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²H solid state NMR of the butane/graphite system

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Recently,¹ we have studied the two dimensional (2D) fluid-solid phase transition of a one monolayer butane film on the graphitized carbon black Graphon (Cabot Corp., Boston, Mass.). It was found that this transition takes place continuously over the temperature range 113 to 125 K. The bulk (3D) melting point of butane is 134.7 K.² The width at half-height of the 2D solid state deuteron spectrum (100 to 112 K) was obtained as 40 ± 3 kHz indicating rapid methyl group rotation. For the 3D solid methyl group rotation has been reported³ to be slow as compared to the line width for temperatures in the range 63 to 88 K. To have a better basis for the examination of differences of the butane molecule mo-

tional behavior in the 2D and 3D solid states we have decided to measure the 3D deuteron spectra for temperatures greater than 88 K.

In order to achieve good quality polycrystallinity of the solid approximately 0.6 g of thoroughly degassed and heat treated Graphon was loaded with a certain amount of butane C₄D₁₀ (Merck, Sharp, and Dohme, Canada) corresponding to ten statistical monolayers or about 2×10^{20} molecules. The deuteron spectra were obtained with the aid of a pulsed NMR spectrometer (CXP 100, Bruker Physik, Karlsruhe, Germany) operated at 13.7 MHz in the quadrature detection mode by Fourier trans-

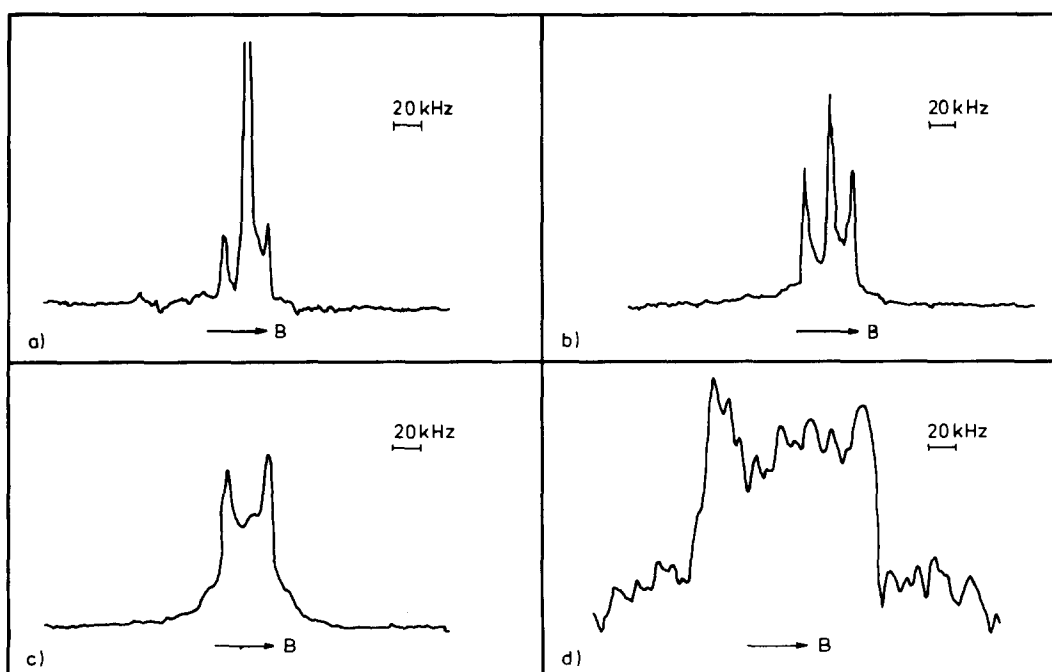


FIG. 1. Deuteron spectra of butane C₄D₁₀/graphitized carbon black. (a) 128 K; (b) 117.5 K; (c) 100 K; (d) 84 K.

forming the average of the quadrupole echoes. The sample temperatures were reproducibly stabilized to ± 0.1 K using a specially designed nitrogen gas flow device.

