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.

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

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

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

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

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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-

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[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).

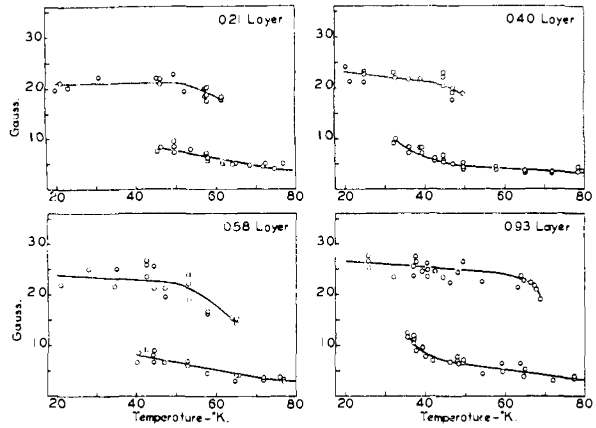

Fig. 1.—Width of n.m.r. line as a function of temperature and number of layers of carbon tetrafluoride.

less the results do show that migration (self-diffusion) and rotation are much freer in a solid monolayer than in bulk and that in the outer of several layers migration and rotation are as free as in the monolayer. Restriction of migration caused by surface heterogeneity also was noted.

Experimental

Apparatus.—The sample container, temperature control and method of detection of the nuclear magnetic resonance line was as described for the investigation in bulk carbon tetrafluoride.[5]

Adsorbent.—The adsorbent used was acid precipitated anatase donated by the New Jersey Zinc Company, Palmerton, Penna., through the courtesy of Dr. C. W. Seller. The sample container was entirely filled with it.

Line Widths and Second Moments.—Line width was defined and measured as for the bulk[5] and second moments were derived from the data by graphical integration.

Results

Except at the lowest temperatures, lines at the higher coverage were arbitrarily resolved into at least two of three components which in order of increasing width will be designated I, II and III as was done for the bulk carbon tetrafluoride.[5] The width of these components is plotted as a function of temperature for the coverages studied in Figs. 1 and 2. While practically constant over most of the temperature range, the component II increases in width from about 2.5 gauss to 4 gauss, the value characteristic of the bulk phase,[5] as the number of layers increases. Likewise the width of component III increases from somewhat less than 10 gauss to somewhat near 11 gauss. Component I, however, at the lower temperatures, is somewhat *wider* for the lowest coverages. This line is present above 55°K. at all coverages. Below about 0.8 layer the broad line does not appear at all. The temperature at which the line II appears on cooling decreases from 65°K. at the monolayer to 45°K. at 0.40 layer and increases to about 50°K. at 0.21 layer. Likewise the temperature of disappearance of line I decreases to 30° K. at 0.40 layer and increases to about 40° K. at 0.21 layer. As will be seen in the discussion, this probably is due to a compression effect in the two dimensional solid due to the higher energy of adsorption on the heterogeneous sites on which the adsorbate rests at the lower coverages.

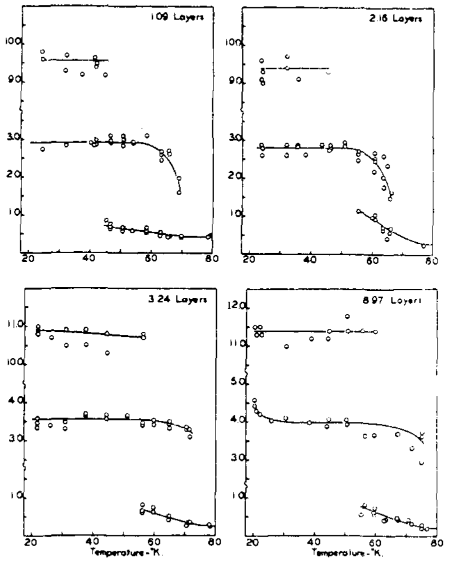

Fig. 2.—Width of n.m.r. lines as a function of temperature and number of layers for carbon tetrafluoride.

Discussion

Calculated Second Moments.—It is best to discuss the data by reference to calculated second moments. The contribution to $\overline{\Delta H^2}$ due to the fluorine atoms on one carbon tetrafluoride molecule (intra contribution) for the rigid molecule and for rotation about C_3, C_2 as well as random axes is made as for the bulk phase[5] and yields the same results. Likewise the value for free rotation yields zero contribution. To obtain a value of $\overline{\Delta H^2}$ due to all causes, the contribution due to the neighboring molecules must be added. Table I lists calculated values of this contribution for certain coverages.

TABLE I

INTERMOLECULAR CONTRIBUTION TO THE CALCULATED SECOND MOMENTS FOR ADSORBED CF_4 ASSUMING EVENLY DISTRIBUTED AND RANDOMLY ORIENTED MOLECULES ON A PLANAR SURFACE

Coverage	$\overline{\Delta H^2}_{\text{Inter}}$, gauss^2
0.40 Layer—rigid	0.02
.58 Layer—rigid	.11
.84 Layer—rigid	.41
1.09 Layers—rigid	1.12
(if rotating generally)	<0.75
3.24 Layers—rigid	~2.5
(if rotating generally)	<1.5

Below a monolayer, molecules were placed at all the corners of squares into which the surface was evenly divided. At and above a monolayer hexagonal close packing was assumed in the first layer and additional molecules placed on top. In all cases marked "rigid" the molecules were randomly oriented. The calculation was made by using the formula of Van Vleck.[6] This is the same as considering the F atoms randomly distributed over spheres of the radius equal to the C–F bond distance. Thus any fluorine atom in one molecule is affected by four fluorine atoms in a neighboring molecule. Each was assumed to be at the "proper"

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(6) J. H. Van Vleck, *Phys. Rev.*, **74**, 1169 (1948).

