Structural Investigations by Means of Nuclear Magnetism. II. Hindered Rotation in Solids

H. S. Gutowsky and G. E. Pake

Additional information on J. Chem. Phys.

Structural Investigations by Means of Nuclear Magnetism.
II. Hindered Rotation in Solids

H. S. Gutowsky* and G. E. Pake†‡

Gibbs Chemical Laboratory and the Lyman Laboratory of Physics, Harvard University, Cambridge Massachusetts

The experimental absorption line widths, for nuclei with spin 1/2, at nuclear magnetic resonance are given as a function of temperature for a number of molecular crystals. Temperatures ranged from 90°K to the melting points of the compounds. In some cases it has been possible to relate observed line structure and transitions in the line width to the existence and frequency of certain types of hindered rotational motion in the solid state. These deductions are based on mathematical considerations of the quantitative effect of such motions on the structure and second moment of an absorption line. It is emphasized that relatively low frequency motion of the order 10^5 cycles/second suffices to narrow the width of an absorption line from its value in the absence of that motion.

1,2-dichloroethane, 1,1,1-trichloroethane, and perfluoroethane were found to have line-width transitions coinciding with changes in crystal form and anomalies in the heat capacity. In 1,2-dichloroethane and perfluoroethane these transitions correspond to rotational motion about the long axis of the molecule. 1,1,1-trichloroethane has a line-width transition corresponding to this type of motion, but the heat capacity anomaly and change in crystal form coincides with a further small decrease in the line width to that characteristic of the liquid. A number of molecules including acetonitrile, methyl iodide, nitromethane, dimethyl mercury, and ammonia have absorption lines at 90°K corresponding to molecular rotation about the C_3 figure axis. Various other data and interpretations are presented for 2,2-dimethyl propane, methanol, ethanol, acetone, methylamine, and the ethyl halides. The possibility of estimating the potential barriers hindering rotation in solids from the line-width transitions is discussed.

1. INTRODUCTION

ROTATIONAL motion of molecules or atomic complexes in solids reveals itself through anomalies or transitions in a number of physical properties,[1,2] chief among which are perhaps the heat capacity, the dielectric constant, and the structure of the crystal lattice. Further evidence is presented by infra-red and Raman spectra, x-ray and electron diffraction, and, recently,[3] by the width of the lines which characterize radio-frequency resonance absorption by the Zeeman levels of nuclei within a given sample. In studying these rotational processes, one seeks data adequate to determine their nature, in addition to indicating their existence. This paper treats methods for extracting information from the structure and second moment of the nuclear magnetic resonance absorption line, which can be combined with other varieties of data to provide further insight into the actual rotational processes.

It is well known[4] that the characteristics of the absorption line depend not only upon the local nuclear configuration, but also upon the motion of a nucleus and that of its neighbors. The determination of the local nuclear configuration in rigid lattices from experimental line shapes is facilitated[4] by Van Vleck's calculation[5] of the second moment of the absorption line in terms of internuclear distances, nuclear spins, and nuclear gyromagnetic ratios. As stated earlier,[6] Van Vleck's calculation can be adapted to possible rotational motions, yielding a second moment dependent upon frequency and type of motion as well as upon the nuclear properties and internuclear distances. Thus, in favorable cases, a comparison between calculated and experimental second moments provides information concerning the rotational process.

2. LINE WIDTH AND THE RATE OF MOLECULAR REORIENTATION

Bloembergen, Purcell, and Pound[7] find the width of the absorption line in terms of the Debye correlation time, τ_c. To facilitate our discussion, we shall employ a *correlation frequency* or reorientation rate, defined as $\nu_c = (2\pi\tau_c)^{-1}$, which one may think of as an average rate at which significant changes occur in the atomic arrangement about a given nucleus. Then BPP Eq. (52) is re-expressed as

$$(\delta\nu)^2 = A^2(2/\pi)\ \tan^{-1}[\alpha(\delta\nu/\nu_c)]. \tag{1}$$

The line width, on a frequency scale, is denoted $\delta\nu$. The factor α is the order of unity and encompasses the uncertainties arising from the integration limits in BPP Eq. (35) and from our inaccurate definition of $\delta\nu$ with respect to line shape. In practice, we shall take $\delta\nu$, or its counterpart δH which is measured on a magnetic field scale, as the separation between outermost points of maximum and minimum slope on the absorption curve. For the Lorentz line shape,[8] $2\pi\delta\nu$ is identical with the quantity $1/T_2$ appearing in the BPP equations.

* Now at Department of Chemistry, University of Illinois, Urbana, Illinois.
† Now at Department of Physics, Washington University, St. Louis, Missouri.
‡ Predoctoral Fellow of the National Research Council.
[1] A. Eucken, Zeits. f. Elektrochemie **45**, 126 (1939).
[2] C. P. Smyth, Chem. Rev. **19**, 329 (1936).
[3] N. L. Alpert, Phys. Rev. **75**, 398 (1949).
[4] Gutowsky, Kistiakowsky, Pake, and Purcell, J. Chem. Phys. **17**, 972 (1949), hereafter referred to as I.
[5] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[6] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **16**, 1164 (1948).
[7] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948), hereafter referred to as BPP.
[8] G. E. Pake and E. M. Purcell, Phys. Rev. **74**, 1184 (1948).

The constant A in Eq. (1) is evidently the width of the absorption line for a rigid lattice $(\nu_c \rightarrow 0)$. As the reorientation rate increases and approaches the rigid-lattice width, A, $\delta\nu$ decreases. Since A is typically the order of 100 kilocycles/sec., the line will be narrowed usually by molecular reorientation at frequencies which are extremely low on a thermodynamic scale.

