[CONTRIBUTION NO. 105 FROM THE CRYOGENIC LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

# Molecular Rotation in Crystals. Line Narrowing in Carbon Tetrafluoride

BY J. G. ASTON, Q. R. STOTTLEMYER AND G. R. MURRAY

RECEIVED JULY 27, 1959

The second order transition at 76.2°K. in solid carbon tetrafluoride has been shown to be due to rotation, as distinct from reorientation, by a study of the effect of the complication produced by reorientation processes. Evidence is presented to show that molecules with almost spherical envelopes have second order rotational transitions. Reduction of the symmetry converts second into first order rotational transitions. Self-diffusion of molecules above the transition has been attributed to rotation of groups of molecules in the crystal.

## Introduction

Several studies have been made in an attempt to relate narrowing of the magnetic resonance line with reorientation and mobility in the solid.[1]

In compounds with a methyl group, reorientation of the methyl group is the main process responsible for the narrowing.[2]

However, up to the present time methane[3] is the only compound with a transition of the type attributable solely to rotation that has been thoroughly investigated. In this case there is a complication produced by reorientation below the rotational transition. Furthermore, owing to the intermolecular contribution to the line width, narrowing produced by rotation or rotational reorientation is small.

Since carbon tetrafluoride seemed likely to be free of these two complications it was decided to study the line width as a function of temperature since its rotational transition already had been studied calorimetrically.[4] This paper gives the results of our investigation.

In the following paper[5] a study is reported of line narrowing in adsorbed monolayers of carbon tetrafluoride which not only throws further light on the problem of rotation in the solid state but also on the nature of monolayers adsorbed on a heterogeneous surface.

## Experimental

**Apparatus.**—The apparatus and cryostat, along with the method of precise temperature control, have been previously described.[6] The sample had a volume of 9 cc. The frequencies were measured by calibration (method of beats) against a frequency meter. The accuracy of the meter was such as to give an accuracy in measuring the line width of 0.3%.

**The Carbon Tetrafluoride Sample.**—The sample contained 0.4% of nitrogen as determined by mass spectrographic analysis. It was provided through the courtesy of Dr. Robert D. Dunlap of the Chemistry Department of the University of Maine.

**Line Widths.**—While the entire line shape could be displayed on an oscillograph, signals proportional to the derivative of the absorption *vs.* field strength curve (n.m.r. line) were recorded on a Leeds and Northrup Speedomax Type G. recorder with a chart speed of 15.22 mm. per minute.

The line width is defined as the distance (in gauss) between the points of inflection in the absorption *vs.* field strength curve (*i.e.*, between the maximum and minimum on the line shape derivative curve). If the line seemed to consist of two components, curves were arbitrarily constructed so as to add up to the observed curve and each treated separately.

From the standpoint of comparison with theory the so-called "second moments" are required. The second moment in frequency units is defined by

$$S_2 = \int_0^\infty \nu^2\, g(\nu)\, d\nu \qquad (1)$$

where $g(\nu)$ has been normalized. With the second moment in units of gauss$^2$, the equation for calculating the second moment from the line shape derivative is

$$\overline{\Delta H^2} = -\frac{\int_{-\infty}^{\infty} (H - H_0)^3\, g'\,(H - H_0)\, d(H - H_0)}{3\int_{-\infty}^{\infty} (H - H_0)\, g'\,(H - H_0)\, d(H - H_0)} \qquad (2)$$

In equation 2 $H$ is the value of the field equivalent to the frequency $\nu$, while $H_0$ is the value equivalent to $\nu_0$ (the frequency of maximum absorption). The function $g(H - H_0)$ is the distribution function representing the absorption and $g'$ is its first derivative.

The second moments were obtained from the derivative curves by graphical integration.

## Results

Figure 1 is a graph of the width of the components of the line against temperature. This figure shows that three lines are involved (I, II and III in order of increasing width). Figure 2 shows the line shape derivative curves of the n.m.r. line in the neighborhood of the transition at 76.2°K. It is clear that there are two distinct molecular environments (possibly phases) during the transition region. The one giving the broader component (II) increases as the transition proceeds and at 73°K. (3° below the heat capacity maximum) makes up the entire sample. At this point (in the cooling) the line (II) is a little over 4 gauss wide.

Figure 3 is a graph of the second moment of the absorption curve against temperature. During the transition at 76.2°K. this is a composite of the second moment of molecules in two distinct environments. Above 76.2°K. the second moment is characteristic of a single line (I) of less than one gauss wide while below 76°K. it is characteristic of a line of about 4 gauss in width (II). The value of $\overline{\Delta H^2}$ at this temperature is about 2 gauss$^2$.

