A Deuteron NMR Study on a Benzene Multilayer on Graphite

B. Boddenberg * and R. Grosse

Lehrstuhl für Physikalische Chemie II, Universität Dortmund, BR Deutschland

Z. Naturforsch. **42 a,** 272–274 (1987); received November 22, 1985

An NMR sample tube was loaded with graphitized carbon black (Graphon) as well as a ten adsorbed layers equivalent of benzene-d_6, and subsequently sealed. The ^{2}H NMR spectra obtained at 298, 170 and 90 K yield the following picture: The multilayer phase with liquid like properties established at 298 K is decomposed at the lower temperatures into a bulk (3D) crystalline phase and an adsorbed phase of, probably, monolayer thickness which can be characterized to exist in the two dimensional (2D) fluid and solid states at 170 and 90 K, respectively.

1. Introduction

A benzene monolayer on graphite, when cooled down from 300 to 70 K undergoes a two dimensional (2D) fluid/solid phase transition in some narrow temperature range at about 130 K [1–3]. If, similarly, a benzene multilayer on graphite is cooled down there is strong indication from NMR spectroscopy [4] and neutron diffraction [2] that below some temperature in the range 230 to 200 K the multilayer has completely collapsed leaving a monolayer surface film in equilibrium with crystallites of bulk (3D) solid benzene. Intimately connected with these observations are the findings by adsorption isotherm studies [5] that below a temperature of about 230 K adsorption of benzene on graphite beyond monolayer coverage is no longer feasible. The present ^{2}H NMR study was undertaken to give clearcut evidence for the above described type of phase separation to occur with a benzene multilayer on graphite at low temperatures.

2. Experimental

The adsorbent used for the present investigation was the graphitized carbon black Graphon (Cabot Corp., Boston, Mass., USA). Its thermal and vacuum pretreatment has been reported elsewhere [6]. Suitable amounts of benzene-d_6 (Merck, Sharp and Dohme, Montreal, Canada) were chilled onto the adsorbent to yield a nominal ten layer film based on the 80 m^2/g N_2-BET surface area of Graphon and the usually employed 0.40 nm^2 benzene molecule cross section.

The ^{2}H NMR spectra were measured at the resonance frequency 52.7 MHz using the spectrometer and techniques described elsewhere [6, 7].

3. Results

Figure 1 shows the deuteron NMR spectra of the nominal ten layer benzene-d_6 on Graphon system at 298 and 170 K. Whereas at the higher temperature a narrow singlet of width at half height of $\delta\nu =$ 350 Hz is obtained, the spectrum at 170 K consist of a singlet ($\delta\nu = 1100$ Hz) superimposed on a typical Pake powder pattern of edge separation $\Delta\nu = 70$ kHz. A careful analysis of the 170 K spectrum reveals a slight upfield shift (to lower frequency) of the singlet with respect to the center of the Pake pattern by 0.75 ± 0.5 kHz, corresponding to $\delta = -15 \pm 10$ ppm.

In Figs. 2a and b are displayed ^{2}H solid state patterns obtained at 90 K by Fourier transformation of quadrupole echos detected in quadrature with cycle times of 10 and 0.2 s, respectively. Spectrum 2a signifies the superposition of two Pake type patterns of edge separations $\Delta\nu = 70$ and 140 kHz whereas with spectrum 2b the broad pattern, obviously, has become saturated leaving the 70 kHz spectrum which exhibits the same characteristic asymmetry as was found with a Graphon sample carrying one monolayer only [6]. The cycle time of 10 s for the detection of spectrum 2a was intentionally set to this value in order to display clearly the two component behaviour and to save measuring time. Actually, the 140 kHz pattern was found to be considerably saturated under this condition.

---

* Reprint requests to Prof. Dr. B. Boddenberg, Lehrstuhl für Physikalische Chemie II, Universität Dortmund, Postfach 500 500, Otto-Hahn-Straße, D-4600 Dortmund 50, West-Germany.

0340-4811 / 87 / 0300-0272 $ 01.30/0. – Please order a reprint rather than making your own copy.

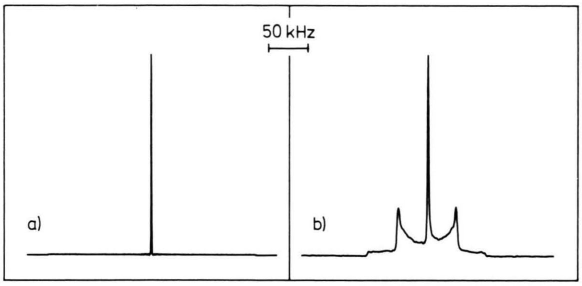

Fig. 1. ^{2}H NMR spectra at 298 K (a) and 170 K (b) of an equivalent of ten layers of benzene-d$_6$ on Graphon.

