

$\text{He}^3(d, p)\text{He}^4$  for 10.5 deuterons with the experimental curves of Brolley *et al.*<sup>20</sup> and Allred<sup>11</sup> and found  $r_0 = 4.3 \times 10^{-13}$  cm. The difference is not considered significant.

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<sup>20</sup> Brolley, Fowler, and Stovall, *Phys. Rev.* **82**, 502 (1951).

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## States of Solid Methane as Inferred from Nuclear Magnetic Resonance\*

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As there are different points of view concerning the molecular dynamical states in solid methane, especially concerning the  $\lambda$ -transition at 20.42°K, we have investigated the manner in which the new method of nuclear magnetic resonance throws light on the problem. Both the one-parameter theory and the method of perturbation were applied to the analysis of the proton resonance data given by Thomas, Alpert, and Torrey.

The characteristic time  $\tau_c$  for molecular reorientation was estimated from the spin-lattice relaxation data, and it was found that above 20°K molecules may be considered to reorient against some fixed hindrances due to neighboring molecules. At about 65°K a marked alteration is present in the dominant mechanism of the above reorientation, which is considered to be either cor-

related or independent molecular rotation. However, below 20°K most of the molecules seem to be in the ground state of rotational oscillation and occasionally (about  $10^7$  times per second) tunnel or flip to neighboring equivalent orientations. It was proposed that we should discriminate between two pictures of the local magnetic field, possibly in relation to the frequency of resonance. This idea was confirmed by reproducing the line width data.

A perturbation calculation, assuming the  $F\bar{4}3m$  arrangement of the molecules and taking account of the above situation, gave the entire shape of the absorption line, which was in close agreement with experimental data observed in the lowest temperature range.

### I. INTRODUCTION

ABOUT ten years ago Clusius, Popp, and Frank<sup>1-4</sup> carried out a series of thermal measurements on solid methane and found a  $\lambda$ -change in the specific heat at 20.42°K. Although many authors have considered the mechanism of the  $\lambda$ -transition since that time, no decisive conclusions seem to have been obtained.

According to the results of x-ray analysis<sup>5</sup> the carbon atoms form a face-centered cubic lattice (see Fig. 1), and scarcely any difference was observed<sup>6</sup> between the lattice structures above and below the  $\lambda$ -point. The only remaining degrees of freedom being those of molecular reorientation, Clusius suggested that the transition should be a rotational one as suggested by Pauling.<sup>7</sup>

Because x-ray analysis could not fully locate the hydrogen atoms in the molecule, it seemed hopeless to

verify the molecular rotation directly, and some indirect verifications have been attempted. These are connected with the thermal behavior of solid methane both above and below the  $\lambda$ -point.

Eucken examined<sup>8</sup> the rotational part of the specific heat and obtained a value of about 3 cal/mole deg between the  $\lambda$ -point and the fusion point, which seems to suggest that the molecules are rotating freely in the classical sense. Theoretical calculations showed,<sup>9</sup> however, that the free rotation of a single molecule may become classical only above 50°K.

At the lowest temperature the value of the zero-point entropy has been used as a starting point. Free rotation is excluded because it would require  $S = S_0 + (2/16)R \ln 5$ , which is definitely greater than the observed value  $S_0 = R \ln 16$ . Since  $2^4 = 16$ , Clusius proposed a random distribution of proton spin over the whole crystal, which implies that a spin is correlated equally with spins in the same molecule and with those in the other molecules. Were this the case, the resultant spin of a molecule could easily be changed, and sublimation from such a state should give a single species having

\* Read on October 8, 1951, at the Sixth Annual Meeting of the Physical Society of Japan.

<sup>1</sup> Clusius, Popp, and Frank, *Physica* **4**, 1105 (1937).

<sup>2</sup> A. Frank and L. Popp, *Z. physik. Chem.* **B36**, 291 (1937).

<sup>3</sup> Kruis, Popp, and Clusius, *Z. Elektrochem.* **43**, 664 (1937).

<sup>4</sup> K. Clusius and L. Popp, *Z. physik. Chem.* **B46**, 63 (1940).

<sup>5</sup> H. H. Mooy, *Commun. Phys. Lab. Univ. Leiden* **213 D**(1931); **216 A**(1931).

<sup>6</sup> A. Schallamach, *Proc. Roy. Soc. (London)* **A171**, 569 (1939).

<sup>7</sup> L. Pauling, *Phys. Rev.* **36**, 430 (1930).

<sup>8</sup> A. Eucken, *Z. Elektrochem.* **45**, 126 (1939).

<sup>9</sup> A. W. Maue, *Ann. Physik* **30**, 555 (1937).

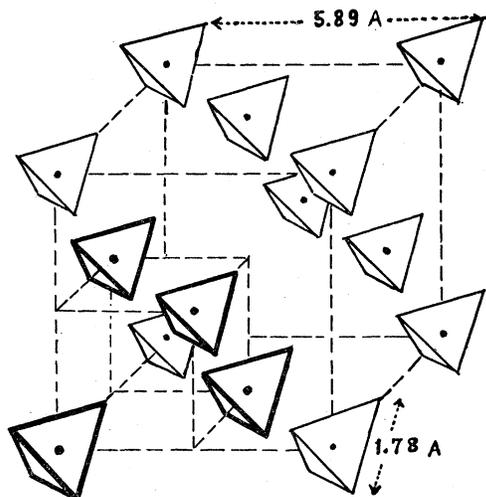


FIG. 1. The crystal structure of solid methane ( $F\bar{4}3m$ ).

the lowest free energy, which seems improbable from our experience with hydrogen. However, recently Nagamiya<sup>10</sup> put forth another reasonable interpretation. He assumed that a molecule is in a state of rotational oscillation, which is quantized by a crystalline field having a definite symmetry due to the configuration of neighboring molecules, and looked for structures which give the proper value of the zero-point entropy. A crystalline field with tetrahedral symmetry was selected, in which molecules should be located parallel to each other, stretching their C—H bonds along the cubic body diagonals (see Fig. 1).

