proton-chlorine spin exchange induced by reorientations of the CCl_3 group. The T_1 is constant in the supercooled high-temperature solid phase of methyl chloroform. There is an anomalous increase in the T_1 at the low-temperature transition in *t*-butyl chloride, indicating a higher molecular mobility during the phase transition than in either stable solid phase. A 2:1 mixture of CH_2DCCl_3 and CH_3CCl_3 gave proton T_1 values only 1.3 to 1.6 times as long as those in normal CH_3CCl_3, whereas the tunneling mechanism suggests a 20-fold increase. Spin exchange between protons in neighboring CH_2DCCl_3 and CH_3CCl_3 molecules accounts for the results and it is proposed that spin exchange may be investigated directly by observing T_1 in appropriate isotopic mixtures of known composition.

I. INTRODUCTION

PREVIOUS studies of the proton magnetic resonance of several tetrasubstituted methanes have given information as to the types of motions occurring within the various solid phases possessed by these substances.[1] Although some quantitative information was obtained from these studies, which were limited to line shapes and widths, the most profitable information was qualitative: kinds of motion rather than rates of motion were disclosed. To find out more about the rates of motion, the present studies of the spin-lattice relaxation time T_1 were performed.

In papers III and IV of this series[2,3] the framework of a theory has been described which for the case of CH_3 group reorientations relates both the line width and the T_1 data to an internal parameter, the tunneling frequency. This tunneling frequency may in turn be related to the potential barrier to rotation experienced by the CH_3 groups. To test this theory as well as to investigate more fully the substances studied, several different kinds of T_1 measurements were made. Both temperature- and frequency-dependence data were obtained. Although there are still discrepancies to be fully explained, there is a good over-all compatibility between the theory and the several kinds of experiments devised to check the theory. In addition, several quite interesting generalizations may be made as to the dynamic state of molecules within the substances studied.

2. EXPERIMENTAL METHODS

The rf pulse apparatus used to measure T_1 has been described elsewhere.[4] The measurements were made with either the method employing two 90° pulses[5] or the null method,[6] which requires a 180° pulse followed by a 90° pulse. The second method, whenever feasible, proved to be somewhat more desirable. It seems to produce more self-consistent results. For long T_1's, however, those of the order of seconds, this method was no longer practical. An error analysis on the first method indicates that between 10 and 20% error is to be expected as a result of the inaccuracies inherent in the observed quantities, if τ, the time between the two pulses, is kept greater than $T_1/2$ and less than $2T_1$. If these limits are overstepped, the error skyrockets. The error inherent in the null method is probably closer to 5%. Some uncertainty arises because of a small induction decay, due to inhomogeneity of the rf field, after the 180° pulse. However, as long as the null point is chosen in a consistent manner, the exact temperature dependence of T_1 is measured, even though the true values may differ systematically from the apparent ones by a constant factor close to unity. The temperature of the sample was measured during the experiments with a thermocouple inserted in a well in the

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‡ Now at Magnolia Petroleum Company, Field Research Laboratory, Dallas, Texas.

[1] J. G. Powles and H. S. Gutowsky, J. Chem. Phys. **21**, 1695 (1953); paper I of this series.

[2] J. G. Powles and H. S. Gutowsky, J. Chem. Phys. **23**, 1692 (1955); paper III of this series.

[3] E. O. Stejskal and H. S. Gutowsky, J. Chem. Phys. **28**, 388 (1958); paper IV of this series.

[4] Buchta, Gutowsky, and Woessner, Rev. Sci. Instr. **29**, 55 (1958).

[5] E. L. Hahn, Phys. Today **6**, **11**, 4 (1953).

[6] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

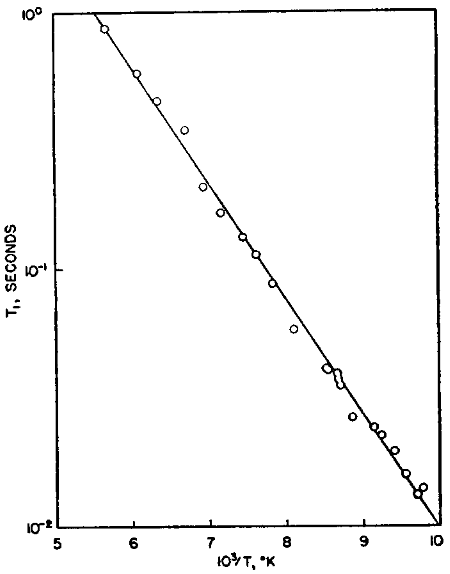

FIG. 1. The temperature dependence of the proton T_1 in solid CH_3CN, plotted as $\log T_1$ *vs* $10^3/T$.

side of the sample tube. Most runs were made upon warming; however, those made upon cooling showed no differences, except for the measurements made upon the supercooled high-temperature solid phase of methyl chloroform.

A word is in order regarding the samples used for the above determinations. There have been indications in previous research that some of these compounds are not completely stable.[1,7] Because of the sensitivity of T_1 to certain kinds of impurities, this was cause for some concern. Bottles of methyl chloroform and *t*-butyl chloride have developed considerable partial pressure of HCl above the liquid after standing at room temperature for a few weeks. To circumvent such occurrences all the samples except neopentane were washed with $CaCO_3$ and water, dried over $Mg(ClO_4)_2$, and fractionally distilled in a 5 ft column packed with glass helices. Neopentane is stable and available commercially in very pure form. We wish to thank Dr. D. C. Smith of the Phillips Petroleum Company for providing the sample of research grade neopentane used in these experiments. All the samples were sealed into the sample tubes under vacuum. This last operation served to reduce the amount of oxygen dissolved in the compound. After preparation, the sample tubes were stored at Dry Ice temperatures until immediately before the T_1 measurements.

3. EXPERIMENTAL RESULTS

Five compounds were studied in the course of these investigations. Four may be considered to be tetrasubstituted methanes. They are methyl chloroform, which was studied most extensively, 2,2-dichloropropane, *t*-butyl chloride, and neopentane. The fifth compound, acetonitrile, was chosen because it offers a good comparison with the other compounds. All the compounds were studied from their melting points down to the limit of either liquid N_2 temperature or the sensitivity of the rf pulse apparatus. Each of the tetrasubstituted methanes exhibits at least one solid phase transition. A proton resonance frequency of 20 Mc/sec was used in the experiments except for studies made of the dependence of T_1 upon resonance frequency in methyl chloroform at frequencies between 16 and 28 Mc/sec.

