^2H NMR Patterns of Methylaromatics Adsorbed on Graphite

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^2H NMR solid state powder patterns were measured at one monolayer coverage of benzene on the non graphitized carbon black Spheron, and of toluene, p-xylene, mesitylene, and mellitene (hexamethylbenzene) on the graphitized carbon black Graphon. Benzene on Spheron, in contrast to Graphon, exhibits a typical Pake type powder pattern shape demonstrating the minor influence of paramagnetic centers on the pattern shapes as well as confirming the formerly introduced shielding anisotropy interaction in the case of graphite. From the highly asymmetric appearance of the ^2H powder patterns for the adsorbed methyl-aromatics on Graphon the flat orientation of these molecules on graphite as well as details of the rotational molecular motions are deduced.

I. Introduction

Most recently, it has been demonstrated that the orientation of adsorbed benzene molecules on microcrystalline graphite substrates can be determined from the characteristic asymmetry of the deuteron NMR solid state powder patterns [1, 2]. This unique possibility emerges from the fact that the deuterons (spin $I = 1$) contained in molecules adsorbed on graphite are subject to a two-fold tensorial interaction, namely an electric via the electric field gradient (EFG) tensor being fixed with respect to the molecular framework, and a magnetic via a shielding tensor being fixed with respect to the solid support frame. The magnetic interaction arises from the polarization in the static Zeeman field of the graphite support due to its highly anisotropic diamagnetic susceptibility tensor.

In a recent theoretical paper [3] the basis was laid for the analysis of NMR powder patterns of any type of molecules adsorbed on graphite. In the present paper these results are used and extended to assess the orientations as well as the rotational dynamics of various aromatic molecules adsorbed on the basal planes of graphite.

II. Experimental

The adsorbents used for the present investigation were the carbon black Spheron and its graphitized version Graphon (both Cabot Corp., Boston, Mass., USA) having specific surface areas of 130 and 80 m^2/g, respectively, as determined from low temperature nitrogen adsorption isotherms using the BET procedure of analysis and the standard $\omega_{N_2} = 0.162\ nm^2$ nitrogen molecule cross section [4]. Graphon consists of agglomerated primary particles of about 25 nm diameter bounded by stacks of graphite like microcrystallites (4 nm × 8 nm) having the (0001) crystal basal planes oriented parallel to the particle external surface [5, 6]. The turbostratically disordered [5] Spheron particles, on the other hand, do not expose such well defined surface planes which property is reflected in the very large energetic heterogeneity of this material [5, 7]. In addition, Spheron in contrast to Graphon exhibits a very large concentration of localized paramagnetic centers of about 10^{20} spins/g [8, 9] rendering this carbon black unsuited for proton (^1H) NMR relaxation studies of adsorbed molecules [7].

The adsorptives used for the present study, all having been purchased from Merck, Sharp and Dohme, Montreal, Canada, except p-Xylene (Sigma Chemie, München, Germany) were as follows. Benzene-d_6 (C_6D_6, 99.6 atom % D); Toluene-d_8 ($C_6D_5CD_3$, 99.6%); p-Xylene-d_6 ($C_6H_4(CD_3)_2$, 99%); Mesitylene-d_{12} ($C_6D_3(CD_3)_3$, 98%); Mellitene (Hexamethylbenzene)-d_{18} ($C_6(CD_3)_6$, 99.4%). Except for degassing, these materials were used as obtained.

The adsorbent materials were put into 10 mm o.d. glass tubes, evacuated at slowly increasing temperature, and finally baked at 450 °C under high vacuum ($\lesssim 10^{-4}$ Pa) for 12 hrs. Such amounts of the adsorptives were transferred into the sample tubes to give one monolayer coverage for each adsorbate. The respective molecule cross section areas needed for this

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calibration were taken from the literature [5, 10] or estimated from van der Waals radii. For use in the spectrometer the sample tubes were sealed off under high vacuum.

The ^{2}H NMR spectra were obtained by Fourier transformation of coherently added quadrupole echoes [11] detected in quadrature at resonance frequency $\nu_0 = \omega_0/2\pi = 52.7$ MHz using the spectrometer and equipment described elsewhere [1].