To verify the above viewpoint and to have a clear understanding of the nature of the transition, the recently developed method of nuclear magnetic resonance offers a powerful and promising tool. For this method is capable not only of giving the geometrical configuration<sup>11,12</sup> of protons but also of throwing light on their dynamical behavior.<sup>13-17</sup> The writer had already pointed out<sup>18</sup> that a methane molecule must be in a state of motion even in its lowest temperature modification, because the absorption line is definitely narrower than that expected for a rigid configuration.<sup>19,20</sup> Recently Thomas, Alpert, and Torrey<sup>21</sup> reported a proton magnetic resonance investigation on solid

<sup>10</sup> T. Nagamiya, *Progress Theor. Phys.* **6**, 702 (1951).

<sup>11</sup> G. E. Pake, *J. Chem. Phys.* **16**, 327 (1948).

<sup>12</sup> Gutowsky, Kistiakowsky, Pake, and Purcell, *J. Chem. Phys.* **17**, 972 (1949).

<sup>13</sup> Bloembergen, Purcell, and Pound, *Phys. Rev.* **73**, 679 (1948).

<sup>14</sup> E. R. Andrew and R. Bersohn, *J. Chem. Phys.* **18**, 159 (1950).

<sup>15</sup> H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **18**, 162 (1950).

<sup>16</sup> R. Newman, *J. Chem. Phys.* **18**, 669 (1950).

<sup>17</sup> E. M. Purcell, *Physica* **XVII**, 282 (1951).

<sup>18</sup> K. Tomita, Read on Nov. 4, 1950 at the fifth annual meeting of the Physical Society of Japan.

<sup>19</sup> N. L. Alpert, *Phys. Rev.* **75**, 389 (1949).

<sup>20</sup> Bitter, Alpert, Poss, Lehr, and Lin, *Phys. Rev.* **71**, 738 (1947); N. L. Alpert, *Phys. Rev.* **72**, 637 (1947).

<sup>21</sup> Thomas, Alpert, and Torrey, *J. Chem. Phys.* **18**, 1511 (1950).

methane, giving not only the absorption line width but also the spin-lattice relaxation time (Figs. 2 and 4). They considered that the possibility of rotational transformation was eliminated, because there is no change in line width at the  $\lambda$ -point. Thus we have several conflicting opinions concerning the  $\lambda$ -transition.

The purpose of the present paper is to put in order the above diverse pictures by carefully analyzing the proton magnetic resonance data and to obtain a clear understanding of the mechanism of the  $\lambda$ -change.

## II. DESCRIPTION BY THE ONE-PARAMETER THEORY

In a chemically saturated molecule like methane, protons are seldom influenced by their surroundings except through the magnetic interaction among themselves. The frequency associated with this interaction is only about 0.1 Mc/sec and that associated with molecular rotation is larger than  $10^4$  Mc/sec; therefore, spin-spin interaction can hardly affect the molecular rotation. Conversely, the rotation of the molecule cannot produce any significant magnetic field at the position of the nucleus, because the molecular charge distribution has no electric dipole moment owing to its high symmetry. Thus the coupling of the molecular motion with the nuclear spin system is involved only implicitly in the time change of the relative nuclear coordinates in the spin-spin interaction.

Magnetic resonance experiments are usually performed in the frequency range of 10 Mc/sec, where the Paschen-Back condition is well established; therefore the resonance line is well defined and perturbations due to spin-spin interaction affect only the attributes of the resonance line—i.e., its width and degree of saturation. Under these circumstances the following classification of the magnetic interaction is useful:

$$V = \sum_{i>j} V_{ij}, \quad (1)$$

$$V_{ij} = \gamma^2 \hbar^2 r_{ij}^{-3} \{ (\mathbf{I}_i \cdot \mathbf{I}_j) - 3r_{ij}^{-2} (\mathbf{I}_i \cdot \mathbf{r}_{ij})(\mathbf{I}_j \cdot \mathbf{r}_{ij}) \} \\ = \gamma^2 \hbar^2 r_{ij}^{-3} (A + B + C + D + E + F), \quad (2)$$

$$\Delta m = 0 \begin{cases} A = -2(I_{iz}I_{jz})P_2^0(\cos\theta_{ij}), \\ B = \frac{1}{2}(I_i^+I_j^- + I_i^-I_j^+)P_2^0(\cos\theta_{ij}), \end{cases} \quad (2.1)$$

$$\Delta m = +1: C = -\frac{1}{2}(I_i^+I_{jz} + I_{iz}I_j^+)P_2^1(\cos\theta_{ij}) \\ \times \exp[-i(\phi_{ij} - \gamma H_0 t)], \quad (2.3)$$

$$\Delta m = -1: D = -\frac{1}{2}(I_i^-I_{jz} + I_{iz}I_j^-)P_2^1(\cos\theta_{ij}) \\ \times \exp[+i(\phi_{ij} - \gamma H_0 t)], \quad (2.4)$$

$$\Delta m = +2: E = \frac{1}{4}(I_i^+I_j^+)P_2^2(\cos\theta_{ij}) \\ \times \exp[-2i(\phi_{ij} - \gamma H_0 t)], \quad (2.5)$$

$$\Delta m = -2: F = \frac{1}{4}(I_i^-I_j^-)P_2^2(\cos\theta_{ij}) \\ \times \exp[+2i(\phi_{ij} - \gamma H_0 t)]. \quad (2.6)$$

