January, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 25—27 (1988)* 25

Invited Paper

Heat Capacity of CH_3D Adsorbed on Graphite at Monolayer Coverages between 0.3 and 7 K

Akira INABA†,* and (the late) James Alexander MORRISON††
Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4Ml, Canada

(Received August 28, 1987)

Heat capacity measurements have been made on CH_3D adsorbed on exfoliated graphite (Grafoil MAT) over the temperature range $0.3<T<7$ K at two surface coverages near a monolayer, to evaluate predictions of the energy states of the adsorbed molecules, based on earlier studies of the properties of bulk solid CH_3D and other isotopic methanes. Two Schottky-type anomalies are observed with maxima at 2 and 0.1 K; these are consistent with the predictions in a general way.

The heat capacities of bulk solid isotopic methanes have been studied over the years with the fundamental object of understanding molecular energy states—especially those associated with hindered rotational motion of the molecules in the solids. In addition to the original publications, several reviews of the studies are available in papers devoted to the discussion of molecular orientational ordering and related matters. For example, Bloom and Morrison published one such review[1)] in 1973. More recently, Yamamoto et al. produced a summary of the theoretical and experimental investigation of solid methane[2)] in terms of a specific quantum mechanical model, developed from a classical study.[3)] The model is particularly valuable in showing how complicated and difficult the methane "problem" is from both the experimental and theoretical points of view. The methane system shows all of the features of the better-known example of the hydrogen/deuterium system[1)] but with more solid phases and phase transitions and a greater number of nuclear spin symmetry species. Finally, a pertinent book on single particle rotations in molecular crystals should be mentioned.[4)]

It is obvious that no one technique—either experimental or theoretical—will provide sufficient information to describe orientational motion in solids fully. In the case of the rotational energy of molecules, the characteristic temperature for rotation is generally low, e.g. $\theta_{\rm rot}<87.5$ K for solid methane. (This can be worked out easily from data in Table 1 of Ref. 1.) Thus, contributions which rotational (orientational) motions make to thermodynamic properties and to the magnitude or separation of energy states depend upon $\theta_{\rm rot}/T$. In practical terms, this means that to exploit measured properties, such as heat capacities, to learn about quantum states of molecular solids, we need to make measurements at low temperatures, typically in the region $T<20$ K. Full details can be found in Refs. 1 and 2.

The so-called Schottky anomaly[5)] has long been used to deduce information about arrays of energy levels from measured heat capacities and has been widely exploited for this purpose for the solid isotopic methanes.[6)] The resulting energies have often been compared and correlated with estimates obtained from measurements of inelastic neutron scattering. In one extensive study[7)] of the sequence of molecules, CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4, expected results were obtained for CH_4 and CD_4 but not for the partially deuterated compounds in one of the solid phases, — viz. in phase III. It is the lowest temperature phase that exists under the equilibrium vapour pressure and is thought to have at least three different site symmetries,[8)] but that is still not established in fact.[9)] The investigation of the discrepancy brought out the following important conclusion which is contained in a direct quotation from Ref. 7.

> "The importance of the partial deuteration is that it defines a molecular axis. Thus, when the molecules interact with sites of lower symmetry, a distinction can be made between orientational levels, where the splitting stems from the change of the molecular axis relative to the site symmetry axes, and tunneling levels, where the splitting arises from overlap between equivalent molecular orientations. It turns out that the neutron scattering and thermodynamic experiments sample the manifolds of energy states in different ways. This is exploited through a model to yield a picture of orientational and tunneling states that is broadly consistent with experimental observation for all of the deuterated methanes including CD_4."

In other words, the combination of heat capacity and neutron scattering data for the solid methanes significantly refined our understanding of orientational and tunneling behaviour in them over what was obtainable from one type of data alone.