III. Theoretical Considerations

In a recent paper [3] it has been shown that with static axially symmetric electric field gradient (**q**) and magnetic shielding (**S**) tensors acting at the site of a deuteron the isotropic powder pattern is determined by two parameters, A and β, where

$$A = \frac{8}{9} \frac{\nu_0 \Delta s}{\mathrm{DQCC}} \tag{1}$$

and β is the angle between the distinct principle axes of the **q** and **S** tensors. In (1) $\mathrm{DQCC} = e^2 q Q/h$ is the rigid deuterium quadrupole coupling constant, $\Delta s = s_{\parallel} - s_{\perp}$ is the shielding tensor anisotropy, and ν_0 is the resonance frequency. This theory was mainly developed in order to account for the asymmetric appearance of NMR patterns obtained from the deuterons of molecules adsorbed on isotropic graphite powders where the magnetic shielding tensor is set up by the action of the Zeeman field on the highly anisotropic diamagnetic susceptibility tensor of graphite [1]. Since the **q** and **S** tensors have their principal axis systems fixed with respect to some molecular and the solid support frame, respectively, the angle β contains the information about the orientation of the molecule with respect to the graphite (0001) surface plane on which the molecule is adsorbed.

As has been pointed out in [3] the treatment leading to (1) remains valid if molecular motions proceed fast on some NMR time scale and lead to axially symmetric motionally averaged tensors as is the case with uniaxial rotations [12]. The time scales of relevance here are $\tau_Q = |\mathrm{DQCC}|^{-1}$ and $\tau_S = (\nu_0 |\Delta s|)^{-1}$, which characterize the quadrupole and the shielding anisotropy coupling strengths, respectively. For the present applications it is required that the residence time of a molecule on a microcrystallite surface plane of well defined orientation in space must be long as compared to τ_Q and τ_S since otherwise both the quadrupole and shielding tensors become practically isotropically averaged by surface diffusion processes [13]. This condition which, in general, can be attained by proper adjustment of the measuring temperature entails that with fast uniaxial molecular rotations the EFG tensor is averaged and the shielding tensor remains static.

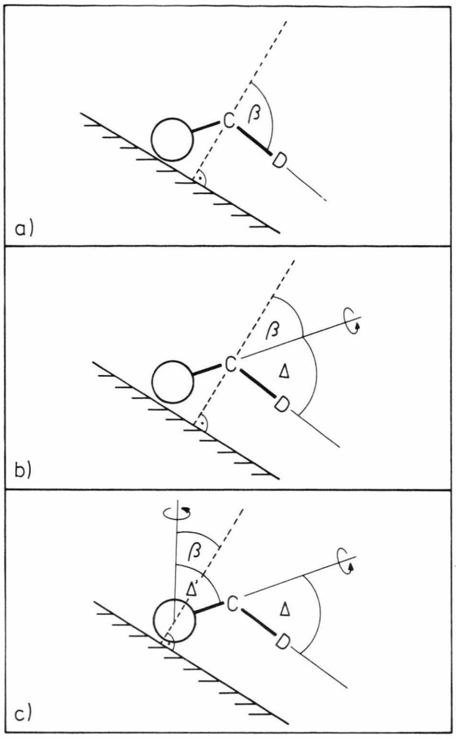

Fig. 1. Schematic representation of molecule/graphite surface arrangement for definition of the angles occurring in (1)–(4). a) Static case, b) uniaxial rotation, c) rotations around two axes.

In view of the present applications three cases are of interest and are depicted in Figure 1. For each of these cases the deuterium quadrupole coupling constant DQCC which has to be introduced into (1) to obtain A, and the angle β are defined in a different manner. The distinct principle axes of the rigid axially symmetric [14, 15] EFG tensor and of the axially symmetric [1] shielding tensor acting at the deuteron sites of the molecules adsorbed on graphite (0001) are in parallel with the C–D bond axis and the normal to the surface, respectively.

Case a (Figure 1a). The orientation of the C–D bond remains static on the time scale τ_Q. Consequently,

$$\mathrm{DQCC} = e^2 q Q/h, \tag{2}$$

and β is the angle between the C–D bond axis and the normal to the surface.