Here  $\mathbf{I}_i$  represents the spin operator of the nucleus  $i$ ,

and  $m$  is the  $z$  component (parallel to the constant field  $\mathbf{H}_0$ ) of the resultant spin of the molecule.  $\mathbf{r}_{ij}$  ( $r_{ij}, \theta_{ij}, \phi_{ij}$ ) is the relative coordinate of spin  $i$  and  $j$ , and the  $P_l^\mu$  ( $\mu=1, 2, 3$ ) are spherical harmonics of the second order. Semi-diagonal elements ( $A$  and  $B$ ) represent adiabatic perturbations and are considered responsible for the spin-spin relaxation, while off-diagonal elements ( $C, D, E$ , and  $F$ ) represent nonadiabatic perturbations which are considered responsible for the spin-lattice relaxation. However, we can observe only the stationary parts of the perturbation; therefore, an appropriate projection is necessary to select such stationary parts. The idea of Bloembergen *et al.* lies in approximating this process by adopting some specified harmonics in the Fourier spectrum of the intensity of perturbation. When we define  $J_k(\nu)$  by the equation

$$\begin{aligned} \langle F_k^*(t)F_k(t) \rangle &= \int_{-\infty}^{+\infty} J_k(\nu) d\nu \\ &= \int_{-\infty}^{+\infty} d\nu \int_{-\infty}^{+\infty} \langle F_k^*(t)F_k(t-\tau) \rangle e^{2\pi i\nu\tau} d\tau, \end{aligned} \quad (3)$$

where

$$F_0(t) = 2 \sum_{i>j} P_2^0(\cos\theta_{ij}(t))/r_{ij}^3(t), \quad (3.1)$$

$$F_1(t) = \frac{1}{3} \sum_{i>j} P_2^1(\cos\theta_{ij}(t))e^{i\phi_{ij}(t)}/r_{ij}^3(t), \quad (3.2)$$

$$F_2(t) = \frac{1}{3} \sum_{i>j} P_2^2(\cos\theta_{ij}(t))e^{2i\phi_{ij}(t)}/r_{ij}^3(t), \quad (3.3)$$

the spin-lattice relaxation time  $T_1$  (which is associated with the transition due to a nonadiabatic perturbation) is given by

$$(1/T_1) = \frac{3}{4}\gamma^4\hbar^2 I(I+1)[J_2(2\nu_0) + 2J(\nu_0)], \quad (4)$$

where  $\nu_0$  is the Larmor frequency and is introduced as a result of the above projection. The spin-spin relaxation time  $T_2$  (associated with the phase diffusion due to an adiabatic perturbation) is given by

$$\begin{aligned} (1/T_2)^2 &= \text{Spur}(\dot{I}_x^2)/\text{Spur}(I_x^2) \\ &= \frac{9}{4}\gamma^4\hbar^2 \frac{I(I+1)}{3} \langle \sum_j \{2P_2^0(\cos\theta_{ij})/r_{ij}^3\}^2 \rangle \\ &= \frac{9}{4}\gamma^4\hbar^2 \frac{I(I+1)}{3} \int_{-\nu_m}^{+\nu_m} J_0(\nu) d\nu, \end{aligned} \quad (5)$$

which is equivalent to the adiabatic second moment of the absorption line.<sup>22</sup> However, as a result of the above projection there appears the quantity  $\nu_m$ , which is the maximum frequency of the spectrum that contributes to the stationary part of the local field.

In our case of solid methane, since the only remaining degree of freedom is that of molecular rotation, we may

<sup>22</sup> J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

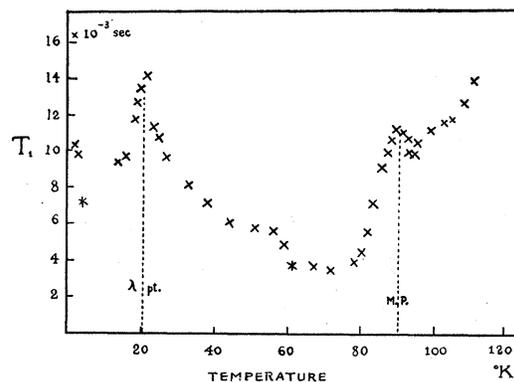


Fig. 2. Observed spin-lattice relaxation time  $T_1$ . (The data indicated by \* seem unreliable as the result of our analysis (see Figs. 3 and 4).)

assume a single time constant  $\tau_c$  (which represents the mean life of the relative orientation of nuclei) at least for the first approximation. This allows us to take a Brownian type correlation function,

$$\langle F_k^*(t)F_k(t-\tau) \rangle = \langle F_k^*(t)F_k(t) \rangle_{Av} \exp(-\tau/\tau_c), \quad (6)$$

from which we can obtain the Fourier intensity by the formula

$$\begin{aligned} J_k(\nu) &= \int_{-\infty}^{+\infty} \langle F_k^*(t)F_k(t-\tau) \rangle \exp(2\pi i\nu\tau) d\tau \\ &= 2\langle F_k^*(t)F_k(t) \rangle_{Av} \tau_c / [1 + (2\pi\nu\tau_c)^2]. \end{aligned} \quad (7)$$

