followed by

$$2AH\cdot \longrightarrow AH_2 + A, \text{ etc.}$$

However, this type of mechanism is consistent with a first-order decay only if all of the intermediate disappeared by forming the pink pigment, which is not consistent with the estimated quantum yields of formation. At moderately high concentrations of water and ascorbic acid, the efficient quenching of the triplet indicates a quantum yield of formation of the intermediate of the order of magnitude of unity, much greater than the observed yield[7] of the pink pigment.

It appears probable, therefore, that under our experimental conditions the intermediate disappears

$$GH_2\cdot \text{ (or } GH^-) + Ox. \longrightarrow \longrightarrow GH + \text{Red.}$$
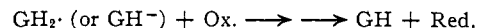
chiefly by reacting with an adventitious oxidant. If the concentration of the oxidant were much greater than that of the intermediate, its rate of decay would be first order, but not if the concentrations were of the same order of magnitude. This condition excludes the possibility that O_2 is the oxidant; since the observed, spontaneous rate of decay of the triplet was normal, indicating an O_2 concentration less than $5 \times 10^{-7}\ M$. It is probable that our samples of ascorbic acid were appreciably contaminated with dehydroascorbic acid and that it acted as the oxidant (compare ref. 3, p. 302). Additional experiments should be performed to test these suggestions.

The Structure of the Nuclear Magnetic Resonance Lines for Methane Adsorbed on Rutile

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A study of the temperature dependence of the nuclear magnetic resonance line characteristics has been made for solid methane and for methane adsorbed on titanium dioxide. This confirms previous conclusions that the line narrowing is due to diffusion processes. Reasons are given for concluding that the data give no information about the rotational process that sets in at the lambda point. The presence of the line of intermediate width well below the lambda point and the appearance of the narrow line only at temperatures well above the lambda point are the only differences from the behavior of carbon tetrafluoride and neither of these is directly connected with the onset of rotation.

I. Introduction

The original nuclear magnetic resonance data of Alpert[1] was at first taken to indicate that the lambda point in methane was not a transition involving rotation or re-orientation. However, Eucken and Veith[2] had previously made a study of the low temperature heat capacities of solutions of krypton in solid methane from below to well above the lambda point from which they had concluded that a rotational transition occurred at the lambda point. A careful analysis of their data indicates that almost completely free rotation exists above the transition.[3]

This investigation was performed in an effort to investigate further the motions in solid methane by a comparison of the behavior of the nuclear magnetic adsorption line of the solid with that when methane is adsorbed on heterogeneous surfaces of high area[4,5] as was done for carbon tetrafluoride.[6,7]

Proton resonance derivative line shapes have therefore been obtained for methane adsorbed on high surface area titanium dioxide at various coverages from 0.33 to 8.06 layers, and also in bulk methane, as a function of temperature. The results are compared with the corresponding ones for carbon tetrafluoride.

II. Experimental

Apparatus.—Details of the apparatus, cryostat, precise method of temperature control,[8] titanium dioxide sample and drying procedure have been described elsewhere.[7]

In the studies on bulk methane the titanium dioxide was omitted from the sample holder in one set of measurements.

The Methane Sample.—The sample contained less than 0.2 mole % impurity as deduced by mass spectrograph analysis.

Line Widths.—The method of recording the derivative of the adsorption has been described.[9] Where a line was considered to consist of two components, curves were arbitrarily drawn so as to add up to the observed curve and each component was treated separately. Figure 1 shows a typical line shape derivative curve. Second moments were obtained from the derivative curves in the usual way.[9]

III. Results

A graph of line width against temperature for bulk methane in the presence of titanium dioxide and without titanium dioxide is given in Fig. 2. Measurements were made on bulk methane after removing the titanium dioxide from the sample container to ascertain the effect of titanium dioxide. The only difference was the absence of the narrow components below 70°K.