3. EFFECT OF ROTATION ON DIPOLAR SPLITTING

If the nuclei which are at resonance reside in a molecule, or atomic complex, which rotates in the crystal lattice, the energy of this system consists of its kinetic energy of rotation together with the potential energy of its position in the lattice and the Zeeman energy of its nuclear magnetic moments in the external magnetic field.

$$\mathcal{3C} = \mathcal{3C}_{\mathrm{orb}} + \mathcal{3C}_{\mathrm{spin}}$$

$$\mathcal{3C}_{\mathrm{orb}} = p^2/2\mathcal{3} + V(\theta, \phi) \qquad (2)$$

$$\mathcal{3C}_{\mathrm{spin}} = -\sum_{j=1}^{n} g_j \beta H_0 I_{zj}$$

The potential function governing the rotation is $V(\theta, \phi)$, and the effective moment of inertia of the system is $\mathcal{3}$, not to be confused with the nuclear spin operator $\mathbf{I}$. The external field $\mathbf{H}_0$ is taken along the z axis.

We suppose that the only significant perturbation arises from the dipole-dipole interaction between spins. This implies that the amplitude of the radiofrequency field, in practice about 10^{-2} gauss, is significantly less than the line width, that electric quadrupole broadening and effects of the electronic spins of paramagnetic atoms are absent or negligible and that magnetic field inhomogeneities (usually about 0.5 gauss) are sufficiently small to permit observation of the true line width. The dipolar perturbation is then

$$\mathcal{3C}^{(1)} = \sum_{j>k} g_j g_k \beta^2 [\mathbf{I}_j \cdot \mathbf{I}_k r_{jk}^{-3} - 3\mathbf{I}_j \cdot \mathbf{r}_{jk} \mathbf{I}_k \cdot \mathbf{r}_{jk} r_{jk}^{-5}] \quad (3)$$

which is shown by the Van Vleck[5] to reduce to

$$\mathcal{3C}_{\mathrm{eff}}^{(1)} = \sum_{j>k} A_{jk} [\mathbf{I}_j \cdot \mathbf{I}_k - 3I_{zj}I_k]$$

$$A_{jk} = \tfrac{1}{2} g_j g_k \beta^2 r_{jk}^{-3} (3 \cos^2\theta_{jk} - 1). \qquad (4)$$

The matrix elements of $\mathcal{3C}_{\mathrm{eff}}^{(1)}$ are computed for the rigid lattice using spin eigenfunctions only and treating the factors A_{jk} as constants. The eigenfunctions of Eq. (2), however, are products of the eigenfunctions of the $\mathcal{3C}_{\mathrm{orb}}$ and those of $\mathcal{3C}_{\mathrm{spin}}$, inasmuch as spin and orbital coordinates are independent. The expectation value of the spin operator in brackets in Eq. (4) is, therefore, evaluated just as for the rigid lattice, but one now requires the expectation value of A_{jk} over the rotational motion of the system.

Inasmuch as the orbital eigenfunctions will not be known in general, we shall limit ourselves here to the rigid restricted plane rotor moving in a potential well

periodic modulo $2\pi/n$ and to situations that permit the use of a classical average over the rotation. Moreover, according to Section 2 the reorientation frequency of a given rotational process should exceed the frequency-width of the absorption line if a unique line width is to exist for that process. In discussing the characteristics of the resonance in moving systems, it is assumed henceforth that this criterion is satisfied.

4. ROTATING PAIRS OF NUCLEAR MAGNETS

The considerations of the preceding section may be applied readily to an isolated pair of like nuclei with spin 1/2 and internuclear separation r. The detailed line shape for the rigid lattice has been computed elsewhere;[9] the absorption line at fixed frequency consists of two components at magnetic fields given by

$$H_0 = (h\nu/g\beta) \pm (3/2)\mu r^{-3}(3 \cos^2\theta - 1). \qquad (5)$$

If the two interacting nuclei move about an axis perpendicular to the line joining them as in Fig. 1, then in the expression for A_{jk} in Eq. (4)

$$3 \cos^2\theta - 1 = 3 \cos^2\phi \sin^2\theta' - 1,$$

where ϕ is the azimuthal or rotational angle of the internuclear vector OP about the rotation axis OA, which makes an angle θ' with the external field. For classical rotation, where $\phi = \omega t$, the average value of $\cos^2\phi$ over the rotation is 1/2, so that

$$\langle 3 \cos^2\theta - 1 \rangle_{\mathrm{rot}} = (3/2) \sin^2\theta' - 1 = (1/2)(1 - 3 \cos^2\theta').$$

Thus, if the frequency of rotation $\omega/2\pi$ is larger than the frequency-width of the rigid-lattice resonance, then the corresponding absorption line has two components at

$$H_0 = (h\nu/g\beta) \pm (3/4)\mu r^{-3}(1 - 3 \cos^2\theta'). \qquad (6)$$

If the two nuclei are in an n-fold potential

$$V(\theta, \phi) = (V_0/2)(1 + \cos n\phi),$$

tunneling may occur as an increasing temperature populates the higher levels within the minima or as the
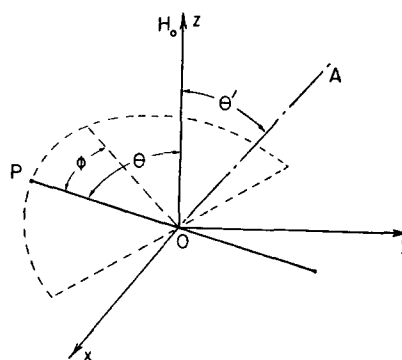

FIG. 1. Model for a nuclear pair in motion about an axis perpendicular to the internuclear axis.

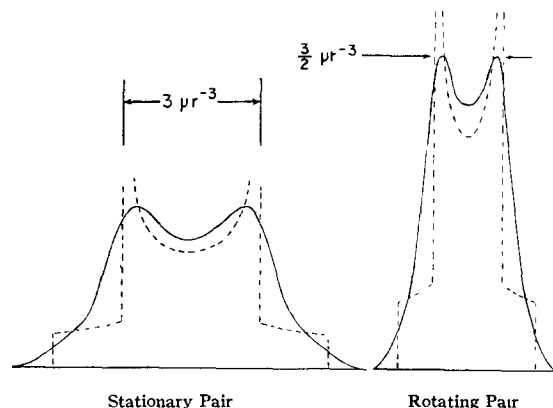[9] G. E. Pake, J. Chem. Phys. **16**, 327 (1948).