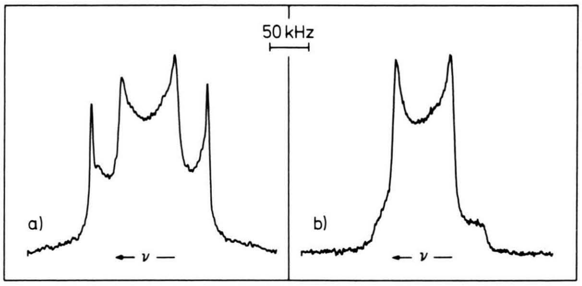

Fig. 2. ^{2}H NMR spectra at 90 K of an equivalent of ten layers of benzene-d$_6$ on Graphon. The spectra were obtained with pulse sequence cycle times of 10 s (a) and 0.2 s (b).

4. Discussion

The appearance of the narrow singlet signal at 298 K indicates clearly the liquid like behaviour of the ten monolayer film. This finding is not surprising since even with one monolayer coverage a narrow singlet, which indicates rapid isotropic reorientational motion on the NMR time scale, is observed [7].

The appearance of the spectrum at 170 K suggests that the singlet and the Pake pattern are due to benzene molecules being in intimate contact with the graphite surface and contained in 3D benzene crystallites, respectively. The assignment of the singlet comes, firstly, from the linewidth which is comparable in value to the width found for the monolayer coverage sample [7], and secondly, from the upfield shift observed, which is typical for hydrogen shifts of molecules adsorbed on graphite [8, 9]. Following the same reasoning as in [7] the narrow singlet is clear indication of 2D fluid behaviour of the adsorbed layer.

The 70 kHz edge splitting of the Pake pattern (Fig. 1b) is unequivocal evidence that hexad axis rotation is fast, whereas all other types of conceivable rotational motions proceed slowly on the NMR time scale [6]. The time scale is set by $\tau_{\mathrm{NMR}} = (e^2qQ/h)^{-1}$, where e^2qQ/h is the rigid deuterium quadrupole coupling constant. With $e^2qQ/h = 186.6$ kHz [10], τ_{NMR} is 5.4 µs. The situation of rapid hexad axis rotation with all other rotational motions being frozen in at 170 K is characteristic for solid benzene as may be deduced from ^{1}H NMR studies on solid benzene [11–14]. Actually, without going into details of the hexad axis reorientation mechanism [14], an order of magnitude estimate of the correlation time of this motion may be obtained using the expression $\tau_c = 6 \cdot 10^{-14} \exp(1800/T)$ derived by Andrew and Eades from proton relaxation studies. From this relation the hexad axis rotation correlation time at 170 K is easily calculated as $\tau_c = 2.4 \cdot 10^{-9}$ s, a value which clearly meets the required condition $\tau_c \ll \tau_{\mathrm{NMR}}$. Thus, there is strong evidence for the assignment of the Pake pattern observed to 3D solid benzene. This notion is substantiated by the completely symmetrical appearance of the pattern, which disapproves the conceivable assignment of the Pake pattern to a surface phase since otherwise a distinct asymmetry should have shown up [6].

The ^{2}H NMR patterns at 90 K shown in Fig. 2 suggest the following interpretation. The 70 kHz edge splitting pattern comes from a 2D solid state monolayer film whereas the 140 kHz pattern is due to 3D solid benzene.

The first of these conclusions follows immediately from the asymmetry of the spectrum 2b, which is practically identical with that obtained for the one monolayer sample [6]. In fact, applying the same model and identical parameters as in [6] the spectrum 2b can excellently be reproduced as is demonstrated in Figure 3a. The model employed considers the molecules to be adsorbed flat on the surface and in rapid hexad axis rotation [6], with parameters $e^2qQ/h = 186.6$ kHz [10] and $\Delta s = +150$ ppm, where Δs is the magnetic shielding anisotropy [6].

Using, again, the correlation time expression of Andrew and Eades mentioned above the correlation time at 90 K comes out as $\tau_c = 2.9 \cdot 10^{-5}$ s, implying $\tau_c \gg \tau_{\mathrm{NMR}}$. Consequently, with $e^2qQ/h = 186.6$ kHz the full static Pake pattern with edge splitting $\Delta\nu = 140$ kHz should result as is actually observed.

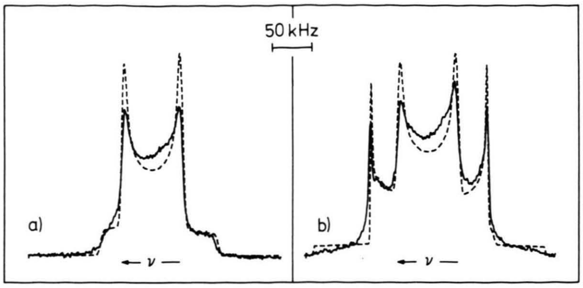

Fig. 3. Theoretical ^{2}H NMR spectra according the models explained in the text superimposed on the experimental spectra of Figure 2.