Excluding intramolecular and lattice vibrations, there are three main types of motion which contribute to the dynamic structure of these relatively simple molecular crystals: CH_3 group reorientations about their symmetry axis; molecular tumbling, i.e., random reorientations involving the heavy atom skeleton of the molecule; and translational motions associated with self diffusion. In this section, the proton T_1 data are presented and it is decided which of these motions dominates T_1 in the various solid phases. Moreover, in the plots of $\log T_1$ *versus* $1/T$ straight-line portions are found in most instances, permitting the determination of an apparent activation energy E_a for the motion in question. The compounds are discussed more or less in order of increasing complexity of the results. Detailed consideration of the CH_3 group reorientation process is deferred until the section after this one.

A. Acetronitrile, CH_3CN

The proton spin lattice relaxation times plotted in Fig. 1 for acetonitrile have the simplest possible form. $\text{Log}T_1$ *versus* $1/T$ is a straight line from the melting point, which is not included in the figure, to 100°K, the lowest temperature at which T_1 was measured. Proton line shape studies[8] indicate that only CH_3 group reorientations occur in this temperature interval. Moreover, we have found no reports of thermal or dielectric constant transitions, and the molecule is rodlike in shape, supporting the conclusion that CH_3 group reorientations determine T_1. The activation energy derived from the slope of the straight line passed through the T_1 data is 2.1 kcal. This calculation is based on the equations[3,8]

$$1/T_1 \propto \tau_c/(1+\omega_0^2\tau_c^2) \qquad (1)$$

$$\tau_c=\tau_0 \exp(E_a/RT), \qquad (2)$$

where τ_c is the correlation time for the motions, τ_0 is an inverse frequency factor, and ω_0 is the resonance angular frequency. The T_1 data in Fig. 1 indicate that τ_c is on the short side of the T_1 minimum predicted by Eq. (1), that is $\tau_c<1/\omega_0\cong 10^{-8}$ sec. This is compatible with the line-width studies[8] which show that τ_c for the CH_3 group reorientations is less than 10^{-5} sec at 80°K.

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[7] Powles, Williams, and Smyth, J. Chem. Phys. **21**, 136 (1953).

[8] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 162 (1950).

B. Neopentane, $(CH_3)_4C$

The T_1 data given in Fig. 2 for neopentane reveal the presence of all three types of molecular motion in the solid. The line widths[1] show that at temperatures between 80° and 200°K both CH_3 group reorientations and molecular tumbling are effective in narrowing the absorption, which has a constant and relatively narrow width of about 3 gauss in this temperature interval. However, the second moment is just beginning to increase at temperatures below 85°K. Tentatively, we assign the low-temperature, straight line portion ($10^3/T$ between 7 and 8.5) of the T_1 data in Fig. 2 to CH_3 group reorientations; the slope corresponds to an E_a of 3.0 kcal. Actually, as we shall see later, there is good reason to believe that some molecular tumbling is also involved in the motions.

Neopentane has a solid phase transition[9] at 140°K (T.P. in Fig. 2). At this temperature T_1 undergoes a large discontinuity in both magnitude and temperature dependence, although the line width is unchanged. The implication is that at temperatures above the transition, the motions are much faster than at lower temperatures but that the same kinds of motion occur in both phases. Also, τ_c is on the short side of the T_1 minimum, indicating that T_1 is probably governed just above the transition by molecular tumbling. At temperatures above 200°K, T_1 starts decreasing, as does the line width. Both effects are assigned to self diffusion. The fact that T_1 decreases with increasing temperature implies that τ_c for this motion is on the long side of the T_1 minimum, i.e., $\tau_c > 10^{-8}$ sec, which is compatible with the line narrowing observed in the same region.

Activation energies for the molecular tumbling and self diffusion in the high-temperature solid can be obtained from the two straight line portions of the $\log T_1$ *vs* $10^3/T$ curve between $10^3/T$ values of 4 and 7 in Fig. 2. The overlapping effects of the two motions complicate the analysis a bit. It was assumed that the T_1 observed was given simply as

$$1/T_1 = (1/T_1)_{\text{self-dif}} + (1/T_1)_{\text{mol reor}}. \qquad (3)$$

In this manner, approximate E_a values of 6.0 and 1.0 kcal were obtained for self diffusion and molecular tumbling, respectively. The importance of self diffusion in the high-temperature solid is supported by x-ray studies which indicate considerable disorder.[10]

There is a sharp rise in T_1 just below the melting point (M.P. in Fig. 2). This could arise from impurities, but it might be a "real" premelting phenomenon in view of the fact that the sample as received was stated to be 99.87 mole % pure.

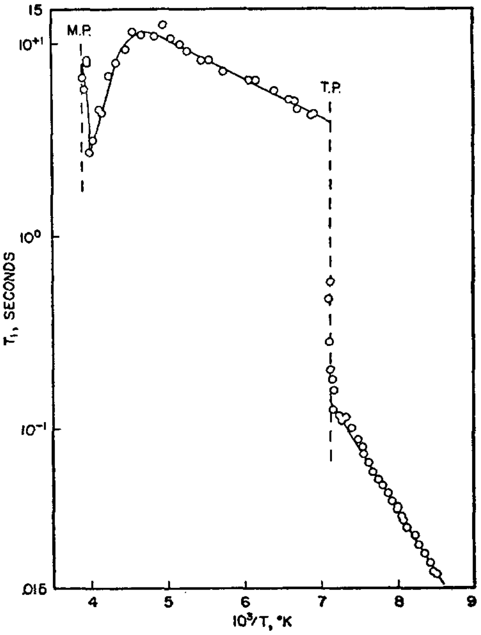

FIG. 2. The temperature dependence of the proton T_1 in solid $(CH_3)_4C$, plotted as $\log T_1$ *vs* $10^3/T$.

C. *t*-Butyl Chloride, $(CH_3)_3CCl$

t-Butyl chloride differs from neopentane in having three solid phases.[11] Between the melting point and the first thermal transition point, the solid has a very narrow proton resonance[1] and a large dielectric constant.[11] Translation as well as molecular tumbling is taking place. The change in dielectric constant and in proton line width are considerable at this first transition point. However, the proton line width in the second solid phase is considerably less than that predicted for molecules in which only CH_3 group reorientations occur. Accordingly, molecular tumbling as well as CH_3 group reorientations occur in this phase. At the second transition there is a small change in dielectric constant and no noticeable change in the line width, suggesting that at temperatures just below the transition, slow molecular reorientations occur about the C–Cl axis but not about axes perpendicular to it. These motions, as well as the CH_3 group reorientations, are frozen out at still lower temperatures, as evidenced by the broadening of proton resonance below 125°K, with no further phase change.