Case b (Figure 1b). Fast uniaxial rotation occurs about a spaced fixed axis around which the molecule as a whole or part of it (internal rotation) is moved. In this case

$$\mathrm{DQCC} = \tfrac{1}{2}(3\cos^2\Delta - 1)\, e^2 q Q/h, \qquad (3)$$

and β is the angle between the rotation axis and the normal to the surface. Δ is the angle between the C–D bond and the rotation axis.

Case c (Figure 1c). On the time scale τ_Q there is fast internal rotation motion and, in addition, the molecule rotates rapidly as a whole. Since these two types of motion can be considered to be stochastically independent

$$\mathrm{DQCC} = \tfrac{1}{2}(3\cos^2\Delta - 1)\,\tfrac{1}{2}(3\cos^2\Delta' - 1)\, e^2 q Q/h, \qquad (4)$$

and β is the angle between the body rotation axis and the surface normal, Δ' is the angle between the two rotation axes considered.

IV. Results

Figure 2, a and b, shows the ^{2}H NMR solid state patterns of benzene adsorbed on Spheron and on Graphon [1] at the temperatures 80 and 90 K, respectively. In both cases the prominent edge splitting is 70 kHz and the total spectral width is 140 kHz. However, whereas with Spheron as the support all spectral features are symmetrically displaced about the spectrum center, the Graphon sample pattern exhibits a distinct asymmetry which may be recognized from the different extension of the "feet" at the outer spectrum portions. It may further be recognized that the pattern shape for benzene on Spheron is more sharply developed than for benzene on Graphon.

In Fig. 3, a to d, are shown the ^{2}H solid state patterns measured for toluene, p-xylene, mesitylene, and mellitene, respectively, adsorbed on Graphon at the temperatures denoted in the figures. Most strikingly, the spectra are strongly distorted and asymmetric with respect to the spectrum centers bearing hardly a resemblance to the usually encountered quadrupole pattern shapes such as for benzene on Spheron (Figure 2a). This behaviour is most strikingly revealed by the system toluene on Graphon.

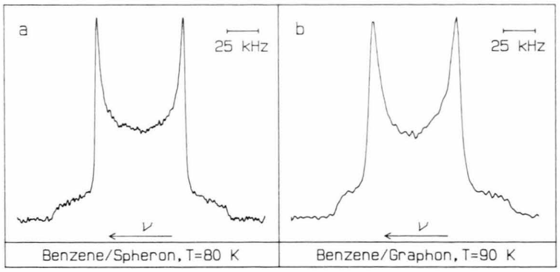

Fig. 2. ^{2}H NMR solid state patterns of benzene adsorbed on Spheron (a) and on Graphon (b), one monolayer coverage.

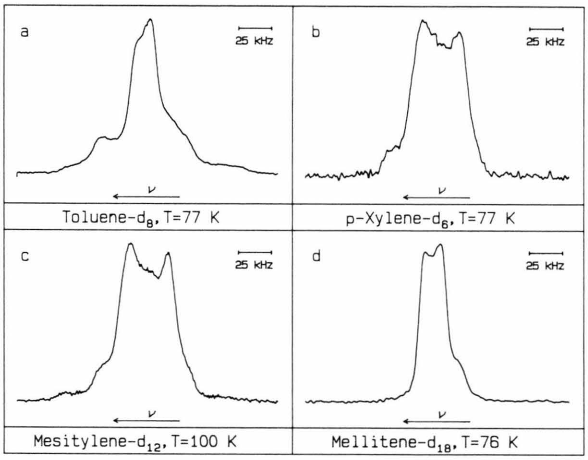

Fig. 3. ^{2}H NMR solid state patterns of toluene (a), p-xylene (b), mesitylene (c), and mellitene (d) adsorbed on Graphon at one monolayer coverage each.

The spectra for benzene, p-xylene, mesitylene and mellitene were found to be independent of temperature both with respect to shape and width between 75 K and about 120, 85, 110, and 170 K, respectively. At even higher temperatures these spectra collapsed into isotropically averaged singlets. The toluene solid state pattern displayed in Fig. 3 was obtained at the lowest temperatures attainable at present (75 K). This pattern changed shape and width with increasing temperature and separation of the pulses generating the quadrupole echoes. At temperatures of about 130 K the powder pattern had completely collapsed into a singlet. In the vicinity of 75 K these changes were, however, found to be only slight. Obviously, some type of motion has not become completely frozen in at 75 K.