FIG. 2. Theoretical line shapes for a nuclear pair with spin 1/2 when stationary and when in motion about an axis perpendicular to the internuclear axis.

potential is altered by lattice changes. In this event, one considers that the system may be found in each of the n minimal positions with equal probability. For $n \geqslant 3$, the expectation value of $\cos^2\phi$ is also $1/2$ over the eigenfunctions

$$\psi = \sum_{r=-\infty}^{\infty} a_r e^{irn\phi}$$

corresponding to a rigid restricted plane rotor in such a potential.[10] In this respect, tunneling is indistinguishable from classical rotation; Eq. (6) gives the doublet positions for both cases and shows the doublet separation is half as great as for the stationary pair.

The dependence of the splitting in Eq. (6) on the orientation of the system with respect to $\mathbf{H}_0$ is similar in form to that in Eq. (5), the axis of rotation replacing the internuclear vector in specifying the orientation. The similarity is more complete for a powder sample, since random orientation of microcrystals provides all values of either θ or θ', whatever the state of motion. For a powdered solid in which the internuclear vector of the isolated pair is stationary at low temperatures but rotates or tunnels at higher temperatures, the absorption line should undergo a transition, becoming half as wide and correspondingly more intense at higher temperatures. The two curves of Fig. 2 represent calculated[9] line shapes corresponding to such a transition. In 1,2-dichloroethane, discussed in Section 7, the proton resonance undergoes just such a transition in which the line retains essentially the same shape but reduces to one-half the rigid-lattice width and becomes noticeably more intense.

5. EFFECT OF MOTION ON THE SECOND MOMENT

A spin system consisting of three protons situated at the vertices of an equilateral triangle occurs in organic

[10] R. Bersohn (private communication); a similar argument holds for the general potential $V(\theta, \phi) = \sum_{r=-\infty}^{\infty} V_r e^{irn\phi}$.

molecules containing methyl (CH_3-) groups. The detailed line structure for an isolated triangular system in rotation about an axis normal to its plane may be determined using the foregoing methods. This problem, as well as its much more difficult counterpart for the rigid lattice, is treated in detail in the accompanying paper by Andrew and Bersohn.[11]

Further additions to the elementary spin system so complicate the detailed analysis that one is led to include the effects of nuclear motion in Van Vleck's calculation of the second moment of the absorption
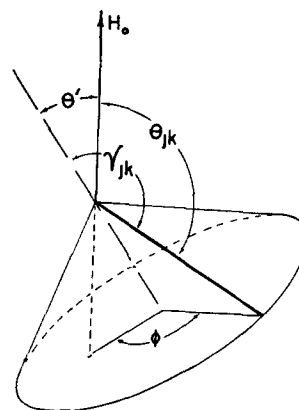

FIG. 3. Model for a nuclear pair in motion about any axis.

line. The considerations of Section 3 permit us to write Eq. (7) of I as

$$\Delta H_2^2 = (3/2)I(I+1)N^{-1}g^2\beta^2 \sum_{j>k} \langle 3\cos^2\theta_{jk} - 1 \rangle^2 r_{jk}^{-6}$$

$$+ (1/3)N^{-1}\beta^2 \sum_{j>f} I_f(I_f+1)g_f^2 \langle 3\cos^2\theta_{jf} - 1 \rangle^2 r_{jf}^{-6}. \quad (8)$$

Here N is the number of nuclei at resonance in the elementary system of spins, and the subscripts f refer to all other nuclear species in the elementary system. The pointed brackets denote the average value of the orbital factor over the motion.

We treat first a classical rotation involving the azimuthal angle ϕ as in Fig. 3. The addition theorem for spherical harmonics[12] yields

$$\langle P_l(\cos\theta_{jk}) \rangle_\phi = P_l(\cos\theta')P_l(\cos\gamma_{jk}), \quad (9)$$

the subscript ϕ denoting an average over the azimuthal angle. The angle γ_{jk} is the angle between the axis of rotation of r_{jk} and r_{jk} itself. For $l=2$, Eq. (9) becomes

$$\langle 3\cos^2\theta_{jk} - 1 \rangle_\phi = (1/2)(3\cos^2\theta' - 1)(3\cos^2\gamma_{jk} - 1) \quad (10)$$

and the second moment for a system rotating about an

[11] E. R. Andrew and R. Bersohn, J. Chem. Phys. **18**, 159 (1950).
[12] See e.g. H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 108, Eq. 3–61.

axis making an angle θ' with H_0 is

$$\Delta H_2{}^2 = (\tfrac{1}{4})(3 \cos^2\theta' - 1)^2[(\tfrac{3}{2})I(I+1)N^{-1}g^2\beta^2$$

$$\times\sum_{j>k} r_{jk}{}^{-6}(3 \cos^2\gamma_{jk}-1)^2+(\tfrac{1}{3})N^{-1}\beta^2$$

$$\times\sum_{j>f} I_f(I_f+1)g_f{}^2r_{jf}{}^{-6}(3 \cos^2\gamma_{jf}-1)^2]. \quad (11)$$

In crystal powders, the axes of rotation are randomly distributed over the sphere of directions; the total effect of all microcrystals is found by averaging over the various values of θ'.