A narrow line of approximately one gauss persists down to about 54°K. for bulk methane in the presence of titanium dioxide. On warming, the broad line begins to narrow at about 60°K. No narrow line component was detected below 54°K. as was reported by Fuschillo and Renton[10] of results obtained in this Laboratory. The broad line component was found to be a little more than 6 gauss wide at its maximum, with and without titanium dioxide, which is about 2 gauss less than that reported by Thomas, Alpert and Torrey,[11] but is in agreement with that found by Fuschillo and Renton. While we speak of this as the broad line, it is actually one of intermediate width in terms of the carbon tetrafluoride results.[9] There is no really broad line observed analogous to that observed for carbon tetrafluoride.

(1) N. L. Alpert, Phys. Rev., **75**, 398 (1949).

(2) A. Eucken and H. Veith, Z. physik. Chem., **B34**, 275 (1936); **38B**, 393 (1937).

(3) L. A. K. Staveley, J. Phys. Chem. Solids, **18**, 46 (1961).

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

(5) W. A. Steele and J. G. Aston, J. Am. Chem. Soc., **79**, 2393 (1957).

(6) Q. R. Stottlemeyer, G. R. Murray and J. G. Aston, ibid., **82**, 1284 (1960).

(7) Q. R. Stottlemeyer, Ph.D. Thesis, The Pennsylvania State University, 1959.

(8) J. G. Aston, B. Bolger, R. Trambarulo and H. Segel, J. Chem. Phys., **22**, 460 (1954).

(9) J. G. Aston, Q. R. Stottlemeyer and G. R. Murray, J. Am. Chem. Soc., **82**, 1281 (1960).

(10) N. Fuschillo and C. A. Renton, Nature, **180**, 1063 (1957). This is an unauthorized report of work done under the direction of the senior author as part of work performed with the financial support of 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.

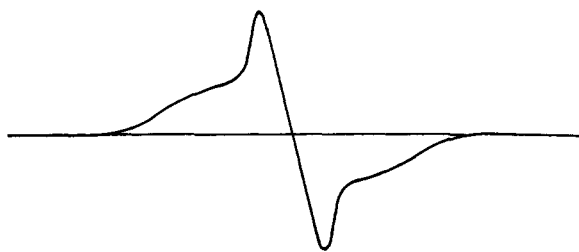(11) J. T. Thomas, N. G. Alpert and H. C. Torrey, J. Chem. Phys., **18**, 1511 (1950).

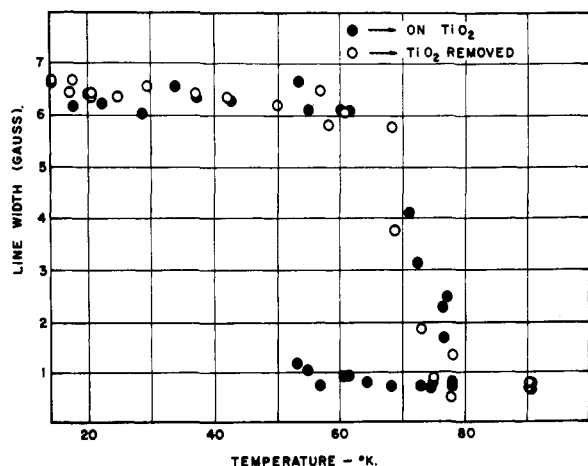Fig. 1.—Line shape derivative curve for bulk methane at 66°K. in the presence of TiO_2.

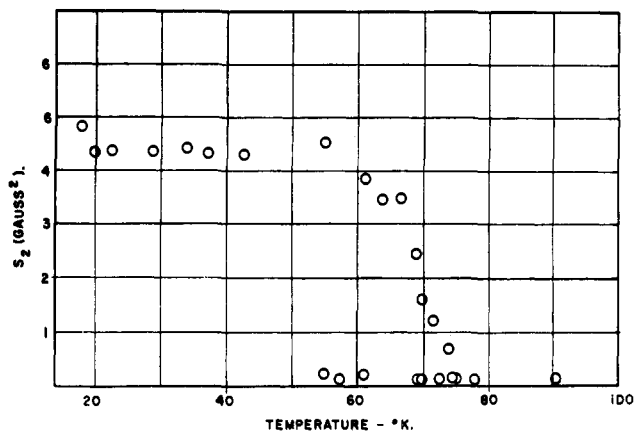Fig. 2.—N.m.r. line width of bulk CH_4 (with and without presence of TiO_2) as a function of temperature.