The T_1 data for *t*-butyl chloride in Fig. 3 are particularly interesting in that three minima are clearly defined, each corresponding mainly to one of the three types of molecular motion. Many more data were obtained for the two low-temperature phases than are indicated in Fig. 3. Those presented are typical of the data omitted; the curves drawn are based on considerably more points than are included in the figure. To a

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[9] J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).

[10] A. H. Mones and B. Post, J. Chem. Phys. **20**, 755 (1952).

[11] Kushner, Crowe, and Smythe, J. Am. Chem. Soc. **72**, 1091 (1950).

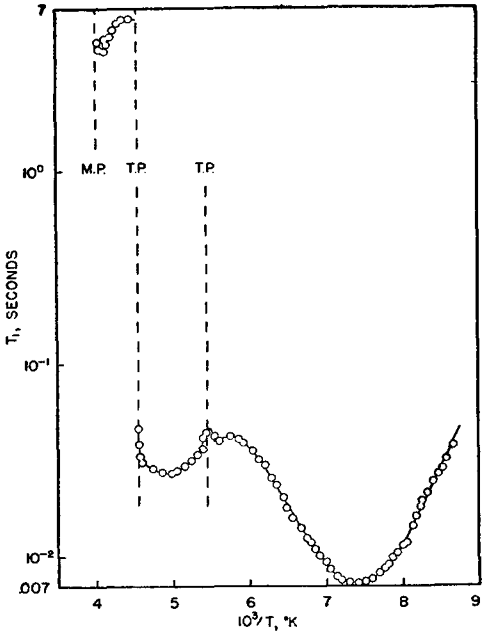

FIG. 3. The temperature dependence of the proton T_1 in solid $(CH_3)_3CCl$, plotted as $\log T_1$ *vs* $10^3/T$.

much lesser extent, similar editing of the experimental data has been exercised on neopentane and methyl chloroform.

The T_1 minimum occurring at the highest temperature is assigned to translational motions. There is curvature in the T_1 plot as the temperature decreases towards the first transition, indicating a contribution from molecular tumbling. This, as well as the shortness of the straight line portion of the high-temperature data, makes it difficult to obtain a reliable value of the activation energy for self diffusion. The observed slope corresponds to an E_a of 2.7 kcal; however, an approximate correction for the effects of molecular tumbling suggests that 5 kcal is more nearly correct.

The T_1 minimum between the two transition points is assigned to molecular tumbling. There is a reasonably good but short straight line portion to the low-temperature side of the minimum; the slope corresponds to an E_a of 1.5 kcal, but this is probably only an approximate value. For reasons to be given, it appears that the molecular reorientations in question occur more frequently about the C–Cl axis than about other axes.

The low-temperature T_1 minimum is due mainly to CH_3 group reorientations. But there is curvature in the plot near the lowest thermal transition, indicating that molecular reorientations are becoming important as well. This is shown also by the apparent activation energies obtained from the slopes of the straight line sections on either side of the T_1 minimum. That at low temperatures is 3.6 kcal while that at higher temperatures is smaller, 2.8 kcal, as would be expected if a second motion were beginning to contribute to T_1. Thus, 3.6 kcal is taken as E_a for CH_3 group reorientation.

Comparison of the observed numerical values of T_1 with calculated values requires an independent accurate means of evaluating τ_c. This is usually difficult except when a T_1 minimum is observed; then the τ_c at the T_1 minimum can be obtained from the first derivative of Eq. (1). The proportionality constant in Eq. (1) is calculated from the molecular structure. The T_1 found in this manner[12] for CH_3 group reorientations is 23 msec, significantly greater than the 7.5 msec observed at the lowest T_1 minimum; however, the calculation assumes that the CH_3 groups are tetrahedral and neglects inter-CH_3 group and intermolecular interactions. Allowing for these approximations and for the contribution from molecular reorientations, the agreement is satisfactory.

Another comparison which can be made involves the ratio of T_1 at the second minimum (27 msec) to the T_1 at the low-temperature minimum (7.5 msec). The ratio predicted[3] between the value of T_1 at a minimum due to CH_3 group reorientation and the T_1 at a minimum due solely to random molecular tumbling is 4/3. The ratio observed is 10/3. The most reasonable interpretation of this is that the T_1 at the second minimum is determined mainly by reorientations about the C–Cl axis;[13] reorientations occur about other axes fast enough to narrow the proton resonance and contribute to the dielectric constant but not fast enough to contribute greatly to T_1.

A final point here is the curious, almost discontinuous increase in T_1 observed at the lower of the two thermal transition points. This little "bump," shown in Fig. 3, is quite reproducible. It seems best explained as the result of slightly faster molecular motion when the crystal form is in the process of changing. When both solid phases are present there would be more grain boundaries and imperfections than in a single phase, and the hindrance to molecular motions would be less.

D. 2,2-Dichloropropane, $(CH_3)_2CCl_2$

Only one thermal transition,[14] at 187°K, is exhibited by solid 2,2-dichloropropane. Between the melting point and the transition, the solid has a very narrow proton resonance[1] as well as a large dielectric constant,[7] indicating that self diffusion as well as molecular tumbling is occurring. At temperatures just below the transition, the dielectric constant is low and the proton

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[12] Gutowsky, Saika, Takeda, and Woessner, J. Chem. Phys. **27**, 534 (1957).

[13] The general methods given in the Appendix of paper IV can be used to make this calculation. Qualitatively, by considering the relative effects of such motions upon the dipolar interactions, it can be seen that reorientations about the C—Cl axis will reduce T_1 less than random reorientations or reorientations about a C—C axis. This is shown in Fig. 13 of I.

[14] A. Turkevich and C. P. Smyth, J. Am. Chem. Soc. **62**, 2468 (1940).

line width[2] corresponds to a "rigid lattice" except for CH_3 group orientations. The latter are frozen out and the proton resonance attains its maximum width at temperatures below 150°K.

The proton T_1 data in Fig. 4 indicate clearly the effects of all three types of motion. In the low-temperature phase, apparently only one motion contributes to T_1; the data fall along a single straight line whose slope gives an E_a of 4.15 kcal, for the CH_3 group reorientations. The slope of this curve is positive, showing that τ_c is on the long side of the T_1 minimum, as it should be in view of the increase in line width at temperatures shortly below the transition.

The T_1 data in the high-temperature phase are very similar to those for neopentane. Near the thermal transition there is a straight line portion of the curve with negative slope, indicating that molecular tumbling is becoming too rapid to affect T_1. The effects of self diffusion then dominate T_1 and the slope becomes positive. And at temperatures just below the melting point there is a pronounced pretransition phenomenon as in neopentane. The actual slopes of the straight line portions assigned to molecular tumbling and self diffusion correspond to E_a values of 2.2 and 4.3 kcal; however, approximate correction with Eq. (3) for the effects of their overlap shows that the true values are more nearly 3 and 6 kcal.