The work was extended by Maki in a theoretical study[10)] of the much more anisotropic example of a monolayer of CH_3D adsorbed on the surface of a graphite crystallite. Information became available from neutron scattering measurements[11,12)] to characterize vibrational/librational/orientational motion of

---

† Permanent address: Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

†† Professor J. A. Morrison passed away on October 20, 1987. This became his last paper. (Editor)

the CH_3D molecules in this system. With that and his model for the bulk solid methanes, Maki was able to calculate the low temperature heat capacity to be expected for CH_3D on graphite.[10] He made a challenge to experimentalists to test his calculations and the present short paper is about a response to that challenge. The agreement between theory and experiment that is found is remarkably good and very satisfying.

For now, we are content to show that the Maki predictions are borne out by experiment. It will be possible in later publications to report the results of more detailed comparisons. There is also information contained in our measurements about conversion between nuclear spin symmetry species of CH_3D but we shall not deal with it here. The dynamics and mechanism of that process are still not known for certain.[13]

Experimental

The calorimeter assembly was installed in a rebuilt Mark V helium dilution refrigerator[14] (Oxford Instruments Ltd.). The calorimeter vessel was constructed of copper and contained graphite adsorbent in it. It carried a small specially designed needle valve[15] through which the gas to be adsorbed could be filled or emptied quantitatively. The germanium thermometer used had been calibrated by the supplier between 0.05 and 8 K based on the T-76[16] from 0.5 to 8 K and on the CMN magnetic scale below 0.5 K.

An exfoliated graphite called Grafoil MAT from Union Carbide was used after purification and outgassing as the adsorbent for the present measurements. It has a specific surface of $24\ m^2\ g^{-1}$ and a bulk density of $0.3\ g\ cm^{-3}$.[17] The preparation and analyses of CH_3D of high isotopic purity by gas chromatography have been fully described.[18] The amount of the gas put into the calorimeter vessel was measured volumetrically with uncertainty of about $\pm 0.2\%$.

One of the main experimental difficulties usually encountered in the heat capacity measurements for such adsorbed system or for small particles is long equilibrium time caused by poor thermal contact between adsorbent/sample and the calorimeter vessel. However, rather unexpectedly, it was found that our calorimeter system could be operated very satisfactorily as experienced many years ago in the heat capacity measurement of small particles of MgO.[19]

The heat capacity of two sub-monolayer samples with 3.014 and 2.590 mmol of the actual amount of CH_3D gas was measured between 0.3 and 7 K. The former corresponds to a coverage of 0.94 monolayer, which slightly exceeds a capacity of the commensurate $(\sqrt{3}\times\sqrt{3})$ structure, and the latter corresponds to a coverage of 0.81 monolayer. The contribution of the monolayer CH_3D to the total heat capacity including the calorimeter vessel was at least 7% at 7 K and amounted up to 95% at 0.3 K.

Results and Discussion

The after-drifts of all of the heat capacity measurements were fitted to an exponential time dependence in order to derive characteristic relaxation times that are plotted as a function of temperature in Fig. 1. About 3 K, they approached those obtained for the calorimeter vessel with graphite alone. The results for the two sets of measurements were indistinguishable and they had a structure with a maximum around 0.7 K, which is different from the behaviour of the bulk CH_3D as investigated by nuclear magnetic resonance[13] as well as by thermal measurements.[20,21]

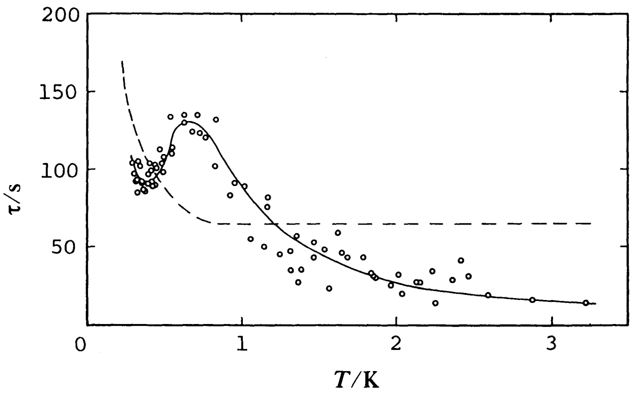

Fig. 1. Relaxation times for thermal equilibration as a function of temperature. ——, the present results for CH_3D/graphite; ------, for the bulk CH_3D.[21]