Since $(1/4)(3 \cos^2\theta' - 1)^2$ averaged over a sphere gives

$$\int_{\theta'=0}^{\theta'=\pi} \tfrac{1}{4}(3 \cos^2\theta' - 1)^2(\tfrac{1}{2} \sin\theta' d\theta') = \tfrac{1}{5},$$

the second moment for a powder is

$$(\Delta H_2{}^2)_{\mathrm{powder}} = \frac{1}{4}\left[\frac{6}{5}I(I+1)N^{-1}g^2\beta^2 \right.$$

$$\times\sum_{j>k} r_{jk}{}^{-6}(3 \cos^2\gamma_{jk}-1)^2+\frac{4}{15}N^{-1}\beta^2$$

$$\left.\times\sum_{j>f} I_f(I_f+1)g_f{}^2r_{jf}{}^{-6}(3 \cos^2\gamma_{jf}-1)^2\right]. \quad (12)$$

For the special case in which all γ_{jk} and γ_{jf} are $\pi/2$, that is, if the rotational axis is perpendicular to all internuclear vectors which figure significantly in the
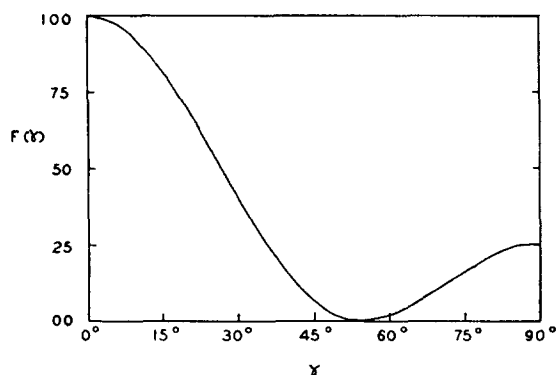

FIG. 4. The dependence of the second moment on the angle γ between the internuclear axis and the axis of motion.

broadening, Eq. (12) reduces to the statement that the second moment for a powder in which such rotation occurs is one-fourth as great as if the lattice were rigid. In the more general case, one applies the factor

$$F(\gamma) = \tfrac{1}{4}(3 \cos^2\gamma_{jk}-1)^2,$$

plotted in Fig. 4, to the individual terms in the summation for the rigid lattice.

The similarity noted in Section 4 between classical rotation and n-fold tunneling for $n \geqslant 3$ applies also to the effect of motion on the second moment. Other cases

may be treated in the same fashion by obtaining the expectation values over the proper orbital eigenfunctions for the terms $\langle 3 \cos^2\theta - 1\rangle^2$ in Eq. (8).

6. EXPERIMENTAL DETAILS

The experimental apparatus and procedure are described in I. Determinations of the second moment give perhaps more insight into a rotational process than do measurements of the line width. However, the calculation of the second moment requires a detailed plot of the absorption line or its derivative,[8] and our cooling apparatus limited such data to fixed temperatures, in this instance room temperature and temperatures corresponding to liquid nitrogen and acetone-dry ice cooling. At intermediate temperatures only the line width was recorded; a single measurement usually required less than 15 seconds. The apparent line width is increased if the field modulation is not sufficiently smaller than the true line width. In graphs of δH versus temperature, the modulation is indicated by a vertical arrow which applies to all measurements in the temperature interval between it and the following arrow.

The intermediate temperatures were reached by permitting the cooling apparatus and sample, previously cooled with liquid nitrogen, to warm. The initial (maximum) rate of warming was about 4° per minute. Above 205°K, where acetone-dry ice was used, the warming rate was greatly reduced by the added heat capacity of the acetone and the smaller temperature differential. The temperature was measured by means of a copper-constantan thermocouple junction placed directly in the sample.

The probable error in a line width measurement is estimated at ±0.3 gauss, and that in temperature is about 1°. Although most determinations were made during warming, occasional checks during cooling showed no hysteresis effects, within the limits of accuracy of the measurements. Of the samples used and not previously referred to in I, most were from commercial sources and of C.P. grade. The dimethyl mercury was infra-red spectroscopically pure and had a boiling point of 92.3–92.5°C. The 2,2-dimethyl pentane (neopentane) was prepared by and available through
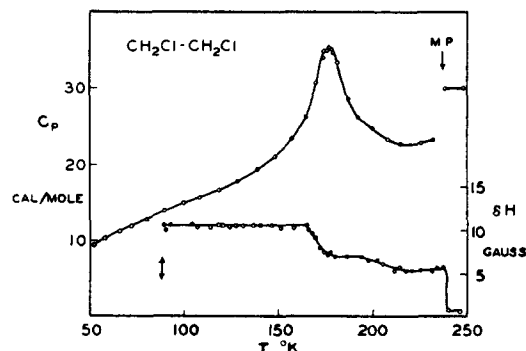

FIG. 5. Line width versus temperature and heat capacity curves for 1,2-dichloroethane.

the courtesy of K. Nozacki; its boiling point was 9.0–9.5°C. The ethanol was absolute, U.S.P.; and the methylamine was anhydrous from Bender and Hobein, München, Germany.

7. 1,2-DICHLOROETHANE: TWO ROTATING PAIRS OF NUCLEAR MAGNETS

The interactions between proton magnetic moments in the 1,2-dichloroethane molecule are found in I to be confined largely to the proton pair in each —CH_2Cl group. Figure 5 shows the experimental line width, δH, of the proton resonance as a function of temperature and includes the heat capacity curve.[13] Detailed line shapes, measured at temperatures of 90° and 205°K are reproduced in Fig. 6. Ordinates of the two curves are not in the same units. The specific heat anomaly at 177°K is approximately coincident with the transition in line width from 10.5 gauss to 6.5 gauss between 165°K and 180°K. A further small decrease of about a gauss occurs near 210°K, above which the line width remains at 5.5 gauss up to the expected sharp transition at the melting point, 238°K.