Inspection of Fig. 1 shows that a third line (line III) of width about 12 gauss appears at 65°K. and that the component II does not disappear until the temperature has been lowered to 55°K. In this region the value of $\overline{\Delta H^2}$ plotted in Fig. 3 is for the entire line. Below 55°K. only there is only one

---

[1] E. R. Andrew, "Nuclear Magnetic Resonance," University Press, Cambridge, Chapter VI, 1955.

[2] J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1695 (1953).

[3] K. Tomita, *Phys. Rev.*, **89**, 429 (1953).

[4] A. Eucken and E. Schroder, *Z. physik. Chem.*, **B41**, 307 (1938).

[5] Q. R. Stottlemyer, G. R. Murray and J. G. Aston, THIS JOURNAL, **82**, 1284 (1960).

[6] J. G. Aston, B. Bolger, R. Trambarulo and H. Segall, *J. Chem. Phys.*, **22**, 460 (1954).

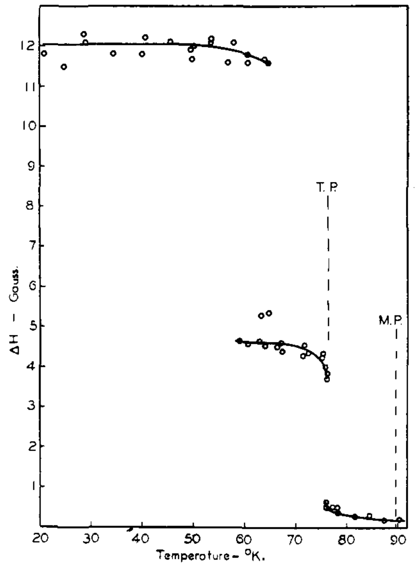

Fig. 1.—N.m.r. line width of bulk $CF_4$ as a function of temperature.

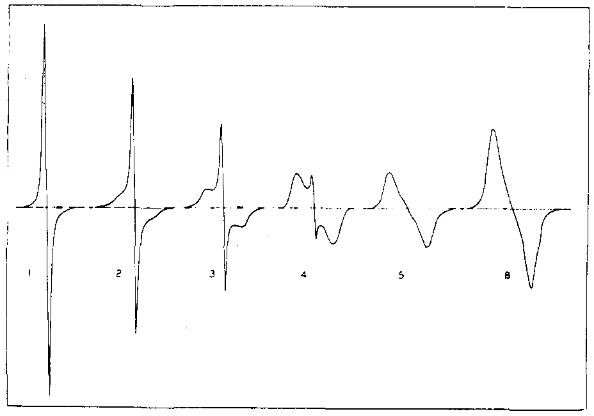

Fig. 2.—Derivatives of n.m.r. absorption lines at temperatures (1) −78°K.; (2), (3) and (4) −76.2°K. in order of increasing amounts in the low temperature form; (5) −75°K.; (6) −73°K.

component III and the significance of $\overline{\Delta H^2}$ is clear. Inspection of the graph of heat capacity *versus* temperature[4] shows that it is at 55°K. that the second order transition starts to occur. Thus, the decrease in $\overline{\Delta H^2}$ is to be connected with the cooperative effect involved in the second order transition. This is generally believed to be rotation of the entire molecule. The case for this point of view will be discussed in the next section from the standpoint of the n.m.r. data.

## Discussion

Before discussing the case of carbon tetrafluoride, it is profitable to discuss a case of line narrowing due to reorientation and examine how this can be eliminated. The line narrowing in 1,1,1-trichloroethane[7] undoubtedly is due to a process involving reorientation of the methyl group, occurring with a correlation frequency.

$$\nu_c = \nu_0 e^{-V/RT} \qquad (3a)$$

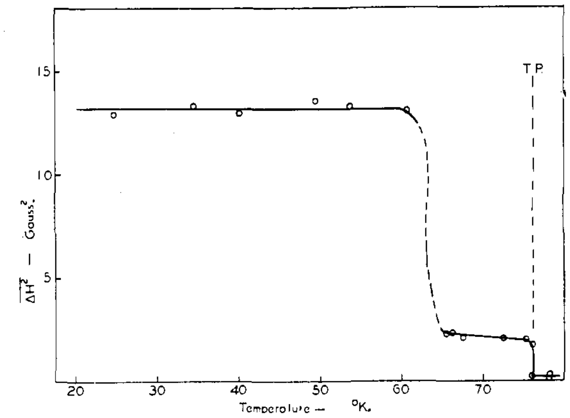

Fig. 3.—Second moments of the n.m.r. absorption as a function of temperature.