Two sets of heat capacity measurements at different coverages are essentially indistinguishable from each other below 3 K. The shape of the Schottky anomalies observed is totally different from that of the bulk CH_3D.[20,21] The heat capacity has a broad maximum around 2 K and probably another one at 0.1 K. It means that the manifold of low-lying energy levels in CH_3D on graphite must be considerably different from that known for the bulk CH_3D.[7]

Complete understanding of the shape of the heat capacity curve would require to work out the energy levels of CH_3D molecules on the surface of graphite. Neutron scattering experiments which are being undertaken will certainly provide useful information toward that end, but the present experimental results alone are sufficient to give an insight into the structure of the energy level manifold. Fuller analysis of the heat capacities together with the experimental details will be reported elsewhere when the neutron scattering results have been rationalized.

The research was supported by a grant from the Natural Sciences and Engineering Research Council of Canada and, in part, by a Grant-in-Aid for Scientific Research administered by the Ministry of Education, Science and Culture of Japan. We are grateful to Dr. M. B. Dowell of the Union Carbide Corporation for the preparation of the Grafoil MAT. We thank Mr. W. Scott for supplying liquid helium efficiently. We also thank Dr. R. K. Thomas and Dr. K. Maki for stimulating discussions and helpful correspondence. One of us (A.I.) would like to thank Professor H. Chihara and Professor M. L. Klein for their continuing advice and encouragement. The other (J.A.M.) wishes to express his long admiration for the high quality of the scientific contributions of Professor Tsunenobu Yamamoto of Kyoto University to our understanding of the methane "problem".

References

1) M. Bloom and J. A. Morrison, "Surface and Defect Properties of Solids," The Chemical Society, London (1973), Vol. 2, p. 140.

2) T. Yamamoto, Y. Kataoka, and K. Okada, *J. Chem. Phys.*, **66**, 2701 (1977).

3) H. M. James and T. A. Keenan, *J. Chem. Phys.*, **31**, 12 (1959).

4) W. Press, "Springer Tracts of Modern Physics," Springer, Berlin (1981), Vol. 92.

5) See for example R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, New York (1949).

6) See Ref. 2. A number of references to details is contained in the reference list of Ref. 7.

7) K. J. Lushington, K. Maki, J. A. Morrison, A. Heidemann, and W. Press, *J. Chem. Phys.*, **75**, 4010 (1981).

8) K. Maki, Y. Kataoka, and T. Yamamoto, *J. Chem. Phys.*, **70**, 655 (1979).

9) W. Press, University of Kiel, private communication (1987).

10) K. Maki, *J. Chem. Phys.*, **74**, 2049 (1981).

11) G. Bomchil, A. Hüller, T. Rayment, S. J. Roser, M. V. Smalley, R. K. Thomas, and J. W. White, *Philos. Trans. R. Soc. London, Ser. B*, **290**, 537 (1980).

12) M. W. Newberry, T. Rayment, M. V. Smalley, R. K. Thomas, and J. W. White, *Chem. Phys. Lett.*, **59**, 461 (1978).

13) J. Higinbotham, B. M. Wood, and R. F. Code, *Can. J. Phys.*, **57**, 1752 (1979).

14) A. Inaba and J. A. Morrison, *J. Phys. Soc. Jpn.*, **54**, 3815 (1985).

15) J. A. Morrison and P. R. Norton, *J. Chem. Phys.*, **56**, 1457 (1972).

16) The 1976 Provisional 0.5 to 30 K Temperature Scale, *Metrologia*, **15**, 65 (1979).

17) A. Inaba, Y. Koga, and J. A. Morrison, *J. Chem. Soc., Faraday Trans. 2*, **82**, 1635 (1986).

18) P. R. Norton, *J. Chromatog. Sci.*, **8**, 411 (1970).

19) W. H. Lien and N. E. Phillips, *J. Chem. Phys.*, **29**, 1415 (1958).

20) J. H. Colwell, *J. Chem. Phys.*, **51**, 3820 (1969).

21) K. J. Lushington and J. A. Morrison, *J. Chem. Phys.*, **69**, 4214 (1978).