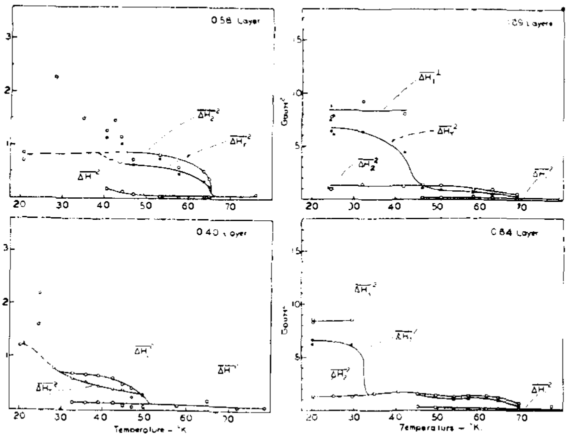

Fig. 3.—Experimental second moments of component lines as a function of temperature and coverage.

average distance. The "proper" average was taken as equal to the distance between fluorine atoms on the spheres of the respective molecules taken to the sixth power and averaged over the spheres. In the cases marked "If Rotating Generally" the calculation was made by an obvious modification of the methods of the previous paper on bulk carbon tetrafluoride.[1] The effect of the titanium atoms with non-zero moment on and near the surface was neglected since it is generally assumed that the surface is mostly oxygen.

The Experimental Second Moments of Compounds. I, II and III.—The second moments, $\overline{\Delta H_1}^2$, $\overline{\Delta H_2}^2$ and $\overline{\Delta H_3}^2$, of the lines I, II and III were obtained by graphical integration of the line shape derivatives as taken from the arbitrarily separated curves. Separation of a complex derivative line into its components was done somewhat intuitively but in such a way that the derivative of each component approximated those of a Gaussian shaped line, with all component derivatives for any frequency adding up to the original derivative. The values thus obtained are graphed in Fig. 3 as a function of temperature for coverages up to a monolayer. For completeness values of the second moment taken over the unresolved line, $\overline{\Delta H_T}^2$, are also included. It is convenient to discuss the widest of these lines first. This corresponds to a rigid lattice. The contribution of the fluorine atoms in a single molecule to $\overline{\Delta H^2}$ is 9.52 g.^{2}.[5] From Table I the effect of fluorine atoms in nearest neighbors adds 1.12 g.^{2} to $\overline{\Delta H^2}$ giving a total of 10.6 g.^{2} The measured value of $\overline{\Delta H^2}$ for the monolayer at temperatures below 40°K. is close to 9 g.^{2}. At 0.84 layer the measured width of $\overline{\Delta H_3}^2$ is still the same (9 g.^{2}) but the broad line does not appear till 30°K. This clearly indicates that condensation occurs in the 0.84 monolayer, giving a condensed phase having the surface packing producing the broad line of the monolayer. Below 0.84 layer the line is absent indicating that this kind of condensation does not occur. It will be shown below that it is unlikely that the broad line is characteristic of the monolayer but more likely is due to patches on the surface on which there are several layers.

The second moment, $\overline{\Delta H_2}$, of line II for the monolayer at the lowest temperatures is about 1.2 gauss^2. If there were completely general rotation the only contribution to $\overline{\Delta H^2}$ would be due to nearest neighbors which, according to Table I, is about 0.7 gauss^2. If rotation occurred about the C_2 axes a further 1.19 gauss^2 would be added which is the contribution to $\overline{\Delta H^2}$ of the other fluorine atoms in the same molecule calculated for bulk carbon tetrafluoride.[5] Thus, it seems likely that the rotation is completely general in the monolayer down to 20°K. The results at 0.84, 0.58, 0.40 and 0.21 layer are not significantly different and show rotation at all temperatures above 20°K.

Since it seems that a layer above is needed to stop rotation the broad line III must be due to patches of surface with at least a second layer.

For 3.24 layers the value of $\overline{\Delta H_2}^2$ for line II is still about 1.2 gauss^2 and this component exists at all temperatures between 20 and 70°K. The component in this case undoubtedly is due to rotation in the outer layer. At this coverage line III exists at all temperatures below 60°K. with a value of $\overline{\Delta H_3}^2$ of twelve gauss^2. This value is close to that of the bulk.[5] Thus below 60°K. the inner two layers are rigid.

Translational Migration below a Monolayer.—Unlike lines II and III the narrow line broadens slowly as the temperature decreases. This indicates that a process analogous to reorientation is responsible for the narrow line. For the coverage of 0.21 layer, the narrow line persists only down to 40°K. whereas for the 0.40 layer the line persists down to 30°K. The effect of high energy sites is to compress the condensed phase and inhibit the reorientation process. This is in keeping with the fact that the first appearance of line II, on cooling, also occurs at a higher temperature (62°K.) for the 0.21 layer than it does for the 0.40 layer (50°K.). Line I persists down to 55°K. for all the multilayers and here also it broadens slowly with decrease of temperature. For the multilayers the line strongly indicates migration in the outer layer.

This evidence for high energy sites confirms the fact that if a high area titanium dioxide surface is half covered with argon the differential heats of absorption indicate a uniform surface.[2]

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