E. Methyl Chloroform, CH_3CCl_3

Thermal[15] and dielectric constant[16] data reveal two transitions in solid methyl chloroform. The large dielectric constant in the high-temperature phase shows that molecular tumbling occurs, and the very narrow proton resonance is evidence of self diffusion with a correlation time no longer than about 10^{-4} sec. At temperatures just below the first transition the dielectric constant is low and the proton line width is large, only slightly less than that predicted for no molecular motions except CH_3 group reorientation. At the low-temperature transition, the line width increases a bit and there is a small anomaly in C_p and in the dielectric constant. All three observations support assignment of the transition to freezing out of CCl_3 group reorientations about the C–CCl_3 axis.

The proton T_1 measurements plotted in Fig. 5 suggest that only two main types of motion govern T_1. At least there is no change apparent in the $\log T_1$ *vs* $10^3/T$ curve at the low-temperature transition. Thus, CH_3 group reorientations appear to determine T_1 in both low-temperature phases, although it is possible that torsional oscillations about C—Cl bonds contribute at the higher temperatures. Data for the low-temperature phases were obtained at several proton resonance frequencies from 16 to 28 Mc/sec in an attempt to learn more about the CH_3 group reorientation mechanism. These will be discussed in the next section. The slope of the straight line low-temperature curve for 20 Mc/sec gives an E_a of 4.1 kcal.

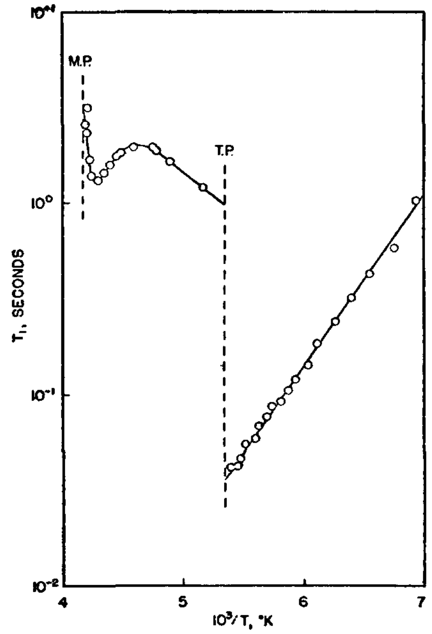

FIG. 4. The temperature dependence of the proton T_1 in solid $(CH_3)_2CCl_2$, plotted as $\log T_1$ *vs* $10^3/T$.

In connection with the high-temperature solid the question arises as to what type of motion governs T_1. The slope of the straight line section between the melting point and the first solid-state transition corresponds to 4.5 kcal which is a possible value for either molecular tumbling or self diffusion. In the other three tetrasubstituted methanes, τ_c for self diffusion in the solid is on the long side of the T_1 minimum. However, the slope of the line in question is negative, indicating that τ_c for the motion dominating T_1 is on the short side of the T_1 minimum. Because of this, it seems more probable that molecular tumbling rather than self diffusion governs T_1.

A curious feature of the T_1 data for methyl chloroform is the behavior of the substance at the main transition point. The high temperature solid phase could be supercooled past the transition. The measurements of T_1 for this phenomenon are also indicated in Fig. 5. No explanation is offered for the apparent constancy of T_1 for the supercooled crystalline form. The most striking aspect of this result is that at the transition there is a change in the slope of the $\log T_1$ *vs* $10^3/T$ plot. In other words, the supercooled phase differs significantly not only from the phase stable at that temperature but also from the parent phase. The molecules are exceptional in that they "know" they are in an unstable thermodynamic state.

Another interesting phenomenon, connecting the

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[15] Rubin, Levedahl, and Yost, J. Am. Chem. Soc. **66**, 279 (1944).

[16] R. W. Crowe and C. P. Smyth, J. Am. Chem. Soc. **72**, 4009 (1950).

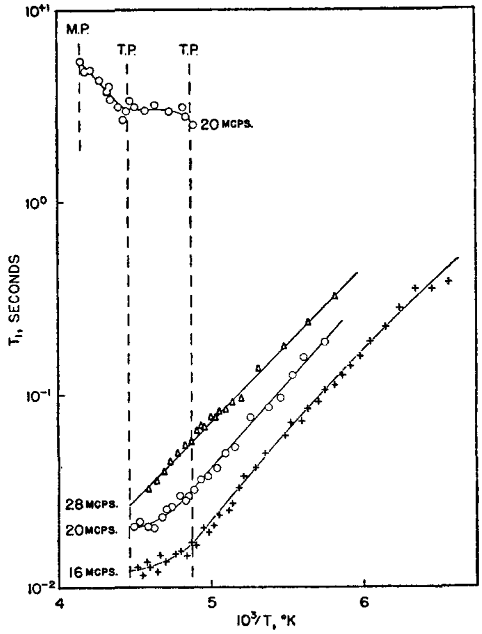

FIG. 5. The temperature dependence of the proton T_1 in solid CH_3CCl_3, plotted as log T_1 *vs* $10^3/T$, for resonance frequencies of 16, 20, and 28 Mc/sec. The data at the top of the figure, between the two T.P.'s, were obtained at 20 Mc/sec on the supercooled high-temperature solid phase; that is, the measurements were made by decreasing the temperature, going on the uppermost curve from left to right.

line width and the pulse experiments, is to be found in an examination of a small detail observed during the pulse experiments. It was noticed that in the low-temperature solid, the Bloch decay following a 90° pulse had a definite structure. This structure is reproduced in Fig. 6. The instrumental transients ("ringing") just after the pulse make it likely that a portion of the nuclear signal is hidden from us. Nevertheless, that portion of the structure which is visible is compatible with the observed line shape; it is the Fourier transform of the "triplet" line shape observed in the steady-state experiments.[1] More detailed studies of free-induction decays in solids have been made independently by Lowe and Norberg.[17]

4. MECHANISM OF THE CH_3 GROUP REORIENTATIONS

A question of some interest concerns the mechanism by means of which the CH_3 groups reorient about their threefold axis. Because of the small mass of the hydrogen atom and the relatively low potential barriers to rotation, it has been proposed[2] that in these molecular solids the CH_3 groups reorient more by tunneling through the barrier than by a classical rotation over the barrier. In paper III, the proton line width was related to an average tunneling frequency ν_t; and the ν_t values inferred from the line widths observed in several tetrasubstituted methanes were compared with those obtained by an approximate quantum mechanical calculation. In paper IV, this tunneling frequency was calculated accurately as a function of temperature for several barrier heights, V_0, with results as shown in Fig. 7, which reproduces part of Fig. 1 in paper IV.