Here  $\langle F_k^*(t)F_k(t) \rangle_{Av}$  expresses the time average and should be calculated by using the orientational wave function  $\phi_R(\theta, \phi)$ . However, as a methane molecule is highly symmetrical in shape, we may safely replace the time average by an average over a sphere. Admitting the above simplifying assumption, we have finally

$$(1/T_1) = K_1 \left\{ \frac{\tau_c}{1 + (2\pi\nu_0\tau_c)^2} + \frac{2\tau_c}{1 + (4\pi\nu_0\tau_c)^2} \right\}, \quad (8)$$

and

$$(1/T_2) = [(3K_1/\pi) \tan^{-1}(2\pi\nu_m\tau_c)]^{\frac{1}{2}}, \quad (9)$$

where

$$K_1 = (3/10)\gamma^4\hbar^2 \sum_{j=2}^4 r_{1j}^{-6}. \quad (10)$$

In this way, the two kinds of relaxation time are reduced to the single parameter  $\tau_c$ .

### 1. Spin-Lattice Relaxation

In contrast to the monotonic variation of the line width with temperature, the spin-lattice relaxation time reveals a rather complex behavior below 90°K (the solidification point), and this suggests its greater sensitivity to the dynamical state of the protons. Accord-

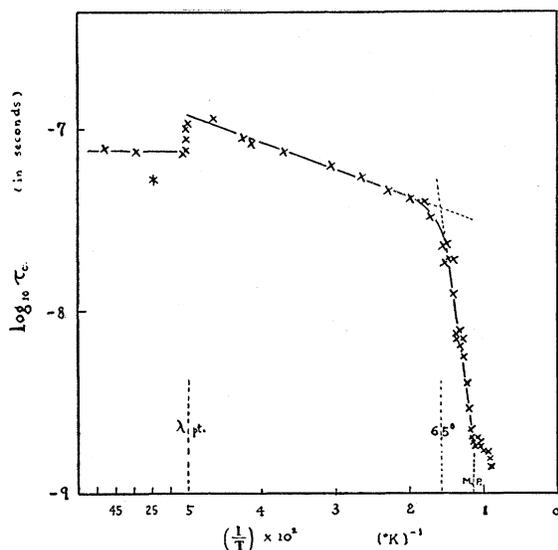


FIG. 3. Characteristic time  $\tau_c$  determined from spin-lattice relaxation. ( $\log_{10}\tau_c$  is plotted against reciprocal temperature.)

ingly, we have chosen the following procedure: By using the spin-lattice relaxation time we first determined  $\tau_c$  as a function of temperature, and then, using this  $\tau_c$ , we calculated the line width to be compared with observation. The first step is not a mere process of parameter fixing, but involves a crucial test of the basic model. For the minimum value of the lattice relaxation time is given by

$$(T_1)_{\min} = (3\sqrt{2}\pi/2)(\nu_0/K_1), \quad (11)$$

which is completely determined by the particular system of nuclei which reorient together as one rigid body, and by the applied frequency. If we take a single molecule as a unit whose reorientation is characterized by the time constant  $\tau_c$ , the minimum relaxation time is calculated to be  $3.5 \times 10^{-3}$  sec, which is nearly equal to the observed value. This assures the validity of our picture, at least in the neighborhood of the minimum (at about 70°K).

By adopting the above picture over the entire temperature range and using (8), we have obtained the results shown in Fig. 3, where  $\log_{10}\tau_c$  is plotted against reciprocal temperature. Figure 3 depends essentially on the nature of solid methane, although  $T_1$  may also depend on the frequency used. It is observed that  $\tau_c$  decreases with increasing temperature, and also that there exist rather sharp changes in the dominant mechanism for spin-lattice relaxation at about 20°K ( $\lambda$ -point), 65°K (this anomaly has not yet been detected by thermal measurements) and 90°K (melting point). The choice of scale enables us to obtain more information about the dynamical behavior of each molecule.

The linear character revealed in the plot above 20°K assures that  $\tau_c$  may be expressed in the form

$$\tau_c^{-1} = \exp(-\theta/T) = \Omega \exp(-\epsilon/kT). \quad (12)$$

Equation (12) suggests that molecular reorientations appear only when the transitions (caused by the thermal agitation) occur between two distinct groups of levels, which are generally quantized by a more or less fixed crystalline field. The orientational flipping in the upper group is considered much more frequent than in the lower group, and  $\epsilon$  is interpreted as the mean separation of the two groups. In the limit of weak quantization, the above process tends to a classical jumping over fixed potential peaks, the height of which is taken to be  $\epsilon$ . The transition in  $\tau_c$  at about 56°K is reproduced fairly well by adding two exponential formulas of the type (12), which seems to favor a classical terminology. The height  $\epsilon$  of the peak and the frequency factor  $\Omega$  in each range was estimated by (12) and are given in Table I. The relative magnitudes of  $\epsilon$  and of  $\Omega$  suggest that in the temperature range (A) (20~65°K) the rate determining passage is rather narrow though it is not very high, whereas in the range (B) (65~90°K) thermal agitation enables a molecule to jump over a broad front though its crest is considerably higher than in the former case. Above 90°K, it is obvious that our model becomes inadequate on account of the possible appearance of migration, but if we assume that only the molecular rotation is responsible for relaxation,  $\epsilon$  and  $\Omega$  are estimated to be between the values in (A) and (B).