The second moment, $\overline{\Delta H^2}$, is related to $\nu_c$ by the equation

$$\overline{\Delta H^2} = \overline{\Delta H^2}_{\text{rest}} + \left[\frac{9\xi}{4\pi^2}\,\gamma^4 h^2 r_0{}^{-6} \nu_c{}^{-1}\right]^2 \qquad (3b)$$

In equation 3b $\overline{\Delta H^2}_{\text{rest}}$ is the contribution due to protons other than those in the reorienting unit, $\xi$ is a numerical coefficient of the order of unity, $\pi_0$ the internuclear distance, and $\gamma$ the gyromagnetic ratio. The barrier height $V$ found from n.m.r. data is 7,000 cal.[7] which is reasonable. Rubin, Levedahl and Yost[8] have estimated the barrier restricting internal rotation of the methyl group *in the gas* as about 3,000 cal. by comparison of the third law entropy with a value calculated from the spectroscopic and molecular data.

Thus, about 4,000 cal. is attributable to the further restriction by the nearest neighbors in the lattice. The meaning of the frequency $\nu_0$ is not clear, but it is reasonable to connect it with torsional oscillation of the methyl group with a frequency $\nu_0$,[9] where $V$ is the $n$ fold barrier hindering the internal rotation

$$\nu_0 = \frac{n}{2\pi}\sqrt{\frac{V}{2I_r}} \qquad (4)$$

with reduced moment $I_r$. The value of $\nu_0$ thus calculated is $10.6 \times 10^{12}$ whereas the value of $\nu_0$ from the n.m.r. data is $8.5 \times 10^{11}$. The latter is approximately a factor of 10 smaller, but the difference may lie in the crude approximation and is not sufficient to throw out the basic connection of $\nu_0$ with the barrier height.

In 1,1,1-trichloroethane, there is a second order rotational transition[7] at 224.2°K., but this is considerably above the temperature at which the n.m.r. line has become comparatively narrow due to the reorientation process, namely, 145°K.

The case of perfluoroethane[7,10] is completely different experimentally. Here there is a rotational transition at 104°K. and this is the temperature of the main line narrowing. The barrier hindering internal rotation in the gas is about the same as for gaseous 1,1,1-trichloroethane,[8] and it may be assumed that the barrier hindering rotation in

---

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

[8] T. R. Rubin, B. H. Levedahl and D. M. Yost, This Journal, **66**, 279 (1944).

[9] K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

[10] E. L. Pace and J. G. Aston, This Journal, **70**, 566 (1948).

the crystal also will be about the same as for crystalline 1,1,1-trichloroethane. The value of $\nu_0$ should, thus, differ from that in 1,1,1-trichloroethane, entirely owing to $I_r$, the reduced moment of inertia.

Since the reduced moment for the perfluoromethyl group in perfluoroethane is about 15 times larger than that of the methyl group in 1,1,1-trichloroethane, the value of $\nu_0$ would be about one fourth that for the methyl group in 1,1,1-trichloroethane. Assuming the barrier height to be the same, this would require a higher temperature to reach values of $\nu_c$ high enough to narrow the n.m.r. line. This temperature is evidently above the rotational transition. At the rotational transition the line narrows because the rotation is essentially free *not because $\nu_c$ is high.*

Inspection of equations (3a) and (3b) makes it obvious that only with a high value of $V$ and consequently with unreasonably high value of $\nu_0$ could the line narrowing with temperature be sharp. Thus, a rapid change in line width is not caused solely by a reorientation process.

We are now in a position to discuss the line narrowing for carbon tetrafluoride.

Inspection of Fig. 3 reveals that the situation resembles that in perfluoroethane.[7] When the transition is complete the value of the second moment should be that for more or less free rotation about all axes, whereas before the transition starts (below 55°K.) there is no rotation at all.

Table I summarizes the calculation of the contribution to $\overline{\Delta H^2}$ of the intra and intermolecular motions of the fluorine atoms for several conditions of motion in the lattice. This table was computed using conventional methods.[7,11]

TABLE I

CALCULATED SECOND MOMENTS FOR SOLID POLYCRYSTALLINE CARBON TETRAFLUORIDE ASSUMING VARIOUS TYPES OF MOLECULAR MOTION

| State of motion | Contribution to $\overline{\Delta H^2}$, gauss$^2$ Intramolecular | Intermolecular |
|---|---|---|
| Rigid lattice | 9.52 | 2.52 |
| Rotation $C_3$ axis | 2.38 | |
| $C_2$ axis | 1.19 | |
| Random axes | 1.90 | |
| Completely general rotation | 0 | <1.50 |
| Translation or migration | 0 | →0 |

From this table it is seen that below 55°K. the value of $\overline{\Delta H^2}$, 12 gauss$^2$ (the sum of the intra and inter contributions), agrees well with experimental value of about 13 gauss$^2$. Immediately above the transition the value found is slightly less than 0.5 gauss$^2$. This is definitely less than the value expected for the intermolecular contribution due to free rotation and may indicate a small degree of translational reorientation or self-diffusion. The slow fall in line width from the transition to the melting point 90°K. does indicate a reorientation process.