V. Discussion

The discussion will be organized as follows. First, from a comparison of the patterns obtained for benzene on Spheron and Graphon several important conclusions will be drawn about the ^{2}H rigid quadrupole constants of adsorbed molecules a well as the role played by paramagnetic centers contained in the adsorbents. Secondly, the ^{2}H patterns measured for the adsorbed methyl substituted aromatics will be analyzed according to the method developed in [3], taking into account the effects of rotational motions as discussed previously. Finally, a comparative view of the spectra obtained will be taken with special emphasis on the individual linewidths.

In general, the patterns can completely be analyzed without introducing a priori assumptions concerning the values of the physical parameters [3]. With the presently studied systems, however, a more convenient approach may be pursued by taking into account the following circumstances. (i) The geometry of the adsorbed molecules can fairly be assumed to be the same as in condensed states since only weak van der Waals forces as in condensed phases are operative. This entails that, at least to first approximation, the values of the rigid quadrupole coupling constants as published in the literature may be used. These were taken as 187 kHz for the ring deuterons as in benzene [16] and 156 kHz for the methyl deuterons as in toluene [15]. (ii) The reorientation rates of methyl groups attached to aromatic rings are well known to exceed by far the value given by $1/\tau_Q$ at temperatures > 70 K [17–20]. Therefore, in the presently studied cases the methyl group deuterons according to (3) and (4) ($\Delta = 70.5^\circ$) give rise to patterns belonging to the cases b) and c) introduced previously. Whether case b) or c) is realized may be assessed from the total widths of the methyl group deuteron parts of the spectra – about 80 kHz in case b), much less than 80 kHz in case c). (iii) A rough estimate of the parameter A from $\nu_0 \Delta s = 7.9$ kHz and DQCC from the spectral widths allows to find out approximately the value β from the type of asymmetry of the pattern [3]. The shielding anisotropy $\Delta s = +150$ ppm as determined for benzene on Graphon [1] is always applied in the discussions to follow.

On the basis of these considerations it is an almost easy task to guess the orientation of the molecules with respect to the surface as well as the rotational dynamical state. Therefore, in the following the correctness of a model guessed is proved by the coincidence of the resulting pattern with experiment. The values of the parameters DQCC, A, β, and $\delta\nu$ (individual linewidth) that were used for the calculations of the theoretical spectra are contained in the figures that follow, others are to be found in the text.

Benzene on Spheron and Graphon (Figs. 2 and 4)

The benzene on Spheron ^{2}H spectrum is a typical example of a pure quadrupole pattern of the Pake type. The theoretical pattern displayed in Fig. 4 which is in optimum coincidence with experiment was obtained with $|\mathrm{DQCC}| = 95$ kHz. Clearly the pattern is *case b* with $A = 0$ and $\Delta = 90^\circ$, hence $e^2qQ/h = (190 \pm 1)$ kHz. The calculated benzene on Graphon pattern, which is shown for comparison is based on the parameters $e^2qQ/h = 186.6$ kHz, $\Delta = 90^\circ$, $\beta = 0^\circ$, $\Delta s = +150$ ppm [1].

These data give unequivocal evidence that both on Spheron and Graphon the adsorbed benzene molecules rotate rapidly about the hexad axis with no other rotational motion being feasible on the time

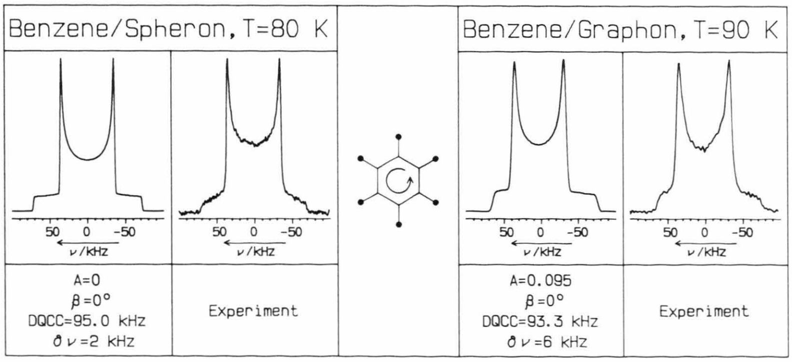

Fig. 4. Comparison of calculated and experimental ^{2}H NMR solid state patterns of benzene on Spheron and on Graphon.