Below the  $\lambda$ -point  $\tau_c$  seems almost independent of temperature, which suggests that molecules are frozen into the lowest group of quantized levels, the width of which is much smaller than  $kT$ . It must be observed that the lowest temperature modification of methane does not give  $\tau_c \rightarrow \infty$  (which is expected when molecules are immovably fixed), but it gives  $\tau_c \sim 10^{-7}$  sec, showing the existence of molecular reorientation at this very low temperature. This remarkable feature is, however, understood if we admit that the lowest group contains a number of levels. For then the transition inside this lowest group may be considered to correspond to the flipping reorientation. In fact, the value of the zero point entropy suggests that the lowest group contains a number of levels, even when quantized by the crystalline field.

## 2. Line Width

To confirm the considerations given above we calculated the line width of resonance absorption along the lines of the one-parameter theory, using values of  $\tau_c$  determined from  $T_1$ . According to Bloembergen *et al.*, the effect of the nonadiabatic perturbation on line

TABLE I. Estimated values of  $\epsilon$  and  $\Omega$ .

Temperature range	Activation energy $\epsilon$ (or $\theta$ )	Frequency factor $\Omega$
(A) 20~65°K	68 cal/mole (34°K)	$4.7 \times 10^7 \text{ sec}^{-1}$
(B) 65~90°K	1380 cal/mole (695°K)	$1.4 \times 10^{12} \text{ sec}^{-1}$
Above 90°K	257 cal/mole (130°K)	$2.0 \times 10^9 \text{ sec}^{-1}$

width becomes appreciable only when  $2\pi\nu_0\tau_c < 1$ . In the present case this corresponds to the range  $T > 70^\circ\text{K}$ , where the observed line width is already very narrow ( $< 0.5$  gauss); therefore we may safely neglect the effect of the lattice relaxation on line width when  $T < 70^\circ\text{K}$ . It should be added that in the formula (9)  $\nu_m$  is a rather ambiguous quantity, and this makes the estimate less accurate than in the case of spin-lattice relaxation. Bloembergen *et al.* took  $\nu_m = (1/\pi T_2)$ , but when applied to our case this formula does not give a good reproduction of line width even in the order of magnitude. In this situation we propose to discriminate between two pictures of local magnetic field, possibly in relation to the frequency which is used in the observation.

(1) In the range where  $\tau_c$  is large, only the quasi-static or *kinematical* picture is observed. In this case the additional field due to magnetic interaction causes an

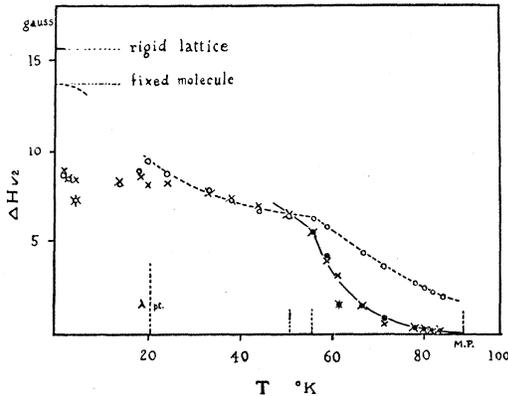


FIG. 4. Half-value width  $\Delta H_{\nu_2}$  calculated from spin-lattice relaxation. (The open circles and the broken line represent the values calculated under the assumption of a quasi-static local field. The closed circles and the full line represent the values calculated under the assumption of a dynamic local field. The crosses represent observed values.)

adiabatic acceleration or decelerations of the main precession, which is expected to appear as a shift or width of the resonance line. However, the effect of the modes of molecular motion which are higher than the applied frequency is averaged out over one cycle of the radiofrequency and cannot be detected as a shift or a width. Therefore it is reasonable to adopt

$$\nu_m = d \cdot \nu_0, \quad (d \sim 1), \quad (13)$$

in this case. In fact, if we take  $d = 0.162$  in this formula, the line width in solid methane is reproduced fairly well, including its local characteristics in the range  $T < 50^\circ\text{K}$  (in Fig. 4 the calculated values are represented by open circles and the broken line). Note that the single formula proves satisfactory both above and below the  $\lambda$ -point.

(2) When  $\tau_c$  becomes small, however, a marked discrepancy appears between the kinematical picture and

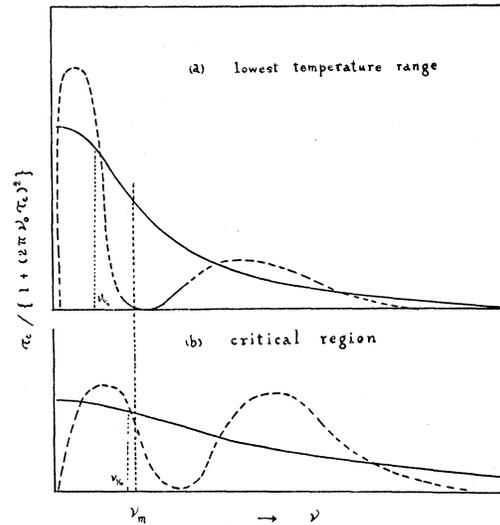


FIG. 5. The frequency spectrum of the intensity of perturbation (schematic). (a) corresponds to the lowest temperature range; (b) corresponds to the critical region.