Also, a calculation was made in paper IV of the dependence of T_1 upon ν_t. The effect of other motions occurring simultaneously was included. In the case of CH_3 group reorientation plus molecular tumbling, the result for a crystal powder, considering the dipolar interactions only within a given CH_3 group, is

$$\frac{1}{T_1}=\frac{3\gamma^4\hbar^2}{40r_0^6}\left[\frac{4\tau_{c_1}}{1+\omega_0^2\tau_{c_1}^2}+\frac{16\tau_{c_1}}{1+4\omega_0^2\tau_{c_1}^2}\right.$$
$$\left.+\frac{3\tau_{c_2}}{1+\omega_0^2\tau_{c_2}^2}+\frac{12\tau_{c_2}}{1+4\omega_0^2\tau_{c_2}^2}\right], \qquad (4)$$

where r_0 is the H–H distance, assumed to be 1.79 A; τ_{c_1} is the correlation time for the molecular tumbling; τ_c is the correlation time for CH_3 group reorientation, given in terms of ν_t as[1] $\tau_c=1/3\pi\nu_t$; and τ_{c_2} is defined by

$$\tau_{c_2}=[(1/\tau_c)+(1/\tau_{c_1})]. \qquad (5)$$

If only CH_3 group reorientations are important, then τ_{c_1} is set equal to infinity, and Eq. (4) reduces to the more familiar expression for a T_1 having a single minimum. The constant in front of Eq. (4) is less sacred than the functional form and may be adjusted to give the proper value of T_1 at the observed minimum, if such adjustment is needed or desired. In this way, one may account for interactions other than those within the methyl groups.

In the first part of this section, Eq. (4) is used to obtain ν_t from the low-temperature T_1 data, and the results are compared with the tunneling calculations. In the second part, the dependence upon ω_0 of the proton T_1 in methyl chloroform is considered in relation to the tunneling mechanism.

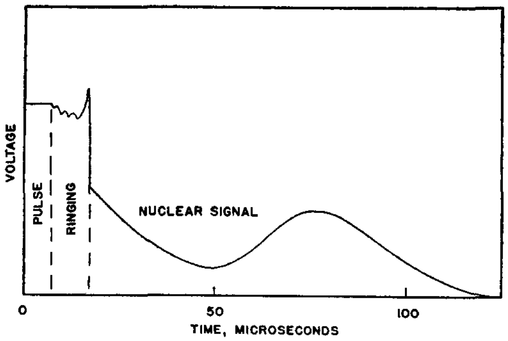

FIG. 6. The Bloch decay of the proton induction signal following a 90° rf pulse applied to solid CH_3CCl_3. The resonance frequency was 25 Mc/sec and the temperature of the sample was about −55°C.

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[17] I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

A. Calculation of ν_t from the Low-Temperature T_1 Data

Acetonitrile

The T_1 data for acetonitrile, in Fig. 1, are not complicated by molecular tumbling, so ν_t was calculated using Eq. (4) with $\tau_{c_1}=\infty$. Because of the absence of a T_1 minimum in the data, a value had to be assumed to complete the calculations. The minimum predicted by Eq. (4), neglecting interactions between neighboring CH_3 groups, is 22.6 msec; however, the T_1 minimum in *t*-butyl chloride is less than 10 msec, which was chosen as a reasonable value for acetonitrile. The ν_t values obtained in this fashion are plotted in Fig. 7. The resulting curve is reasonably compatible with the theoretical ones; it corresponds to a barrier to CH_3 group rotation of about 900 cm^{-1} (2.6 kcal).

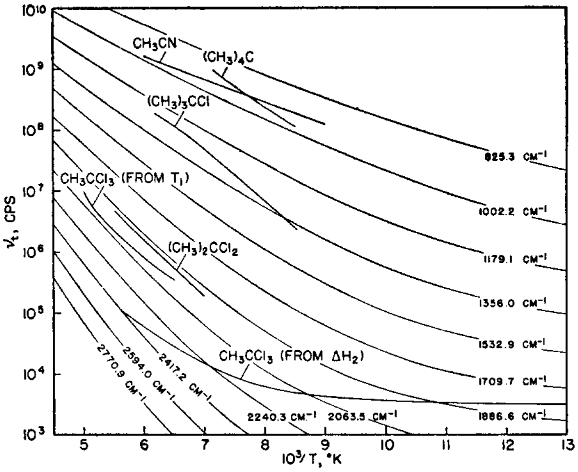

FIG. 7. Log ν_t *vs* $10^3/T$ obtained in a quantum mechanical calculation, see reference 3, for several barrier heights. Included for comparison are experimental curves obtained by calculating ν_t with Eq. (4) from the temperature dependence of the proton T_1 observed in several compounds. In addition, for CH_3CCl_3 there is a second curve obtained from the observed temperature dependence, see reference 1, of the line width ΔH_2.

Neopentane

No low-temperature T_1 minimum was observed in neopentane. It was decided to use the value of 7 msec found for *t*-butyl chloride, in view of the structural similarity of the compounds. Otherwise, the calculations of ν_t from T_1 were made as for acetonitrile, and a curve showing the results is included in Fig. 7. This curve gives the poorest agreement with the tunneling theory of any of the compounds studied. Not only is the slope wrong with respect to the theoretical curves but also the barrier to rotation estimated from Fig. 7 is about 900 cm^{-1} (2.6 kcal) which is less than the activation energy of 3 kcal obtained directly from the T_1 data.

Several factors may be responsible for the discrepancies. A likely one is the contribution of molecular tumbling to T_1 in the low-temperature solid. The activation energy for molecular tumbling in the high-temperature solid is only 1 kcal and a value about threefold larger in the low-temperature solid would result in an appreciable contribution to T_1 and an increase in the apparent activation energy. Another possibility is that the barrier itself decreases at higher temperatures, decreasing τ_c and increasing the apparent activation energy. Intermolecular forces add significantly to the barrier, as evidenced by the 2.1-kcal activation energy found for CH_3CN, and this term would be temperature dependent. Of course, this mechanism applies to all of the compounds and there is no obvious reason why it should be most important for neopentane.