scale of several microseconds. The asymmetry of the benzene on Graphon pattern clearly reveals the flat orientation of the molecules with respect to the graphite basal planes whereas the symmetrical appearance of the pattern with Spheron as the support does not allow any conclusion about the orientation. Evidently, these findings ar a consequence of the different structures of the two blacks used with well developed microcrystallite graphite patches on Graphon in contrast to Spheron. The remarkable difference of individual line widths observed for the two blacks will be addressed to below.

Further interesting conclusions may be drawn from the above reported results. (i) The very good agreement of the rigid quadrupole coupling constant for the supported benzene molecules on Graphon with the single crystal value reported in the literature [16] is not unexpected in view of the above mentioned weak interaction character of the surface forces. It is, therefore, rather surprising that for benzene on Spheron a larger coupling constant than 187 kHz has to be introduced in order to explain this spectrum. The reason for this effect is not clear at present. (ii) The pure quadrupole pattern appearance for benzene on Spheron proves that the quadrupole Hamiltonian is by far dominating over the Hamiltonian describing the coupling of the deuterons with the electron spins of the support paramagnetic centers. This is in contrast to a recent study on lipid bilayer systems where the doping with paramagnetic ions leads to strong deuteron/electron spin coupling showing up in unusually large pattern asymmetries [21]. Since with Spheron, exhibiting much higher paramagnetic center concentration than Graphon, deuteron/electron couplings, obviously, come not into play it is proven that the pattern anisotropy for Graphon is not due to such effects.

Mesitylene on Graphon (Figs. 2 and 5)

The 3:1 ratio of the methyl to ring deuterons as well as the presence of rapid methyl group rotation immediately predict the dominance of the methyl group resonance pattern. The 80 kHz width of this subpattern (Fig. 2) suggests the *case b*) situation with $\beta > 54^\circ$ (magic angle) since the "foot" is more developed on the high than on the low frequency side of the pattern [3]. In fact, excellent agreement of the calculated subpattern shape with experiment is obtained (Fig. 5) with the notion of flat orientation ($\beta = 90^\circ$) of the molecules on the graphite basal planes. The pattern due to the ring deuterons, which is hardly to be seen is *case a*, thus substantiating the view of flat orientation. These results, obviously, mean that the molecules are prevented from rotating about the threefold symmetry axis normal to the ring plane on the NMR scale.

Mellitene on Graphon (Figs. 2 and 6)

As compared to mesitylene, the pattern width is considerably smaller and the greater extension of the "foot" now appears on the low frequency side of the pattern (Figure 2). Obviously, it is a *case c* situation with $\beta < 54^\circ$. The explicit calculation using the parameters given in the figure with $\Delta = 70.5^\circ$, $\Delta' = 90^\circ$ gives very good agreement with experiment. Consequently, the mellitene molecules are lying flat on the surface and – with rapidly rotating methyl groups attached – rotate fast around the sixfold symmetry axis normal to the molecular plane.

p-Xylene on Graphon (Figs. 2 and 7)

Since this pattern is similar to the methyl deuteron subpattern of mesitylene (*case b*) it is concluded that the p-xylene molecules are adsorbed flat with no allowance given for rotation about any body axis on the time scale $\tau_Q = 10\,\mu$s.

Toluene on Graphon (Figs. 2 and 8)

As the sequence of calculated spectra in Fig. 8 shows, the composite pattern that compares well with experiment is obtained with the notion of flat orientation and both rapid methyl group and body rotation about an axis normal to the molecular plane. Thus a *case b* (ring deuterons)/*case c* (methyl deuterons) combination is realized.