Figure 1 shows the spectra obtained at several selected temperatures between 84 and 128 K. At the upper end of this interval a slight hysteresis with respect to the direction of the temperature change was observed which may be due to nonperfect establishment of equilibrium conditions. At 132 K a single narrow line of about 2 kHz width was obtained. It is seen that between 100 and 128 K the spectra are superpositions of a Pake type powder doublet and a singlet, the latter being slightly upfield shifted (about 1 kHz) with respect to the center of the doublet. The doublet which grows in intensity at the expense of the singlet with decreasing temperature exhibits a temperature independent splitting of 37 ± 3 kHz. Below 100 K the spectrum was observed to broaden considerably. At 84 K the spectrum consists of a broad doublet of splitting 120 ± 10 kHz and a broad central line of not well resolved shape which again seems to be slightly upfield shifted with respect to the center of the doublet. Since it was not intended to study such broad lines in detail the receiver bandwidth was retained comparatively narrow thus leading to line shape distortions beyond 30 kHz to either side of the center of the spectrum.

The spectra may be most reasonably interpreted in thermodynamic terms following essentially the reasoning of Berezin *et al.*⁴ If with decreasing temperature the chemical potential of the 3D solid (μ_{3D}) falls below that of the adsorbed layer (μ_s) butane is desorbed to form 3D solid crystallites anywhere in the sample container giving rise to the doublet signal the splitting of

which is typical for rapid methyl group rotation.⁶ Since μ_s generally decreases with surface coverage the amount of 3D solid increases continuously with decreasing temperature. The upfield shift of the singlet which is attributed to the adsorbed layer is due to the magnetic fields emanating from the graphite support because of its comparatively large diamagnetic susceptibility.^{1,5} At 84 K methyl group rotation of the 3D solid has, obviously, sufficiently slowed down to cause the drastic broadening of the spectrum. The splitting corresponds to the deuteron quadrupole coupling constant of 169 kHz as found by Burnett and Muller.³ The central broad line is attributed to one monolayer butane which is now in a 2D solid state. The probable slight upfield shift supports this assignment.

On the basis of the present results it is suggested to use a suitable and carefully conditioned adsorbent as filler material to obtain high quality powder spectra in cases where the desired polycrystallinity cannot be achieved otherwise. We are testing "soft surface" materials, e.g., suitably chemically modified silicas, in order to get rid of the undesired first layer spectrum component.

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Determination of the spectrum of recoil energies for chlorine atoms generated by the $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ nuclear process

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When energetic chlorine atoms are generated for studies of hot atom reaction dynamics or to radio-label molecules by the (n,γ) nuclear reaction, both recoil ^{36}Cl and ^{38}Cl are produced. The natural abundance of stable chlorine isotopes is ^{35}Cl (75.77%) and ^{37}Cl (24.23%).¹ ^{38}Cl is a useful radio isotope for studies of hot atom reactions because it decays by γ -ray emission with the relatively short half-life of 37.3 min, and it has been used extensively in gas phase studies in this laboratory with hydrocarbons^{2,3} and hydrogen.^{4,5} ^{36}Cl , on the other hand, is impractical for such gas phase studies because of its long lifetime, $t_{1/2} = 3.1 \times 10^5$ years,¹ which requires a much larger number of nucleogenic atoms for statistically significant detection and the correspondingly longer irradiation time resulting in

excess radiation damage to the reaction mixture of interest. Crystalline inorganic materials of interest in solid state chemistry, however, are usually quite radiation resistant, and ^{36}Cl is now being used to elucidate information about crystal defect and other solid state phenomena.⁶ While ^{38}Cl can also be used for such studies and kinetics and mechanisms of solid state reactions in $\text{K}_2[\text{ReBr}_6]/\text{K}_2[\text{ReCl}_6]$, mixed crystals have been reported,^{7,8} its short half-life precludes many of the normal inorganic chemical procedures. In general, a complete description of hot atom recoil energies is useful in simulations of these solid state experiments.⁶⁻⁸

The recoil spectrum for the distribution of energies imparted to ^{36}Cl atoms from the $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ nuclear