In I, the 90°K curve of Fig. 6 is integrated and fitted to a computed curve, like that of Fig. 2, which corresponds to a proton-proton separation of 1.71 ±0.02A in a stationary —CH_2Cl group. The constancy of the line width between 90°K and 165°K indicates that the molecule remains effectively stationary in the lattice over that temperature interval. The transition near 177°K to a line approximately half as wide suggests motion about an axis perpendicular to the vector between protons. Further evidence is presented by the curves of Fig. 6, which agree in form with those of Fig. 2 and which correspond closely to the respective
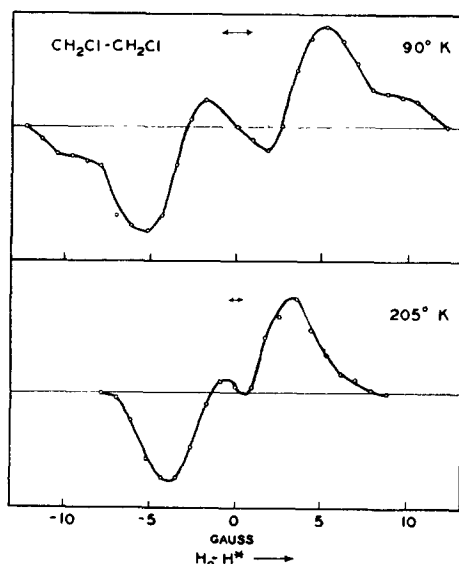

FIG. 6. Derivative curves of the proton magnetic resonance absorption line in 1,2-dichloroethane at 90°K and 205°K.

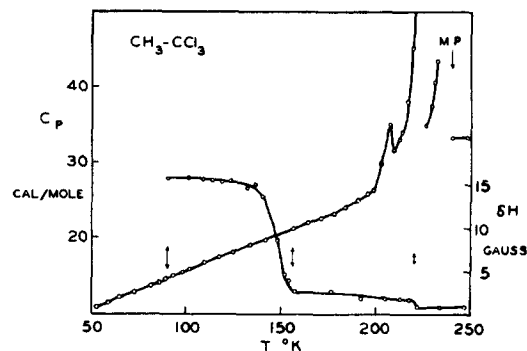[13] K. S. Pitzer, J. Am. Chem. Soc. 62, 331 (1940).

FIG. 7. Line width *versus* temperature and heat capacity curves for 1,1,1-trichloroethane.

doublet separations, $3\mu r^{-3}$ and $(3/2)\mu r^{-3}$, of Eqs. (5) and (6). One concludes that in solid 1,2-dichloroethane, at temperatures between 165°K and its melting point of 238°K, there is rotation or threefold or sixfold tunneling about an axis perpendicular to the lines connecting proton pairs at each end of the molecule. This axis is presumably not quite along the C—C bond, for the heavier Cl atoms tip the principal axis; in any event the axis remains perpendicular to the internuclear vector as required by this interpretation of the data.

The information gained from the line shape in 1,2-dichloroethane affords an opportunity for comparison with the more generally useful second moment considerations. The rigid lattice second moment of 18.2 gauss^2 (see I) may be divided into three major parts: the pair interaction, 14.2 gauss^2; the interaction with other nuclear magnets in the same molecule, 2.5 gauss^2; interactions with neighboring molecules, 1.5 gauss^2. Applying Eq. (12), the postulated motion should reduce the 14.2 gauss^2 contribution by 1/4, and the remaining 4 gauss^2 by approximately 2/3, giving $\Delta H_2{}^2 = 6.3$ gauss^2. Three detailed line plots (including that of Fig. 6) yield 7.2, 6.9, and 5.8 gauss^2 at 205°, 210°, and 218°K, respectively, reasonably consistent with the proposed rotation or tunneling.

The implication of the above data that there is no rotation about an axis perpendicular to the C—C bond below the melting point is consistent with dielectric constant measurements.[14]

The heat capacity anomaly is not fully explained by the motion that narrows the resonance. According to Section 2, the reorientation frequency at the center of the line-width transition is approximately the frequency-width of the rigid lattice resonance:

$$\nu_c(177°K) \cong \delta\nu = (\nu/H_0)\delta H = 40 \text{ kc/sec.}$$

Such a frequency is too low to account in itself for the heat capacity anomaly. However, it might initiate a change in crystal structure which could account for the anomaly.

These experiments do not indicate whether the observed motion involves rotation of one end of the

[14] A. H. White and S. O. Morgan, J. Chem. Phys. 5, 655 (1937).
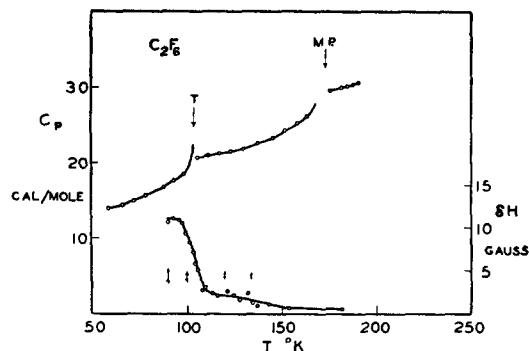
FIG. 8. Line width *versus* temperature and heat capacity curves for perfluoroethane.

molecule with respect to the other as well as motion of the molecule as a whole. The barrier to internal rotation[15] in the gas is about 3000 cal. mole^{-1}; since the heat of fusion is only 2100 cal. mole^{-1}, it is suggested that the predominant motion involves the molecule as a whole.

8. 1,1,1-TRICHLOROETHANE

The absorption line derivative of the proton resonance for this substance at 90°K has been given in I and is discussed in the accompanying paper.[11] Line width is plotted against temperature in Fig. 7, along with heat capacity data.[16] Both the shape[11] and the observed second moment,[4] 18.7 gauss^2, of the absorption line at 90°K correspond to a rigid lattice, with slight narrowing possibly attributable to tunneling of the CH_3-group with respect to a fixed —CCl_3 group. The rigid lattice second moment computed from theory is about 23 gauss^2, of which 21.2 gauss^2 arise from the three protons in the methyl group.