A closer examination of Figs. 5 to 8 reveals that the methyl group deuteron patterns resp. subpatterns calculated with the parameter values cited are somewhat broader than those obtained from experiment. This effect is most clearly seen in the cases of mellitene (Fig. 6) and toluene (Fig. 8) on Graphon, where besides methyl group rotation the body rotation also proceeds fast on the NMR time scale. Actually, a similar observation has been made with solid mellitene [22], where the effective quadrupole strength derived from the powder pattern at room temperature with rapid C_6 motion is by about 15% smaller than expected from the low temperature data. Recent experi-

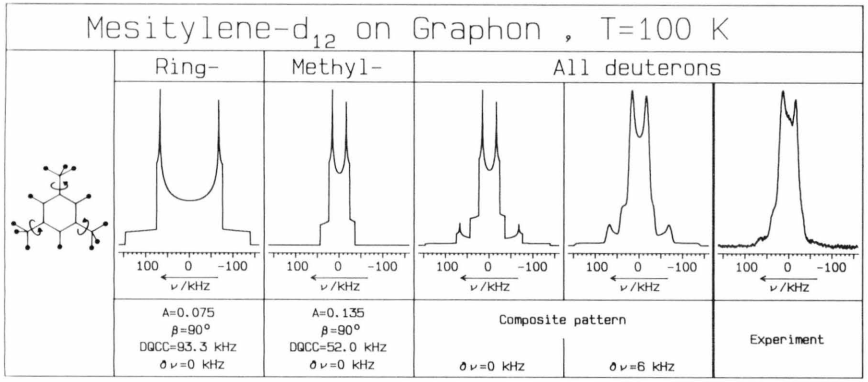

Fig. 5. Calculated ^{2}H NMR solid state patterns of mesitylene on Graphon and comparison with experiment.

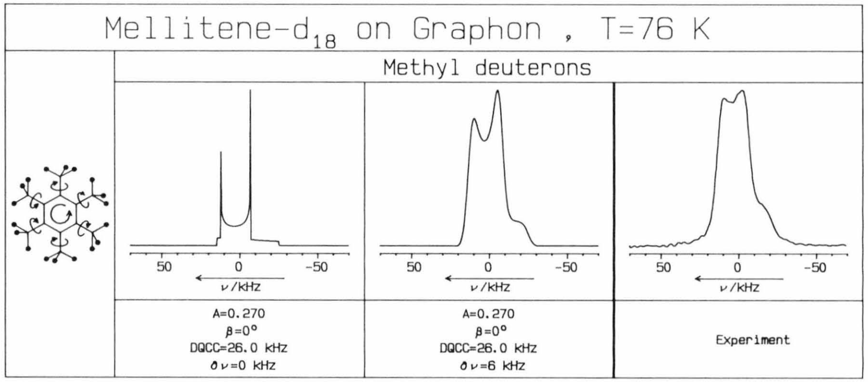

Fig. 6. Calculated ^{2}H NMR solid state patterns of mellitene on Graphon and comparison with experiment.

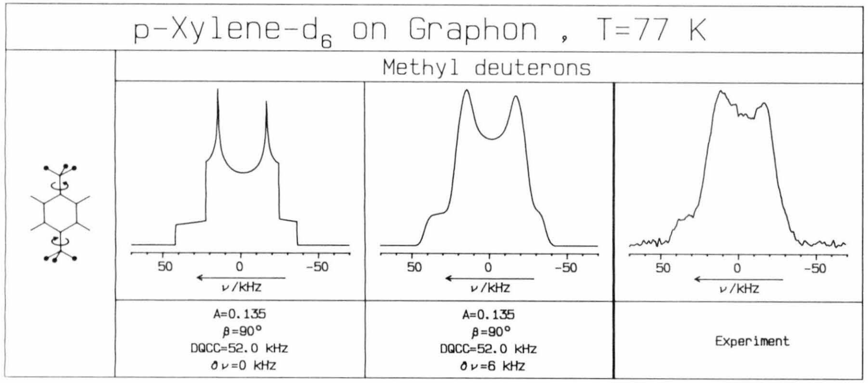

Fig. 7. Calculated ^{2}H NMR solid state patterns of p-xylene on Graphon and comparison with experiment.