The ^{2}H spin lattice relaxation time T_1 for the anisotropic hexad axis rotational motion can easily be estimated to be 20 s using known expressions [15, 16] as well as the correlation time evaluated before. This result is in full accordance with the observation of complete and only partial saturation of the 140 kHz pattern if cycle times of 10 and 0.2 s, respectively, are applied in the experiments. Thus, the 140 kHz pattern assignment to 3D solid benzene is confirmed.

Figure 3b shows superimposed on the experimental spectrum of Fig. 2a the theoretical spectrum on the basis of the foregoing discussion, which is the composite of the asymmetrical 70 kHz pattern as in Fig. 3a and a symmetrical 140 kHz Pake pattern. It was assumed that all portions of the 140 kHz component spectrum are equally partly relaxed which assumption is a over-simplification as is well known [17]. Taking account of this circumstance the agreement of experiment and theoretical model is considered to be excellent. However, an isotropic upfield shift of 30 ppm ($\delta = -30 \pm 10$ ppm) of the 70 kHz with respect to the 140 kHz pattern was introduced in order to attain this very good agreement. This shift corresponds to $\delta^{\mathrm{TMS}} = -23 \pm 10$ ppm on a TMS shift scale if the shift difference of solid benzene relative to TMS is tentatively assumed to be temperature independent and to agree with the usually employed liquid benzene shift. This value excellently agrees with the findings for n-butane on Graphon at 120 K ($\delta^{\mathrm{TMS}} = -22$ ppm [8]). Thus, the shift introduced appears not to be accidental but reflects the 2D solid/3D solid two phase situation encountered at the temperature 90 K.

5. Conclusion

In the present paper it has been demonstrated that ^{2}H NMR provides a convenient tool to differentiate bulk and surface phases on graphite which are in equilibrium with each other in a closed volume system. This favourable circumstance is due, on the one hand, to the single spin character of the deuteron spin Hamiltonian which renders the analysis of the resulting ^{2}H NMR spectra a comparatively easy task, and on the other hand to the large values of the isotropic shielding constant and the shielding anisotropy provided by the graphite support. Efforts are being made presently to exploit this favourable possibility for the study of other multilayer systems with graphite as support.

Acknowledgements

Financial support of this work by "Deutsche Forschungsgemeinschaft" and "Fonds der Chemischen Industrie" is gratefully acknowledged.

[1] M. Monkenbusch and R. Stockmeyer, Ber. Bunsenges. Phys. Chem. **84,** 808 (1980).
[2] P. Meehan, T. Rayment, R. K. Thomas, G. Bomchil, and J. W. White, J. Chem. Soc., Faraday Trans. I, **76,** 2011 (1980).
[3] U. Bardi, S. Magnanelli, and G. Rovida, Surf. Sci. **165,** L 7 (1986).
[4] B. Boddenberg and J. A. Moreno, Ber. Bunsenges. Phys. Chem. **87,** 83 (1983); J. A. Moreno, Dissertation, Universität Hannover, 1977.
[5] Y. Khatir, M. Coulon, and L. Bonnetain, J. Chim. Physique **75,** 789 (1978).
[6] B. Boddenberg and R. Grosse, Z. Naturforsch. **41 a,** 1361 (1986).
[7] R. Grosse and B. Boddenberg, Z. Phys. Chem., NF, in press.
[8] G. Neue, Dissertation, Universität Dortmund, 1983.
[9] J. Tabony, Progr. NMR Spectrosc. **14,** 1 (1980).
[10] F. S. Millett and B. P. Dailey, J. Chem. Phys. **56,** 3249 (1972).
[11] E. R. Andrew and R. G. Eades, Proc. Roy. Soc. London A **218,** 537 (1953).
[12] U. Haeberlen and G. Maier, Z. Naturforsch. **22 a,** 1236 (1967).
[13] J. Wendt and F. Noack, Z. Naturforsch. **29 a,** 1660 (1974).
[14] F. Noack, M. Weithase, and J. von Schütz, Z. Naturforsch. **30 a,** 1707 (1975).
[15] H. W. Spiess, in "NMR. Basic Principles and Progress", edited by P. Diehl, E. Fluck, and R. Kosfeld, Springer, Berlin 1978, Vol. 15, p. 55.
[16] H. Pfeifer, in "NMR. Basic Principles and Progress", edited by P. Diehl, E. Fluck, and R. Kosfeld, Springer, Berlin 1972, Vol. 7, p. 53.
[17] D. A. Torchia and A. Szabo, J. Magn. Res. **49,** 107 (1982).