Finally, one of our basic assumptions in calculating the theoretical curves probably breaks down rather badly for neopentane. It was assumed that the potential barrier to rotation was sinusodial and time independent. However, in a neopentane molecule there undoubtedly is a great deal of interaction among the methyl groups. This "cog-wheeling" of the CH_3 groups could produce deviations from the behavior predicted for the simple model. The situation here is sufficiently complex that it would perhaps be better to stop with the classical activation energy determination and let well enough alone.

t-Butyl Chloride

As before, we use the T_1 data near the low-temperature minimum to add another curve to Fig. 7. Although the agreement with theory again leaves something to be desired, we can estimate a barrier to rotation of about 1300 cm^{-1} (3.7 kcal). The rather unsatisfactory fit can be attributed to the same causes as those suggested for neopentane.

2,2-Dichloropropane

Below the thermal transition point, the T_1 data have been treated as in the previous cases. These data contribute another curve to Fig. 7. Again the T_1 minimum is absent. In lieu of better information, 22.6 msec, the calculated value for an isolated methyl group, has been arbitrarily taken as the value of T_1 at the minimum. The barrier indicated from these data is 1900 cm^{-1} (5.4 kcal). The fit between the theoretical curves and the experimental one is quite encouraging.

Methyl Chloroform

The 16 Mc/sec T_1 data in Fig. 5 were used to calculate the ν_t curve in Fig. 7, for the low-temperature solid phase of methyl chloroform. With no clear-cut T_1 minimum present to indicate the amount of inter-CH_3 group interaction to allow for, a value of 18 msec was used; it is the value calculated for an isolated CH_3 group. The data for the other resonance frequencies yield very similar curves which provide no new information. The general shape of these curves fits the family

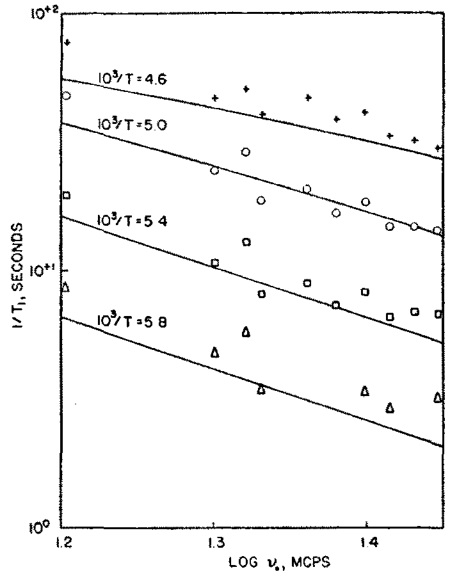

FIG. 8. The dependence of T_1 upon the proton resonance frequency, ν_0, for several temperatures, observed in the low-temperature phase of CH_3CCl_3 and plotted as log $1/T_1$ *vs* log ν_0 (in Mc/sec). The points represent experimental data while the solid lines are theoretical curves calculated as described in Sec. 4B.

of theoretical curves fairly well. The barrier to rotation indicated is 2000 cm^{-1} (5.7 kcal).

In paper III, the root-second-moment, ΔH_2, of the observed proton absorption was used to calculate ν_t in the low-temperature phase. This calculation has been repeated, over a somewhat wider temperature range, and a curve giving the results is included in Fig. 7. There is considerable discrepancy between this curve and the general trend of the family of theoretical curves given there, but that it is curved at all is encouraging. The barrier to rotation indicated by this curve is unclear, but it is some place in the vicinity of 2100 cm^{-1} (6 kcal). The most important feature is that there is a significant difference between the tunneling frequencies obtained from the line widths and from the T_1 data.

This sort of behavior was anticipated in paper IV, when we discussed the combination of two or more spectral density functions to produce a more complex one. We referred to the possibility that perhaps only some of the lower torsional states should be added together in the calculation of a correlation time for CH_3 group reorientation. The upper states could be introduced separately. For lower frequencies, near to zero frequency, this would increase the spectral density function and give a value for ν_t lower than would be predicted by the simple theory, as observed. For higher frequencies, the effect would be much less noticeable. If each of the upper states is considered to possess its own correlation time, and if the frequency under consideration is greater than most of the important levels, i.e., those contributing appreciably to the calculated single tunneling frequency, there is negligible difference between this approach and the simple theory. Calculations of ν_t from the line widths in those compounds where it is possible give results similar to those for methyl chloroform. There seems little point in giving details, particularly as molecular tumbling is so closely associated with the low-temperature line-width changes in neopentane and *t*-butyl chloride.

Mono-Deutero Methyl Chloroform

Substitution of a deuterium atom for one of the hydrogens in the methyl group increases its moment of inertia about the C_3 axis by a factor of 4/3. This is equivalent to a 4/3 increase in V_0, which decreases ν_t by a factor of about 1/10 as may be seen in Fig. 7. Classical motions do not have nearly as great a dependence upon mass as does tunneling. Therefore, in principle it is possible to make a definitive test of the tunneling mechanism by comparing the proton T_1 for CH_2D group reorientation with that for CH_3. An unsuccessful attempt was made to do this using a sample[18] containing about a 2:1 mole ratio of CH_2DCCl_3 to CH_3CCl_3. The proton T_1's were measured in the mixture at 20 Mc/sec giving results which are very similar to those in Fig. 5 for CH_3CCl_3 at 20 Mc/sec except that the T_1's in the mixture are 1.3 times longer in the high-temperature phase, and from 1.3 to 1.6 times longer in the low-temperature phases, the difference increasing at lower temperatures.

In the two low-temperature phases, the T_1 in pure CH_2DCCl_3 would be increased tenfold by the 1/10 decrease in ν_t, and increased by another factor of two, because each proton has only one proton neighbor in CH_2D rather than two as in CH_3. In the high-temperature phase, T_1 is governed by molecular tumbling which should be unaffected by the deuterium substitution; however, one would still expect the twofold increase in T_1 caused by decreasing the number of proton neighbors, in CH_2D, from two to one.

The experimental results can be explained on the basis of spin exchange[19] between protons in neighboring CH_2DCCl_3 and CH_3CCl_3 molecules. The rate of such exchange is given approximately by the intermolecular dipolar broadening of the proton resonance. In the two low-temperature phases this is 10^3 to 10^2 sec^{-1}, much faster than $1/T_1$ for protons in CH_3CCl_3 so that the latter provide thermal contact with the lattice for *all* protons in the mixture, and the T_1 observed is the weighted average[19]

$$(1/T_1)_{\text{obs}}=(f_a/T_{1a})+(f_b/T_{1b}), \qquad (6)$$

where f refers to the proton fractions contained in molecular species a and b. In the high-temperature phase, spin exchange would be much less effective, but

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[18] Karplus, Anderson, Farrar, and Gutowsky, J. Chem. Phys. **27**, 597 (1957).

[19] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. **29**, 804 (1958).

then T_1 is also two orders of magnitude longer, so Eq. (6) should still apply.