The line width above the transition which occurs near 145°K is much too small to correspond to the expectation for a simple motion of the methyl group about the axis of least moment of inertia. The low value of 0.7 gauss^2 for the second moment of an absorption line plotted at 208°K supports this view. Line shape studies at intermediately low temperatures would be helpful in attempting to settle on the combination of motions responsible for the narrowing.

At 220°K, the line narrows further to a width of about a gauss which persists through the melting point at 240.2°K. Both the specific heat[16] and the dielectric constant[17] confirm the excitation of new degrees of freedom: the former exhibits a 1786 cal. mole^{-1} anomaly at 224.2°K and the latter rises sharply with increasing temperature at 224°K, where the crystal also becomes isotropic. Gradual decrease of the dielectric constant below 220°K as temperature is decreased to 150°K supports the presence of residual low frequency motion below the transition.

[15] W. D. Gwinn and K. S. Pitzer, J. Chem. Phys. **16**, 303 (1948).
[16] Rubin, Levedahl, and Yost, J. Am. Chem. Soc. **66**, 279 (1944).
[17] A. Turkevich and C. P. Smyth, J. Am. Chem. Soc. **62**, 2648 (1940).

9. PERFLUOROETHANE

The derivative of the fluorine absorption line at 27.22 Mc/sec. is given in I for this substance at 90°K. Line width and the heat capacity[18] are plotted against temperature in Fig. 8. The second moment of 15.1 gauss^2 observed at 90°K corresponds to a rigid lattice.[4] Between 95°K and 110°K the line narrows from 11 gauss to 2.5 gauss, remaining fairly constant up to about 130°K where it further decreases to 0.5 gauss and then remains unchanged through the melting point, 173°K.

The first line-width transition parallels the heat capacity anomaly[18] at 104°K. The width between 130° and 160°K seems too low to correspond to motion about the C—C axis alone, but second moment values are necessary to settle this point. The further drop at 135°K evidently marks the onset of low frequency reorientation qualitatively similar to that in the liquid, since the line width is unchanged on melting.

10. THE TRIANGULAR ROTOR

Several absorption lines observed at 90°K probably correspond to rotation or tunneling of a triangular configuration of equidistant protons about an axis normal to their plane. Methyl groups contributed such lines in acetonitrile, methyl iodide, nitromethane, and dimethyl mercury; ammonia also gave such a line.

Figure 9 reproduces the derivative curve of the proton resonance in acetonitrile; the second moment is 6 gauss^2. The other compounds showed similar shape, though the fine structure was less well defined. Second moments observed at 90°K appear in Table I, along with computed values corresponding to motion about the C_3 axis of the molecules. Intermolecular broadening is not included in these computations, which are based on C—H distances of 1.10A and tetrahedral angles in the methyl groups. The N—H bond in NH_3 is taken[19] to be 1.014A and the pyramid height 0.381A. Allowing for
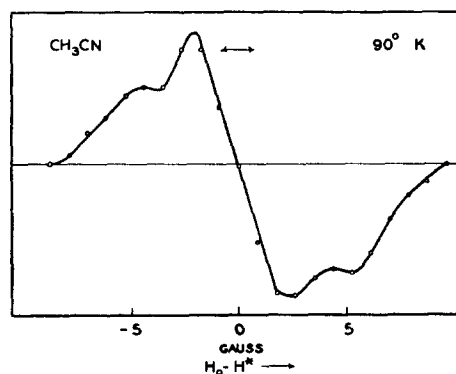

FIG. 9. Derivative curve of the proton magnetic resonance absorption line in acetonitrile at 90°K.

[18] E. L. Pace and J. G. Aston, J. Am. Chem. Soc. **70**, 566 (1948).
[19] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 439.
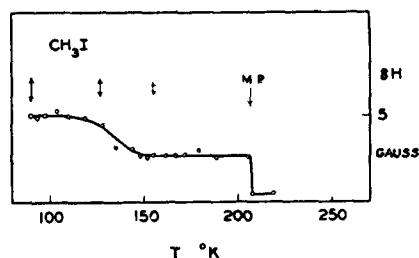
FIG. 10. Line width *versus* temperature curve for methyl iodide.

intermolecular broadening, the proposed motion is reasonably well supported by the table; computed second moments would be four times as great for the stationary molecule. The detailed analysis[11] of the line shape for acetonitrile indicates also the existence of the proposed motion.

Methyl iodide is the only compound of the group for which the line width was measured as a function of temperature. As indicated by Fig. 10, rotation, possibly of the C−I vector, sets in at 125°K. No dielectric constant data known to the authors extends below 175°K.

TABLE I. Observed and theoretical values of $\Delta H_2{}^2$ for triangular rotors.

Sample	Theoretical intramolecular	Observed
CH_3CN	5.3 gauss^2	6.0 gauss^2
CH_3I	5.4	8.4
CH_3NO_2	5.4	7.0
$Hg(CH_3)_2$	5.3	8.7
NH_3	9.7	9.7

to bear on the question. However, the dielectric constants of nitromethane[20] and ammonia[2, 21] do not indicate rotations about an axis perpendicular to the figure axis, nor do their heat capacity curves[22, 23] show any anomalies.

11. OTHER COMPOUNDS STUDIED

The change of line width with temperature was examined for the proton resonance in a number of other compounds. Various data are reproduced in Figs. 11, 12, and 13.

Ammonium salts.—Line-width transitions were first observed in detail for the proton resonance in several ammonium compounds. A summary of these data has been presented earlier.[6]

2,2-Dimethyl propane.—The heat capacity[24] is compared with the line-width curve in Fig. 11. Our lowest attainable temperature was incapable of freezing out

whatever motions lead to the 2.5 gauss line between 93°K and 193°K. The decrease to 1.5 gauss at 200°K implies further rotation of the molecule. One suspects that the nearly spherical symmetry of the molecule permits a high degree of rotational freedom to which the narrow lines in this solid may be attributed. The heat capacity anomaly at 140°K has no counterpart in the line width. Some evidence exists for a change in crystal form near this temperature.[25]

Methanol.—The molecule is interesting in that the line width (Fig. 12) is insensitive to temperature between 85°K and the melting point at 175.2°K, yet a specific heat anomaly[26, 27] and a dielectric constant transition[28] have been reported between 155°K and 160°K. It is possible[29] that these effects are associated with rotation of the hydroxyl group within the solid, as suggested by the small entropy of transition. If so, the line width, predominately contributed by the methyl group which might continue in motion, would be little affected.