the observations. (In methane this point is located at about  $50^\circ\text{K}$ , where there is no anomaly in  $\tau_c$ .) An essentially *dynamical* treatment seems necessary in this case. However, we can also include this case in the scheme of the semi-phenomenological theory if we adopt a cooperative or correlated limit for  $\nu_m$ , the procedure of Bloembergen *et al.* being one such example. However, in our case of methane their assumption proves to be inadequate, while a good reproduction of the line width is obtained if we assume

$$\nu_m = e / (T_2)^n, \quad (14)$$

and take  $e = 0.184$  and  $n = 1.44$  above  $50^\circ\text{K}$ , as is shown in Fig. 4. (The calculated values are represented by solid circles and the full line.) It should be noted that this set of values is satisfactory over two regions which are different in the dominant mechanism for lattice relaxation.

In the transition region of the above two pictures, the line width becomes about one half that of a fixed molecule [the latter is estimated to be 13.6 gauss by taking  $\nu_m \rightarrow \infty$  in (9)]. This seems to suggest that in this region the relative importance of the cut-off modes becomes comparable with the ones retained in (9). Conversely, if we tentatively set the critical region by the above condition, we have, according to (9),

$$\nu_m = \nu_{\frac{1}{2}} \equiv \tan(\frac{1}{8}\pi) / 2\pi\tau_c, \quad (15)$$

which is also written as

$$(\tau_c^* \nu_0) = \tan(\frac{1}{8}\pi) / 2\pi d = 0.420. \quad (16)$$

The fact that  $(\tau_c^*)^{-1} \sim \nu_0$  seems to suggest the significance of the critical condition. The observed value for  $\tau_c^* \nu_0$  is 0.386, which is of the same order as (16) but somewhat smaller. This fact may be understood if





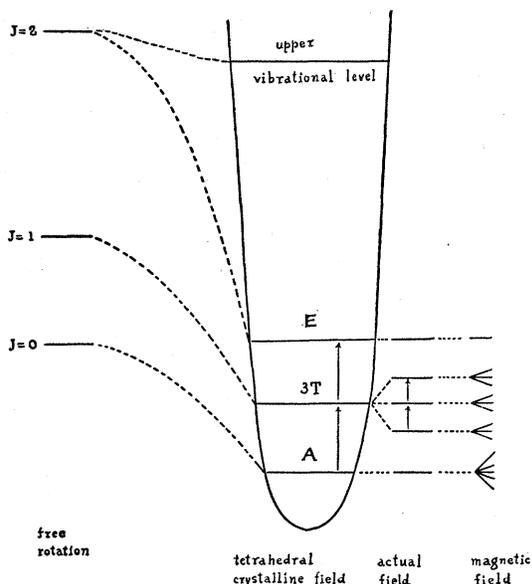


FIG. 6. Level scheme of a methane molecule under the crystalline field (schematic).

### 1. *Meta*-Methane (*A*)

Since the matrix elements themselves are a symmetric combination of  $A_{ij}$ , we have  $a_2 = a_1 = a_0 = 0$  and no local field is present in this case. Therefore a resonance is expected exactly at the Larmor frequency. If we estimate the transition probability by the formula

$$J(M \rightarrow M') = |\langle M | \sum_{i=1}^4 I_{ix} | M' \rangle|^2, \quad (22)$$

we find

$$J_{\text{meta}}(\pm 1 \leftrightarrow 0) = \frac{3}{2}, \quad (23)$$

and

$$J_{\text{meta}}(\pm 2 \leftrightarrow \pm 1) = 1, \quad (24)$$

and finally we have

$$J_{\text{meta}}(\text{total}) = 5. \quad (25)$$

### 2. *Para*-Methane (*E*)

No resultant magnetic moment is present in this kind of molecule; therefore, it drops out of our magnetic observations.

### 3. *Ortho*-Methane (*T*)

Since the trace of the 3-dimensional matrix is zero, the secular equations may be written directly in standard forms. For the case  $M=1$ , we have explicitly

$$x^3 - \frac{3}{16}x + \frac{1}{32} \cos \Psi(\theta, \varphi) = 0, \quad (26)$$

where

$$\cos \Psi(\theta, \varphi) = 1 - (27/2) \sin^2 2\phi \cdot \cos^2 \theta \cdot \sin^4 \theta \quad (26.1)$$

represents the dependence on the constant field direc-

tion. Equation (26) has three real roots:

$$x_1 = \frac{1}{2} \cos(\Psi/3), \quad (27.1)$$

$$x_2 = -\frac{1}{2} \cos[(\pi - \Psi)/3], \quad (27.2)$$

$$x_3 = -\frac{1}{2} \cos[(\pi + \Psi)/3]. \quad (27.2)$$

For the case  $M=0$ , the matrix elements are similar to the case  $M=1$  except in sign and a factor 2; therefore we obtain three roots:

$$x_1' = -2x_1, \quad (28.1)$$

$$x_2' = -2x_2, \quad (28.2)$$

$$x_3' = -2x_3, \quad (28.3)$$

in the same way. Concerning the transition  $M = \pm 1 \leftrightarrow M = 0$ , only levels with the same suffix can be combined by the selection rule, and we have absorption lines at

$$\eta_i = 3x_i \quad (i = 1, 2, 3) \quad (29)$$

with respect to the Larmor frequency. Each of the three lines have the same intensity

$$J_{\text{ortho}}(\pm 1 \leftrightarrow 0) = \frac{1}{2}. \quad (30)$$

and accordingly we have

$$J_{\text{ortho}}(\text{total}) = 3. \quad (31)$$

The dependence of the line position on the direction of the constant field in the case of a single crystal is shown in Fig. 7(a).