At the T_1 minimum and in the high-temperature phase, only the decrease in dipole-dipole interactions affects T_1, and T_1 (CH_2DCCl_3) equals $2T_1$ (CH_3CCl_3). In these cases Eq. (6) leads to the prediction that T_1 in CH_2DCCl_3 whould be 1.4 times longer than that in CH_3CCl_3. The observed ratio, 1.3, is somewhat less, as would be the case if the fraction of CH_2DCCl_3 were less than that assumed. The increase in the T_1 ratio from 1.3 to 1.6 at low temperatures is qualitatively what one would expect on the basis of the tunneling model. Moreover, the predictions are brought closer to experiment if the minimum ratio 1.3 is used in Eq. (6) to calculate the fraction of protons in CH_2DCCl_3. Unfortunately the uncertainties in the composition of the sample as well as the poorer quality of the T_1 data, because of the lower concentration of protons in the sample, are such that it can not be said that the experiment establishes the mechanism of the CH_3 group orientation. But it demonstrates the importance in the spin lattice relaxation of spin exchange and leads to the suggestion that the latter may be measured directly in appropriate mixtures of known isotopic composition. Moreover, the original experiment is still sound in principle and one pitfall has been explored.[20]

B. Dependence upon ω_0 of T_1 in CH_3CCl_3

The dependence of T_1 upon the proton resonance frequency was investigated in the low-temperature solid phase of methyl chloroform with the hope that anomalies attributable to the tunneling might be found. If the torsional levels of the CH_3 group are not broadened into a Debye spectrum by lattice vibrations, and if the splitting of a pair of levels coincides with the resonance frequency, then an anomaly should appear[3] in the dependence of T_1 upon ω_0. However, no effects of this nature were found in measurements of T_1 as a function of temperature at ten different resonance frequencies from 16 to 28 Mc/sec. Three such curves are included in Fig. 5; the others are very similar. A summary of the results is presented in Fig. 8 which shows the frequency dependency of T_1 at several temperatures. Figure 8 was prepared by picking T_1 values for these temperatures from smooth curves drawn through the data obtained in the constant ω_0 experiments. Because of the difficulty in analyzing the errors inherent in the frequency dependence data, the best comment to be made is that the scatter apparent in the data is probably the best indication of the error present.

Although the T_1 data in Fig. 8 fall along smooth curves with no evidence of major anomalies, closer inspection reveals systematic deviations from predictions based on the tunneling theory. Assuming a barrier to rotation of 2063.5 cm^{-1}, the corresponding theoretical curve in Fig. 7 has been used to obtain the apparent value of the tunneling frequency for each temperature used in Fig. 8. From Eq. (4) we can then obtain a theoretical curve giving the dependence of T_1 upon ω_0 for each temperature. The theoretical curves are plotted in Fig. 8 along with the experimental points. Although it is difficult to identify clearly any trend in the details of the frequency dependence of T_1, we can see indications of a slightly enhanced Fourier spectrum both at the lowest and the highest temperatures represented. The highest temperature is well within the region in which it was postulated that there was motion occurring in excess of simple methyl group reorientations. Thus we would expect an enhanced spectral density and a shorter T_1. The source of the low-temperature increase in Fourier spectral density is not quite as clear.

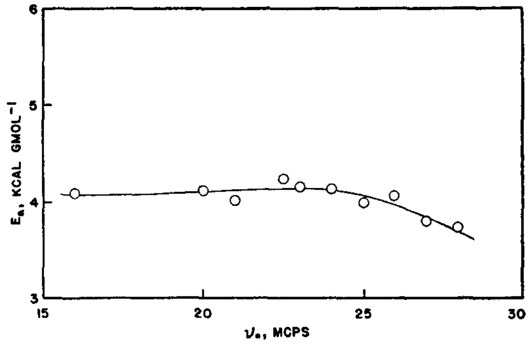

FIG. 9. The dependence upon ν_0 of E_a, the apparent activation energy for CH_3 group reorientations, obtained from the slope of log T_1 *vs* $10^3/T$ observed in the low-temperature phase of CH_3CCl_3.

A somewhat different presentation of the observed frequency dependence of T_1 is given in Fig. 9. Activation energies obtained from the slopes of the logT_1 *vs* $10^3/T$ plots for the low-temperature phase are plotted as a function of the resonance frequency ν_0. One would expect E_a to be independent of ν_0, as it is between 16 and 26 Mc/sec; however, at frequencies above 26 Mc/sec there is a distinct downward trend in E_a. This means that the systematic deviations of T_1 at low temperatures to shorter values as just mentioned becomes significant when ν_0 is greater than 26 Mc/sec. It is, of course, possible to attribute these effects to complexity in the coupling of the torsional and lattice motions, according to the second model for T_1 given in paper IV. However, the fact that E_a starts to change at 26 Mc/sec suggests that spin exchange between protons and chlorine nuclei[19] may be the cause.

The Zeeman splitting of the chlorine nuclear quadrupole energy levels is dependent upon orientation of the CCl_3 group in the magnetic field. Reorientation of the CCl_3 group enables the chlorine resonance frequencies to be brought into coincidence with that of the protons.

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[20] The lability of methyl chloroform makes it difficult to prepare pure CH_2DCCl_3. The sample used here was made by adding DCl to $CH_2{=}CCl_2$. Its stoichiometric composition was close to CH_2DCCl_3; however, enough exchange occurred to produce a mixture of isotopic species more nearly statistical in nature. The presence of CHD_2CCl_3 and CD_3CCl_3 produces minor effects which were neglected in the discussion.

TABLE I. A summary of the activation energies for molecular motions and of the barrier to CH_3 group reorientation obtained from proton T_1 measurements on the solid phases of several substituted methanes.

Motion	CH_3CCl_3	$(CH_3)_2CCl_2$	$(CH_3)_3CCl$	$(CH_3)_4C$	CH_3CN
CH_3 group, V_0	5.7 kcal	5.4 kcal	3.7[a] kcal	2.6[a] kcal	2.6 kcal
CH_3 group, E_a	4.1	4.1	3.6	3.0	2.1
Molecular tumbling	4.5[b]	~3.	~1.5	1.0	...
Self diffusion	...	~6.	~5.	6.0	...

[a] Probably too low because of molecular tumbling; see Secs. 4A and 4B.

[b] There is some uncertainty as to whether molecular tumbling or self diffusion governs T_1 in the temperature interval from which this value is obtained.