It now only remains to discuss the line shape during the transition.

An inspection of Fig. 2 shows that *on cooling* nothing happens to the narrow line (I) until the transition starts (76.2°K.) and then the line of intermediate (4 gauss) width (II) starts to develop. By the time most of the transition is over (73°K.) line I has practically disappeared. This clearly indicates the development of regions in the crystal with a new environment. Since the transition is not isothermal, it would not be proper to speak of these regions as a phase. From the very nature of the second order transition, the new region which develops during it must suffer continuous modification (either in domain size or in nature as well as in amount). From Fig. 2 it would appear that modification is in size since component II does not change much in width as it increases in intensity. Finally, toward the very end of the transition, the component III of width about 12 gauss appears (65°K.) and this line grows at the expense of component II which does not disappear till the temperature has reached 55°K. Lines I, II and III are not all present together.

Inspection of Table I shows that $\overline{\Delta H^2}$ calculated for rotation about a $C_2$ axis is less than 2.7 gauss$^2$ depending on the evaluation of nearest neighbor contribution. In the region from 73 to 65°K. the measured second moment is about 2 gauss$^2$. From steric considerations motion about a $C_2$ axis is of course most probable.

It is thus fairly clear what happens when carbon tetrafluoride is warmed starting at 55°K. First rotation starts about the $C_2$ axis. When this has sufficiently reduced nearest neighbor interference, rotation about all axes starts and finally when the transition is complete rotation is practically free.

It would merely require additional rotation of *groups* of carbon tetrafluoride molecules (as a whole) to produce the additional narrowing. The net result of rotation of groups of molecules is of course essentially the same as of self diffusion of which

TABLE II

DATA ON SOLID AND LIQUID PHASES OF "MOLECULES GLOBULAIRE"

| Compound | Transition temperatures[a] Lower °K. | Upper °K. | Melting temp., °K. | $\Delta S$ of fusion E.u.[b] |
|---|---|---|---|---|
| Methane (6) | 20(S)<br>157† | ..... | 90.0 | 2.47 |
| Carbon tetrafluoride (7) | 76(S)<br>354† | ..... | 89.5 | 1.84 |
| Perfluoroethane (8) | 104(S)<br>893† | ..... | 173.0 | 3.70 |
| Carbon tetrachloride (9) | 225(S)<br>1095† | ..... | 250.3 | 2.40 |
| Tetramethylmethane (8) (10) | 140(S)<br>616† | ..... | 256.0 | 3.03 |
| Cyclohexane (11) (12) | 186(S)<br>1598† | ..... | 279.8 | 2.24 |
| 2,2-Dimethylbutane (13) | 127(F)<br>1289† | 141F<br>68† | 174.2 | 0.79 |
| Cyclopentane (14) | 122(F)<br>1165† | 138(F)<br>83† | 179.7 | 0.80 |
| 2,3-Dimethylbutane (13a) | 136(F)<br>1552† | ..... | 145.2 | 1.32 |
| *t*-Butylchloride (15) | 183(S)<br>410† | 220(S)<br>1390† | 248.2 | 1.90 |

[a] (S) or (F) denotes second or first order transition; † is heat of transition in cal. mole$^{-1}$. [b] Cal. deg.$^{-1}$ mole$^{-1}$.

---

(11) E. R. Andrew and R. G. Eades, *Proc. Roy. Soc.* (*London*), **A216**, 398 (1953).

this is a possible mechanism. The effect of this is to reduce the nearest neighbor contribution to zero. Clear evidence of such an effect has been obtained[12] for the mixture of two moles cyclopentane and one mole of neohexane in which there is a second order transition beginning at 55 and ending at 65°K. During this transition it has been shown that the unit of two molecules of cyclopentane and one molecule of neohexane starts to rotate.

The foregoing leaves little doubt that in the case of carbon tetrafluoride the second order transition really does represent the onset of fairly free rotation of the molecule made possible because of its spherical symmetry.