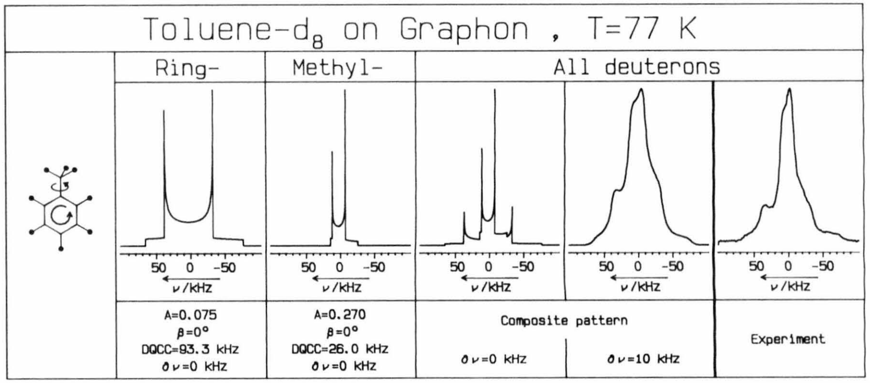

Fig. 8. Calculated ^{2}H NMR solid state patterns of toluene on Graphon and comparison with experiment.

ments [23] have shown that the effective EFG tensor of rapidly rotating methyl groups in solid mellitene has an asymmetry parameter of about 0.1 and the *zz*-axis out of the plane of the molecule. Taking over this notion for the presently discussed mellitene and toluene on Graphon cases, a reduction of the effective quadrupole coupling strengths as suggested by the experimental findings is readily conceivable. With a non-axially-symmetric EFG tensor only slight modifications of the presently used theory have to be applied [24]. A more detailed discussion will be postponed to a forthcoming publication. Undoubtedly, however, the conclusions arrived at present are not touched by these considerations.

The systems that have been studied may be put into three categories according to the values of the individual linewidths $\delta\nu$ (Figs. 4 to 8) that were applied to the calculated patterns in order to get into optimum coincidence with experiment: benzene on Spheron ($\delta\nu = 2$ kHz); benzene, p-xylene, mesitylene, and mellitene on Graphon (6 kHz); toluene on Graphon (10 kHz).

The individual line width found for benzene/Spheron is typical for carefully processed polycrystalline solid powders [25]. This value seems to account for the total of the dipolar couplings experienced by the ^{2}H nucleus. Similar linewidths have been found for benzene on boron nitride [1] and benzene on alumina [26]. The $\delta\nu = 6$ kHz linewidths observed for the second of the above mentioned groups, therefore, is mainly not due to such couplings. This broadening seems to be caused by some distribution of the isotropic shielding constant and the shielding anisotropy as consequence of the finite sizes of the microcrystalline surface patches which the molecules are adsorbed on. This notion, which had been put forward in [1] is confirmed in the present work with the coincidence of the $\delta\nu$ values obtained for benzene, p-xylene, mesitylene, and mellitene on Graphon.

The interpretation of $\delta\nu = 10$ kHz linewidths observed for toluene on Graphon is more involved. Besides the broadening due to the magnetic shielding heterogeneity it is, most probably, the onset of isotropic motional averaging that causes this broadening. Strictly speaking, introducing merely a line broadening into the pattern calculations is a crude approximation that has only a heuristic basis and is not expected to give completely satisfactory results.

Most interestingly, the molecules that give the 6 kHz individual line widths possess symmetries that should allow a close packed arrangement on the graphite surface whereas toluene is expected to resist such an ordering. In fact, for benzene such a close packed arrangement in registry with the graphite surface plane lattice has been proven to exist [27–29] whereas for toluene an incommensurate 2D solid for temperatures in the range 130 to 70 was observed [30]. In this 2D solid, probably, molecular translational motions are feasible at such rate to lead to the onset of motional narrowing of the powder patterns as was discussed previously.

VI. Conclusions

In the present paper it is demonstrated that from the asymmetry of the ^{2}H solid state powder patterns obtained for molecules adsorbed on graphite the molecular orientation with respect to the surface can be deduced. It has become evident that the presence of internal rotors such as methyl groups is particularly useful because the asymmetries of the related subpatterns are strongly pronounced. In principle, however, the method appears applicable to any type of molecule provided the exchange of molecules between surface patches of well defined orientation in space can be suppressed.

Acknowledgements

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