The solid samples used in the observations had been simply condensed from tank methane and cannot be considered as single crystals. Therefore a polycrystalline average was taken, assuming that every direction of a definite figure axis with respect to the constant field is equally probable. Then the probability with which an absorption line appears in the interval  $\eta \sim \eta + d\eta$  is given by

$$W_{\eta \Delta \eta} = \frac{1}{4\pi} \int \int_{\eta \leq \eta(\theta, \varphi) \leq \eta + d\eta} \sin \theta d\theta d\varphi. \quad (32)$$

The results of the calculation, which is given in the Appendix, are shown in Fig. 7(b). Although generally we must take proper account of the mixing ratio of the three kinds of methane, this is proved by Maue<sup>6</sup> to be proportional to the spin weight only, on account of the statistical correlations. Therefore the correct relative weight is given by (25) and (31). After the polycrystalline average is taken, the area under the *ortho*-methane distribution should be normalized to be 3, when that of *meta*-methane (integrated value of  $\delta$ -function) is normalized to be 5. In Fig. 7 the scale unit is

$$3\gamma^2 \hbar^2 / 2\gamma^3 = 7.472 \text{ gauss}. \quad (33)$$

Hitherto we considered an aggregate of isolated molecules, but now we must take into account the interactions between molecules. The effect on a proton

of protons in the neighboring molecules is much smaller and less distinct than the effect of those in the same molecule, and we may take it into account as a broadening of each skeleton line, the resulting shape of which is expected to be proportional to

$$\frac{1}{\langle\langle\Delta H^2\rangle_r\rangle^{\frac{1}{2}}} \exp\left\{-\frac{(H-H_0)^2}{2\langle\Delta H^2\rangle_r}\right\}. \quad (34)$$

Here  $\langle\Delta H^2\rangle_r$  is the second moment (in gauss<sup>2</sup>) due to all protons except those in the same molecule. Assuming that the close neighbors (which play a dominant role) form a single crystal ( $F\bar{4}3m$ ), this is calculated to be (7.34) gauss<sup>2</sup>. Such Gaussian members, which are weighted by the polycrystalline average distribution, were summed to give the entire shape of the resonance. The presence of orthomethane broadens the foot of the Gaussian shape and the final result is shown in Fig. 8 (full line), which is in close agreement with the observed line contour at 1.29°K and 1.42°K.<sup>24</sup> This result is considered to be another independent support of our

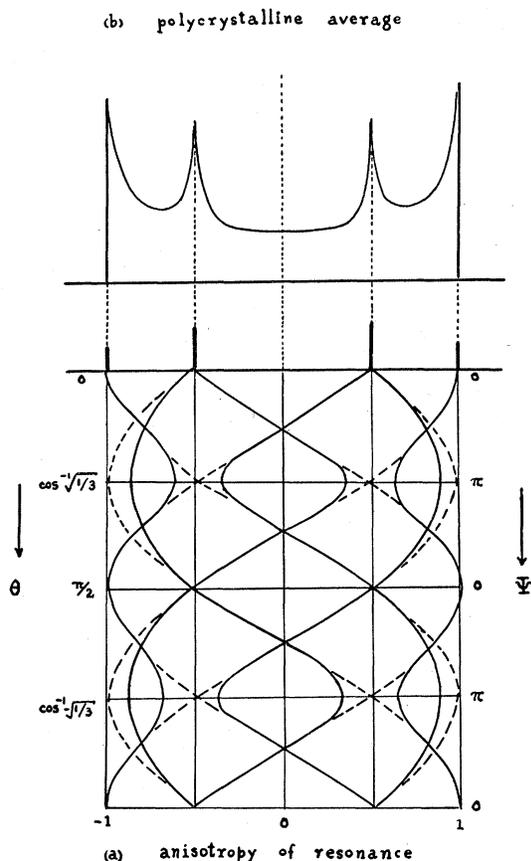


FIG. 7. Anisotropy of the resonance, (a), and the polycrystalline average (b). [Note that the same figure is obtained either when  $H_0$  lies in one of the cubic planes ( $\theta = \pi/2$ ,  $\varphi = 0$ , or  $\varphi = \pi/2$ ) or along one diagonal of the cubic body.]

<sup>24</sup> N. L. Alpert, private communication.

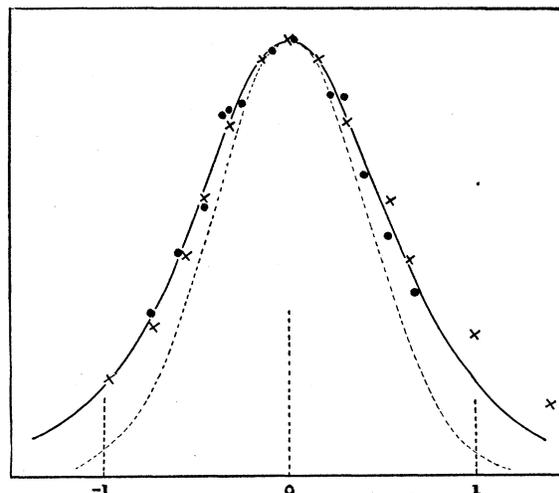


FIG. 8. The absorption line shape below the  $\lambda$ -point (the crosses represent the observed data at 1.29°K and the closed circles represent those observed at 1.42°K, both by Alpert, reference 24). The calculated results are shown by the full line, while the broken line represents the contour when there is only meta-methane. The scale unit equals 7.472 gauss.

viewpoint, which was proposed in the previous section and interpreted in this section.