It is likely that all molecules with spherically symmetrical envelopes behave in this way and this is substantiated by Table II in which (in the second and third columns) the natures of the transitions are given in brackets alongside their temperatures for molecules that rotate in the solid state. The heat of transition is given immediately below the transition temperature. An (S) denotes second order and an (F) denotes first order. When the symmetry is not quite spherical (oblate spheroid or pear shaped) the transition becomes first order since a *higher* degree of coöperation is necessary to allow rotation to occur at all. This coöperation involves self-diffusion as has been pointed out by Rushworth[13] for cyclopentane since the line above the n.m.r. transition becomes very narrow.

That there is a high degree of self-diffusion just below the melting point for most compounds with first order rotational transitions is evident from the entropies of fusion shown in Table II. When there is fully excited rotation but no self-diffusion, the compounds give the communal entropy of $R$ (2 cal. deg.$^{-1}$ mole$^{-1}$). If there is an appreciable amount of self-diffusion in the crystal, part of this entropy already has been gained before fusion and the entropy of fusion is much smaller than $R$.

**Acknowledgments.**—We wish to thank the Chemistry Branch of the Office of Ordnance Research, The Chemistry and Physics Branches of the Office of Naval Research and the Chemistry Branch of the National Science Foundation for financial support that made this research possible.

---

[12] R. N. Selby and J. G. Aston, THIS JOURNAL, **80**, 5070 (1958).

[13] F. A. Rushworth, *Proc. Roy. Soc.* (*London*), **222**, 526 (1954).

UNIVERSITY PARK, PENNA.

---

[CONTRIBUTION NO. 106 FROM THE CRYOGENIC LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PA.]

# The Structure of Nuclear Magnetic Adsorption Lines for Carbon Tetrafluoride Adsorbed on Rutile

BY Q. R. STOTTLEMYER, G. R. MURRAY AND J. G. ASTON

RECEIVED JULY 27, 1959

Evidence has been presented for two dimensional condensation. It has been shown that for carbon tetrafluoride adsorbed on a surface there is rotation in the outer layer at all temperatures down to 20°K. In all cases there is migration (self-diffusion) in the outer layer down to 55°K. At about half a monolayer this migration persists down to 30°K. Below this coverage heterogeneity restricts the migration.

## Introduction

A surface of high area is heterogeneous because on it there are sites consisting of holes, corners and edges in which an adsorbed molecule is exposed to more than one surface. As a result, the differential heats of adsorption on the rough surface at low coverages are several times those at high coverages where only the flat surface is involved.[1,2]

This effect tends to obscure surface condensation effects on a heterogeneous surface. When the surface is uniform, it has been shown[3] that there is a surface critical temperature above which the surface layer does not condense but below which the surface consists of a "condensed" and a gaseous phase. This temperature is roughly half the bulk critical temperature.

This investigation was carried out in an attempt to throw further light on these effects by studying the nuclear magnetic resonance line of carbon tetrafluoride adsorbed on high area rutile. By such a method molecular rotation and migration (self-diffusion) could be detected and the effect in condensed fractional monolayers compared with that in bulk.

An attempt already has been made to do this using methane,[4] but the narrowing of the n.m.r. line due to rotation of the methane molecule is slight and the effect of barrier penetration complicates the results. An investigation on bulk carbon tetrafluoride[5] has shown that these complications do not occur for this substance, so it was chosen for the present investigation.

In order to get a sufficiently strong signal at fractions of a monolayer, it was necessary to use a sample of high area. This introduced the effect of heterogeneity at high coverage in addition to effects occurring in the two dimensional condensed phase characteristic of a smooth surface. Neverthe-

---

[1] J. G. Aston, R. J. Tykodi and W. A. Steele, *J. Phys. Chem.*, **59**, 1053 (1955).

[2] W. A. Steele and J. G. Aston, THIS JOURNAL, **79**, 2393 (1957).

[3] T. L. Hill, "Advances in Catalysis," Vol. IV, Edited by P. H. Emmett, Academic Press, Inc., New York, N. Y., 1950.

[4] (a) N. Fuschillo and J. G. Aston, *J. Chem. Phys.*, **24**, 1277 (1956); (b) a report of incomplete work hastily carried out on methane under a contract with the Office of Ordnance Research in the senior author's laboratory at the Pennsylvania State University has also appeared. N. Fuschillo and C. A. Renton, *Nature*, **180**, 1063 (1957). This work is being repeated.

[5] J. G. Aston, Q. R. Stottlemyer and G. R. Murray, THIS JOURNAL, **82**, 1281 (1960).