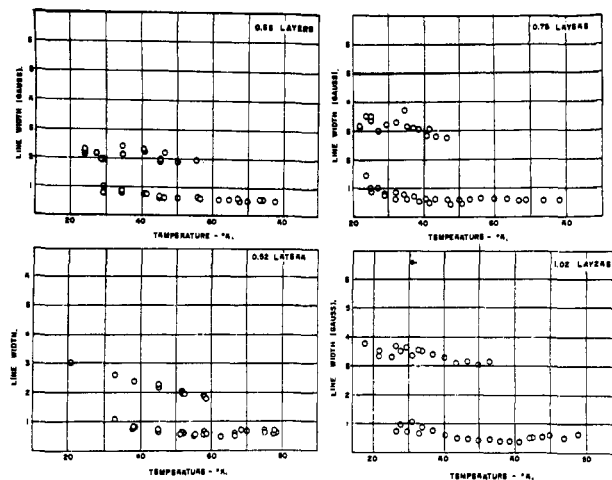Fig. 3.—Second moments of the n.m.r. absorption as a function of temperature.

Fig. 4.—Width of n.m.r. line as a function of temperature and number of layers of methane.

Fig. 5.—Width of n.m.r. line as a function of temperature and number of layers of methane.

Figure 3 is a graph of the second moment against temperature for the bulk phase with titanium dioxide. Without titanium dioxide the line widths are almost identical so no second moments were calculated. The maximum width of the broad line component corresponded to a second moment of a little less than 4.5 gauss.[2]

The width of the components for various coverages of adsorbed methane is plotted as a function of temperature in Fig. 4 and 5. As expected, the width of the broad line increased from about 2 gauss to about 6 gauss, the value characteristic of the bulk phase, as the number of layers increased. Except for the 2.10 and the 3.03 coverages, the narrow line component was constant at a value of about one gauss. For 2.10 and 3.03 layers the narrow line component persisted to the lowest temperatures. For decreasing coverages below 0.75 layer the narrow line disappeared at increasingly higher temperatures. However, the line was present at all temperatures above 32°K. for all coverages. The
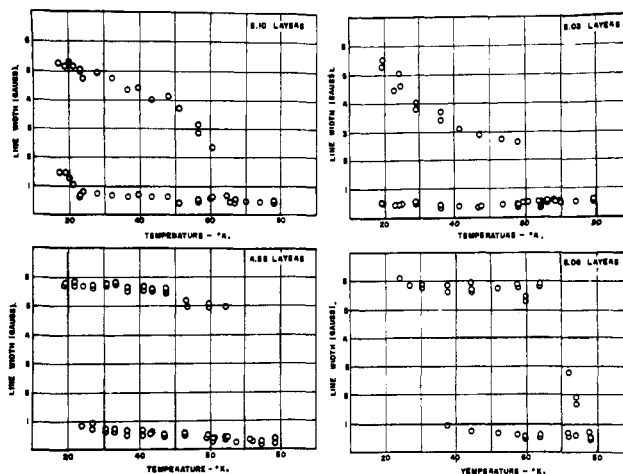
temperature at which the broad line appears on cooling decreases from about 52°K. at the monolayer to 45°K. at 0.75 layer, but increases to about 56°K. at 0.33 layer.

IV. Discussion

As in previous work[10,11] no change in the derivative line width is observed in passing through the lambda point at 20.4°K. A theoretical analysis has been made by Tomita[12] explaining the small value of T_2 obtained[9] as being due to the flipping of methane molecules to neighboring equivalent orientations. This flipping is said to occur with sufficient frequency to average out the intramolecular contribution to the line width at temperatures well below the lambda point. Thus the possibility of hindered or free rotation being associated with the lambda point cannot be excluded due to the absence of a line width transition at this temperature.

Table I lists the calculation of the contribution to the second moment of the intramolecular and intermolecular motions of the hydrogen atoms for several conditions of motion in the bulk material. This table was computed using the modified Van Vleck second moment formula.[9,13,14] The contribution to ΔH^2 due to the hydrogen atoms in one molecule (intramolecular contributions) for the rigid molecule and for rotation

(12) K. Tomita, Phys. Rev., **89**, 429 (1953).