Ethanol.—Whereas the line width in methanol does not become small until melting occurs, that in ethanol (Fig. 12) drops from a value of 10 gauss at 90°K to a width fixed by magnet inhomogeneities at a temperature 35°K below the melting point. No anomalous behavior of the heat capacity[26] has been observed above 90°K and detailed dielectric data below the melting point are lacking.

Acetone.—The methyl groups in this molecule apparently undergo low-frequency reorientation even at 90°K. The gradual decrease in line width (Fig. 12) to the melting point suggests a slow onset of rotation, in agreement with the frequency dependence[30] of the dielectric constant down to about 145°K.

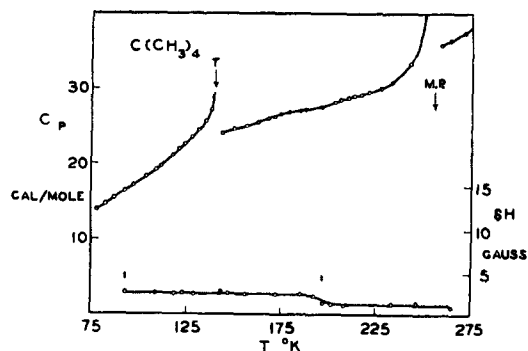*Methylamine.*—This molecule is of interest in con-

FIG. 11. Line width *versus* temperature and heat capacity curves for 2,2-dimethyl propane.

[20] C. P. Smyth and W. S. Walls, J. Chem. Phys. **3**, 557 (1935).
[21] C. S Hitchcock and C. P. Smyth, J. Am. Chem. Soc. **55**, 1296 (1933).
[22] W. M. Jones and W. F. Giauque, J. Am. Chem. Soc. **69**, 983 (1947).
[23] Clusius, Hiller, and Vaughen, Zeits f. physik. Chemie **B8**, 427 (1930).
[24] J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).

[25] W. Wahl, Zeits. f. physik. Chemie **88**, 129 (1914).
[26] G. S. Parks, J. Am. Chem. Soc. **47**, 338 (1925).
[27] K. K. Kelley, J. Am. Chem. Soc. **51**, 180, 1145 (1929).
[28] C. P. Smyth and S. A. McNeight, J. Am. Chem. Soc. **58**, 1597 (1936).
[29] C. S. Hitchcock and C. P. Smyth, J. Am. Chem. Soc. **56**, 1084 (1934).
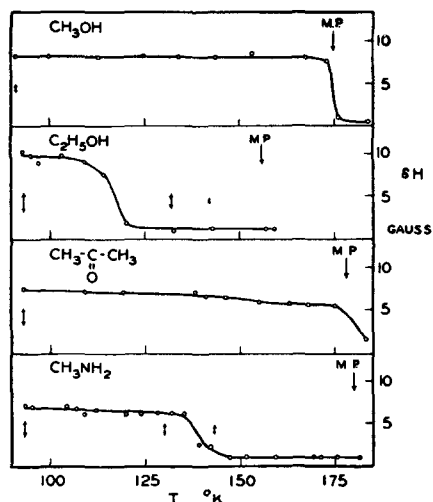[30] S. A. McNeight and C. P. Smyth, J. Am. Chem. Soc. **58**, 1718 (1936).

Fig. 12. Line width *versus* temperature curves for methanol, ethanol, acetone and methylamine.

nection with the high rotational mobility reported in I for ethane and disilane in the solid state.

The second moment of the proton resonance observed at 90°K is 20 gauss,[2] intermediate between the 40 gauss[2] expected for a rigid lattice and the 13 gauss[2] expected for motion about the $C-N$ axis. There is a small decrease in the line width (Fig. 12) from 7 gauss at 90°K to 6 gauss at 125°K; a second moment measurement at the latter temperature is desirable. The line becomes narrow between 135°K and 150°K, remaining so up through the melting point at 180°K. The dielectric data[30] have been interpreted as opposing the proposed existence of molecular rotation in the solid, although the dielectric constant is frequency dependent. Hysteresis effects in the heat capacity[31] further obscure the state of affairs in this substance.

Ethyl halides; Impurity effects.—Figure 13 reproduces line-width curves for ethyl chloride, ethyl bromide, and ethyl iodide; these curves presumably indicate impurity effects. For all three, the dotted curves represent data obtained from old samples which had been opened and standing in the laboratory for several months; the bromide and iodide were deeply colored by free halogen. Freshly opened samples yielded the solid curves.

Both the observed line shape and second moment of ethyl chloride at 90°K indicate a rigid lattice. Although additional second moment data are needed to verify the conclusion, each curve has a transition from a probable rigid-lattice line to one about half as wide, which may correspond to rotation or tunneling about the $C-C$ axis. The effect of impurity on the rate at which reorientation frequencies become great is pronounced.

The transitions in the purer samples occur within 10° of each other, near 115°K, and over like intervals of

about 30°. No anomaly is observed in the low temperature heat capacity[32] of ethyl chloride.

12. DISCUSSION

Some general correlations and queries arise from the data reported above. It appears that light symmetrical groups, even when attached to a heavier framework, can exhibit rotation or tunneling about their figure axes for temperature ranges as great as 100° to 150° below the melting point of the solid. The fact that dimethyl mercury shows motion about the linear $C-Hg-C$ axis at least 150° below its melting point while 1,1,1-trichloroethane does not at only 100° below its melting point suggests that internal hindrance is also important. The results concerning the dependence of motion, over two or three degrees of rotational freedom, on the symmetry of a system are in general accord with conclusions drawn from other data.[2] In addition, molecules such as ethane, disilane, perfluoroethane, and methylamine appear to have unexpected rotational mobility in the solid. Such data as these indicate experimentally the various degrees of hindrance to motion offered by the potential barriers within solids.