In this event, spin exchange and energy transfer can occur between protons and chlorine nuclei. This will reduce the proton T_1 providing the chlorine T_1 is shorter. It was pointed out in the foregoing that CCl_3 group reorientations occur in the intermediate temperature phase. It is likely that they will still be fast enough in the low-temperature phase to be effective in inducing spin exchange; reorientation frequencies as low as 1 cps can produce significant effects.[19] Moreover, measurements[21] of the Cl^{35} T_1 in methyl chloroform at 77°K and in *t*-butyl chloride between 77° and 125°K suggest that the Cl^{35} and Cl^{33} T_1's are at least two orders of magnitude shorter than that of the protons in CH_3CCl_3 in the temperature range in question, 170° to 220°K. Thus, the reorientation-induced spin exchange mechanism can shorten the proton T_1. The lowest proton resonance frequency at which this could occur is 25.6 Mc/sec; it is determined by the Cl^{35} pure quadrupole resonance frequency, which is 37.8 Mc/sec at 77°K. Also, it is plausible that the effectiveness of the spin exchange in lowering the proton T_1 would improve at the lower temperatures, as it must to decrease E_a. If the CCl_3 group reorientations are too fast ($\tau_c \ll 10^{-2}$ sec) the angular factors governing the spin exchange probability lead to a reduction in the effect. Moreover, the effectiveness of the mechanism increases at higher proton frequencies, as shown by Fig. 2 in reference 19; this would account for the dependence upon ν_0 of E_a.

5. DISCUSSION AND CONCLUSIONS

In an attempt to compare the various results obtained, we assemble Table I. In it are listed the four chlorine-methyl substituted methanes in the order of decreasing chlorine content, and acetonitrile. Corresponding to each compound are the various activation energies and barrier heights which we have been able to deduce. We inspect this table in search of a general scheme. It seems quite clear that for methyl group rotation both the barrier to rotation and the observed activation energy decrease with decreasing chlorine content. This seems also to be the case for the activation energies related to the more general molecular tumbling. This is as we might expect. A chlorine atom can be expected to offer more resistance to a nearby rotating methyl group than another methyl group similarly situated. The two are similar in size, but the methyl group is capable of moving out of the way somewhat to accommodate the rotation of the methyl group under inspection. A similar, qualitative trend in the barriers to molecular rotation has been noted[7] in studies of the dielectric dispersion in methyl chloroform, 2,2-dichloropropane, and *t*-butyl chlorine. Electric dipole-dipole forces no coubt contribute to this tend, as suggested.[7]

The activation energies for self diffusion in the solid are alike within the experimental uncertainties for the three compounds for which values were obtained, 2,2-dichloropropane, *t*-butyl chloride, and neopentane. These molecules have quite similar sizes and shapes, approximately spherical, so it is reasonable that their diffusion characteristics be similar. Activation energies for self diffusion in the liquid phase do not appear to be available for any of the compounds treated in this study. The closest appears to be 2,2-dimethyl butane for which the value observed[22] is 2.7 kcal/mole, comparing favorably with the values of 5 to 6 kcal found here for the solids.

A more subtle point to consider is the reasonableness of the values of the barriers to methyl group rotation and the associated activation energies which are inferred from these investigations. The activation energies E_a for those motions which are deemed to be methyl group reorientation are understandably low as are the apparent limiting frequencies for infinite temperature. It may be seen in Fig. 1 of paper IV that at low temperatures the apparent activation energy of the tunneling frequency decreases. Also, we see that at low temperatures the apparent infinite temperature limit is quite small. The next question is whether the rather large values for the barrier to rotation V_0 are reasonable. In the gas phase, methyl chloroform has an internal barrier to rotation of 1017 cm^{-1} (2.91 kcal),[23] while the value obtained here for the solid is 5.7 kcal.

Acetonitrile was included in the list of compounds studied for the sole purpose of investigating this question. Clearly there is no internal barrier to rotation within the acetonitrile molecule itself. Yet, there is definitely a barrier to rotation demonstrated by the T_1

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[21] D. E. Woessner (unpublished results).

[22] McCall, Douglass, and Anderson, Phys. Fluids **2**, 57 (1959).

[23] K. S. Pitzer and J. L. Hollenberg, J. Am. Chem. Soc. **75**, 2219 (1953).

data. This must result from the intermolecular forces within the crystal. It is fortuitous but nonetheless encouraging that the intermolecular V_0 in acetonitrile (2.6 kcal) is virtually the same as the difference between the V_0 value for solid methyl chloroform (5.7 kcal) and the intramolecular V_0 (2.9 kcal). The results for *t*-butyl chloride and neopentane are complicated by interactions between methyl groups, and also by molecular tumbling, but the same general model applies qualitatively to all four tetrasubstituted methanes. Microwave studies of $(CH_3)_3CH$ and $(CH_3)_3CF$ give internal barriers to CH_3 group rotation of 3.9 and 4.3 kcal/mole, respectively.[24] These barriers are large enough to account for τ_c in neopentane and *t*-butyl chloride being about the same magnitude for molecular tumbling as for CH_3 group reorientation.

Although these results show that the tunneling mechanism is plausible for CH_3 group reorientation, it can not be claimed that other possibilities have been eliminated. In order for the tunneling to participate in the spin lattice relaxation there must be relatively strong coupling between torsional and lattice motions, including molecular reorientations.[3] It may well be that such coupling, rather than ν_t, is the most important factor determining T_1 in these experiments. Data obtained over a wider range of temperature and resonance frequency could add to our understanding not only of the dynamic structure of molecular crystals but also of the mechanisms for energy transfer within the solid. At very low temperatures the coupling among the various degrees of freedom in the solid would be reduced and it might then prove possible to observe anomalies in the dependence of T_1 upon ν_0. The possibility of proton-chlorine spin exchange, introduced to account for the dependence upon ν_0 fo E_a for CH_3 group reorientation in CH_3CCl_3, is incidental to the main concern of this research; however, it, along with the results for the mono-deutero methyl chloroform, does draw attention to the need for investigating the importance of spin exchange among protons.

Two observations bear upon the kinetics of phase transitions in solids. One is the constant T_1 observed in the supercooled high-temperature phase of methyl chloroform. The motion dominating T_1 in the high-temperature phase is molecular tumbling, so the implication is that supercooling does not affect the rotational mobility of the molecules. The anomalous increase in the T_1 at the low-temperature transition in *t*-butyl chloride indicates a higher degree of molecular mobility during the phase transition than in either stable phase. This is similar to observations of increased molecular rotation during the supercooled rotational transition of 2,3-dimethyl butane,[25] which was interpreted in terms of a transition about Frenkel holes.

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[24] D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. **29**, 914 (1958).

[25] H. Segall and J. G. Aston, J. Chem. Phys. **23**, 528 (1955).