(13) H. S. Gutowsky and G. E. Pale, J. Chem. Phys., **18**, 162 (1950).

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

about C_3, C_2, as well as random axes for all coverages of adsorbed methane, is of course the same as for the bulk phase. Likewise, the value for free rotation yields zero contributions. Table II lists calculated values for the contribution due to neighboring molecules for several coverages.

TABLE I

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

State of motion	Intramolecular contribution	$\overline{\Delta H^2}$, gauss² intermolecular
Rigid lattice	10.88	2.05
Rotation or reorientation		
C_2-Axis	1.36	
C_3-Axis	2.67	
Random axis	2.18	
Completely general rotation	0	<1.57
Translation or migration	0	→0

TABLE II

INTERMOLECULAR CONTRIBUTION TO THE CALCULATED SECOND MOMENTS FOR ADSORBED METHANE ASSUMING EVENLY DISTRIBUTED AND RANDOMLY ORIENTED MOLECULES ON A PLANAR SURFACE

Coverage	$\overline{\Delta H^2}$, gauss²
0.33 layer, rigid	0.02
0.52	0.12
1.02	1.11
(If rotating generally)	<0.75
3.03 layers, rigid	2.42
(If rotating generally)	<1.30

In the calculation molecules were placed at all corners of squares into which the surface was evenly divided for coverages below a monolayer. At and above a monolayer hexagonal close packing was assumed in the first layer and additional molecules placed on top. For the rigid cases the molecules were assumed to be randomly oriented. The calculations were made in the manner described previously.[6,9]

In the case of the bulk methane from Fig. 2 it is seen that below 60°K. the value of $\overline{\Delta H^2}$, 4.5 gauss², agrees well with the value of 4.23 gauss² obtained from the values for the assumed rigid lattice intermolecular interactions along with intramolecular contributions due to reorientation about random axes as obtained from Table I. A broad line of width corresponding to a second moment of 13 gauss² due to a completely rigid lattice is absent for reasons mentioned already. Immediately above 60°K. the experimental value is only about 0.2 gauss² due to diffusion as expected for the bulk phase from the results of Thomas, Alpert and Torrey[11] as interpreted by Tomita.[12]

The broad line widths in the bulk phase in the presence and absence of titanium dioxide are identical except that diffusion is present below 70°K. in the presence of titanium dioxide. This indicates that for some reason, not clearly understood, some diffusion takes place on the boundary surface layer except at the very lowest temperatures.

It is evident from Fig. 4 that coverages below a monolayer exhibit a narrow line component that broadens with a decrease in temperature indicating, as in the case of carbon tetrafluoride adsorbed on titanium dioxide,[6] that a diffusion process analogous to reorientation is responsible for the narrow line. Below a monolayer the narrow line persists to *lower* temperatures with *increasing* coverage. The effect of high energy sites is to compress the condensed phase and inhibit the diffusion process.

From Fig. 4 and 5 it is seen that the broad line component increases from 2 gauss for the 0.33-layer coverage to 6 gauss for the 8.06-layer coverage, while the narrow line component remains almost constant for the various coverages.

The narrowing of the line of intermediate width for the bulk material, as for carbon tetrafluoride,[6,9] to a width one gauss or less is certainly due to diffusion processes made possible by the loosening of the lattice due to rotation.

Thus it seems evident for the bulk material that while some sort of hindered rotation of the methane molecule is responsible for the lambda point, a re-orientation process is responsible for the absence of a broad line having a moment of about 13 gauss.[2] We hasten to add that the evidence for this is, first, that the narrow line is too narrow to be due solely to a rotational process. Second, the persistence of this narrow line for the outer surface layer of a multilayer coverage down to very low temperatures, along with the broad line due to the inner layers, exactly analogous to the behavior with carbon tetrafluoride in that the intermediate line is present below the completion of the second-order transition, whereas in the case of methane it does not appear until well above, is confusing but in no way invalidates the argument. The narrow line is due to increased ability to diffuse in the surface layer or in the bulk and has nothing to do with the onset of rotation.

The only real difference from the carbon tetrafluoride is that the line of intermediate width is present well below the transition.