More detailed information regarding the hindering potentials should follow from refinements of the experimental methods and qualitative notions developed thus far. In a given system, the structure of an absorption line depends on the frequency and type of motion, which, in turn, are functions of temperature and the potentials in the solid. Therefore, in principle one should be able to relate the temperature dependence of
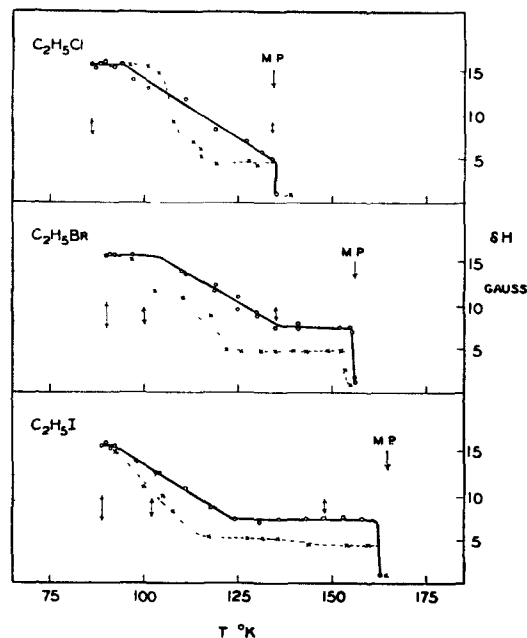

Fig. 13. Line width *versus* temperature curves for ethyl chloride, bromide and iodide.

[31] Aston, Siller, and Messerly, J Am. Chem. Soc. **59**, 1743 (1937).

[32] J. Gordon and W. F. Giauque, J. Am. Chem. Soc. **70**, 1506 (1948).

the line structure to the potentials. Semi-quantitative information is obtainable from the present data and the earlier results of Bloembergen, Purcell, and Pound.[7] Equation (1) of Section 2 was obtained via BPP as a description of the line width in terms of the spectrum of random motions comprising thermal agitation and expresses the result that $\delta\nu$, for a perfectly homogeneous field, approaches zero asymptotically as ν_c increases above the rigid-lattice width A. To treat a transition from one definite line width to a narrower line characteristic of a specialized motion, an *ad hoc* adjustment of Eq. (1) is obtained by writing[33]

$$(\delta\nu)^2 = B^2 + C^2(2/\pi)\,\tan^{-1}(\alpha(\delta\nu/\nu_c)). \quad (15)$$

The rigid lattice width is then
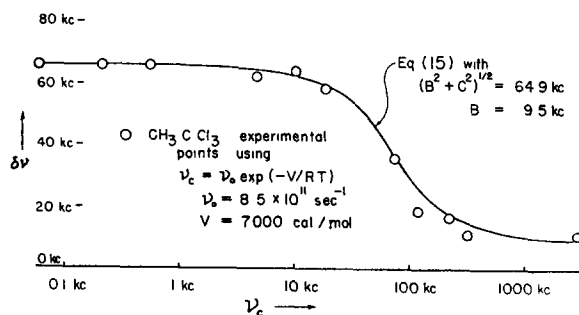
$$A = (B^2 + C^2)^{1/2}.$$

Fig. 14. The correlation frequency ν_c as a function of the line width $\delta\nu$, in frequency, for 1,1,1-trichloroethane.

In Fig. 14, the experimental line width *versus* temperature curve is fitted to Eq. (15) by assuming that ν_c varies with temperature as

$$\nu_c = \nu_0 e^{-V/RT}, \quad (16)$$

a form met in the theory of rate processes.[34] The quantity V is analogous to the activation energy and should be closely related to the barrier hindering rotation.

The curve in Fig. 14 is fitted by $\nu_0 = 8.5 \times 10^{11}$ sec.$^{-1}$ and $V = 7000$ cal. mole^{-1}. These numbers probably have no significance beyond order of magnitude, but they are

surprisingly near the values one can obtain from an approximate treatment[35] of the hindered rotor. The success of so rudimentary an effort as that associated with Fig. 14 suggests that rigorous theory might be developed along these lines. One should note that Eq. (16) ought not in general to be a rigorously valid expression for the reorientation or correlation frequency if tunneling is the mechanism involved; in this event ν_c would be expressed as a sum of properly weighted tunneling rates over the various populated levels within the n-fold potential well.

Another aspect of interest concerning the line-width transitions in the solid is whether or not they are cooperative phenomena. Although the potentials restricting motion are probably a function of that motion, low frequency motions such as we observe do not appear to be cooperatively coupled to as great an extent as melting phenomena. Solids such as methanol and the ethyl halides which have pre-melting broad lines, exhibit line-width transitions at the melting point that are practically discontinuous. In contrast the lower temperature line-width transitions are very gradual indeed. Moreover, the approximate non-cooperative treatment outlined above appears capable, on further refinement, of affording a reasonable interpretation of the observations. The coincidence of heat capacity and line-width transitions suggests that if the rotational frequency is the non-cooperative, slowly increasing inverse function of line width portrayed in Fig. 14, then the excess heat at the transitions must be due to structural changes. In this connection, it is to be noted that most such coincidences occur when the motion involves a fairly large moment of inertia and spatial extent, and then there is usually a concurrent, perhaps cooperative change in crystal structure.

13. ACKNOWLEDGMENT

[33] R. Bersohn has pointed out that by introducing a separate correlation time associated with the specialized motion into the considerations of BPP, Eq. (15) can be derived explicitly and the factors B and C evaluated.

[34] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 548.

[35] Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), p. 358.