#### IV. DISCUSSION AND CONCLUSION

As the result of the above analysis, we now have the following picture of the dynamical state of the molecules in solid methane.

##### 1. Below the $\lambda$ -Point (20°K)

(a) Molecules are located parallel to each other, stretching C-H bonds along the cubic body diagonals; or, more precisely, they are definitely confined to the ground state of the rotational oscillation.

(b) However, several states belong to the lowest level group on account of the figure symmetry, and a molecule resonates among them because of its small moment of inertia. This results in the occasional flipping of molecules to neighboring equivalent orientations (about  $10^7$  times per second on the average), and thus the spin-lattice relaxation time is rather short in this substance even at the lowest temperature.

(c) As the frequency of the flipping which is accompanied by a change in the resultant spin of a molecule is much larger than the Larmor frequency, the consequent local field cannot be detected as line width. Thus the observed width is only 57 percent of that which is expected for fixed molecules.

##### 2. Between the $\lambda$ -Point (20°K) and the Fusion Point (90°K)

(a) The  $\lambda$ -change in the specific heat at 20°K is associated with a rotational transformation, but the liberated motion is a hindered rotation rather than a free rotation.

(b) In the range between 20°K and 65°K, molecules are considered to rotate in gear with each other, slowly but less forcibly; while, in the range between 65°K and 90°K, molecules are considered to rotate more rapidly and independently, but occasionally collide with each other rather violently. The transition at about 65°K involves only the change in the dominant mechanism of relaxation and not a change in the degrees of freedom, for there is no anomaly in the thermal behavior in this region.

To examine the validity of the above pictures, and to make sure of the generality of the idea which leads us to them, it is most desirable to perform several more systematic experiments on methane. For example: (1) Careful measurements of line width using several different frequencies are necessary, because by such experiments discrimination will be obtained between phenomena depending on the frequency used and those inherent in the nature of the material. (2) Experiments on single crystals are desirable, for, by elaborating the fine structure of the resonance absorption, we may be able to test our model more conclusively. Also the direct determination of the proton lattice is desirable, if the method of neutron diffraction is available. (3) Similar measurements on deuterated methane, especially on CD<sub>4</sub>, are needed. This will serve as another method to confirm the assumptions regarding the crystalline field, and will tell us about the electronic structure in the neighborhood of the deuteron.

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#### APPENDIX.

Solving for  $\varphi$  in terms of  $\eta$  in a form  $\phi = \varphi(\theta, \eta)$ , (32) becomes

$$W_\eta = \frac{1}{4\pi} \int_{(\text{allowed region})} \frac{\partial \varphi(\theta, \eta)}{\partial \eta} d(\cos\theta), \quad (\text{A.1})$$

which is convenient for calculation. Confining ourselves to the case of  $\eta_1$  and putting

$$\gamma_1 = \frac{2}{3}\eta_1 = \cos(\Psi/3), \quad (\frac{1}{2} \leq \gamma_1 \leq 1), \quad (\text{A.2})$$

$$\Theta(\theta) = \cos^2\theta \sin^4\theta, \quad (\text{A.3})$$

and

$$f_1(\gamma_1) = (2/27)(1 + 3\gamma_1 - 4\gamma_1^3) \geq 0, \quad (\text{A.4})$$

we obtain

$$\frac{\partial \varphi}{\partial \gamma_1} = \frac{|\partial f_1 / \partial \gamma_1|}{4[f_1(\Theta - f_1)]^{3/2}}, \quad (\text{A.5})$$

from which it becomes clear that the integration in (A.1) should be taken over the regions where  $\Theta \geq f_1 \geq 0$ . Changing the variable to

$$\xi = \cos^2\theta, \quad (\text{A.6})$$

and making use of the roots  $\alpha_1, \alpha_2, \alpha_3$  ( $\alpha_1 \geq \alpha_2 \geq \alpha_3$ ) of the equation

$$\Theta = f_1, \quad (\text{A.7})$$

(A.1) can be integrated to give

$$\begin{aligned} W_{\gamma_1} &= \frac{1}{4\pi} \frac{|f_1'|}{f_1^{3/2}} \int_{\alpha_3}^{\alpha_2} \frac{d\xi}{[(\alpha_1 - \xi)(\alpha_2 - \xi)(\xi - \alpha_3)\xi]^{3/2}} \\ &= \frac{1}{4\pi} \frac{|f_1'|}{f_1^{3/2}} \frac{2}{[(\alpha_1 - \alpha_3)\alpha_2]^{3/2}} K(k^2), \end{aligned} \quad (\text{A.8})$$

where

$$k^2 = [(\alpha_2 - \alpha_3)\alpha_1] / [(\alpha_1 - \alpha_3)\alpha_2], \quad (\text{A.9})$$

and  $K(k^2)$  is a complete elliptic integral. Although we have confined ourselves to the case of  $\frac{1}{2} \leq \gamma_1 \leq 1$ , the same formula may be applied also to the entire range of  $\gamma$ . Taking into account the common probability of transition, we finally obtain the results shown in Fig. 7(b).