A Deuteron NMR Study on the Rotational Dynamics and the Orientation of Benzene Molecules Adsorbed on Graphite and Boron Nitride

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The 52.7 MHz deuteron (^{2}H) solid state NMR spectra of benzene-d_6 adsorbed on microcrystalline boron nitride and on two graphitized carbon blacks (Graphon and Sterling MT) were measured at temperatures between 75 and 120 K. Both on boron nitride and on the graphitized carbons the benzene molecules exhibit hexad axis rotation which is fast on the NMR time scale. From the spectra of benzene on the graphitized carbon blacks it is deduced that the molecules are oriented with their planes parallel to the graphite basal planes exposed. At the deuteron sites the shielding tensor which is set up by the action of the static field on the susceptibility tensor of the graphite microcrystallites possesses a shielding anisotropy of +150 ppm and +200 ppm for the Graphon and Sterling MT blacks, respectively.

1. Introduction

Several years ago we reported the first detailed spectroscopic study on benzene adsorbed on graphite [1] by proton magnetic resonance relaxation spectroscopy proposing a $\sqrt{7} \times \sqrt{7}$ benzene overlayer structure at low temperatures (< 150 K) with the molecules being oriented perpendicular to the surface, and carrying out rapid reorientational motions about a two-fold symmetry axis normal to the surface. In subsequent years the benzene/graphite system was repeatedly studied with the aid of a variety of spectroscopic and diffraction methods such as neutron scattering and diffraction [2–4], Penning ionization electron spectroscopy (PIES) [5], and, most recently, low energy electron diffraction (LEED) [6]. In the diffraction works, the unit mesh found by us was confirmed, the notion of perpendicular molecular orientation, however, abandoned in favour of a orientation parallel to the surface.

The most convincing electron spectroscopic and diffraction studies [5, 6] using single crystal graphite surfaces as the substrates have prompted us to investigate anew the benzene/graphite system by NMR techniques using the deuteron (^{2}H) as the probe nucleus. This work is undertaken under the auspices (i) to clear up the conflicting conclusions drawn about the orientation of benzene molecules on graphite, (ii) to check the suitability of the graphitized carbon black Graphon used by us as substrate for molecule/graphite interaction studies, (iii) to get knowledge on the rotational dynamics of the adsorbed benzene molecules. Should the model of parallel orientation be confirmed by ^{2}H NMR, then the static view provided by PIES and LEED gives certainly an incomplete description of the system as can already be deduced from our ^{1}H relaxation measurements [1].

In recent years, Fourier transform ^{2}H solid state NMR spectroscopy has proven to be extremely well suited for the study of the rotational dynamics of molecules and molecular subgroups in the solid state [7]. In contrast to the proton the deuteron is practically not subject to magnetic multispin interactions but is coupled, in general, almost exclusively to the intramolecular field gradient tensor at the nuclear site on behalf of its electric quadrupole moment. This entails that one gets rid of the very complicated magnetic dipolar interactions encountered in proton magnetic resonance applied to adsorbed layers on the surfaces of finely divided solids [1].

In the present study we are looking on the benzene/graphite system on a time scale of the order of microseconds (the reciprocal of the spectral width) which is many orders of magnitude larger than the time scale of the electron spectroscopic and diffraction methods. The gain of information about the system under this view must be paid for by the

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lack of information about the lateral arrangement of the molecules in the adsorption layer. Therefore, ^{2}H NMR spectroscopy is complementary rather than competitive to methods using electrons as probes.

2. Theory

A deuteron (spin $I = 1$) is considered to be contained in a molecule which is physically adsorbed on a (ideally infinitely large) surface plane of a diamagnetic solid with susceptibility tensor $\boldsymbol{\chi}$. Besides the Zeeman coupling in an applied strong magnetic field $\boldsymbol{B}_0$ whose direction defines the z-axis of the laboratory frame of reference (L) the deuteron experiences a quadrupole coupling via the electric field gradient (EFG) tensor $\boldsymbol{q}$ at the nuclear site, and a magnetic coupling via a shielding tensor $\boldsymbol{S}$ which is set up by the action of $\boldsymbol{B}_0$ on the susceptibility tensor $\boldsymbol{\chi}$. Assuming that $\boldsymbol{S}$ does not contain an antisymmetric constituent [8] and hence may be split into the isotropic part $\boldsymbol{S}^{(0)} = s_{\text{iso}}\boldsymbol{1}$ and the traceless symmetric part $\boldsymbol{S}^{(2)}$, and neglecting other couplings, e.g. dipolar and intramolecular chemical shielding, the nuclear spin Hamiltonian (in units h) may be written as [8]

$$\mathscr{H} = -\nu_0 (1 - s_{\text{iso}}) I_z + \mathscr{H}_{\text{Q}} + \mathscr{H}_{\text{s}} , \tag{1}$$

where $\nu_0 = (\gamma/2\pi) B_0$ and γ is the deuteron gyromagnetic ratio, s_{iso} is the isotropic shielding constant. I_z is the L frame z component of the nuclear spin operator, and $\mathscr{H}_{\text{Q}}$ and $\mathscr{H}_{\text{s}}$ are the Hamiltonians describing the quadrupole coupling and the magnetic coupling mediated by $\boldsymbol{S}^{(2)}$, respectively. Introducing the principle axis coordinate (PAS) frames (P) of the tensors $\boldsymbol{q}$ and $\boldsymbol{S}$, a crystal coordinate frame (C) which is rigidly fixed in the surface with z-axis perpendicular to the surface plane, and taking into account in (1) the secular part of $\mathscr{H}$ only, the Hamiltonians $\mathscr{H}_\lambda (\lambda = \text{Q, S})$ may both be written in the irreducible spherical tensor notation as [9, 10]

$$\mathscr{H}_\lambda = C^\lambda T^\lambda_{20} \sum_{\substack{m,n\\=-2}}^{2} \varrho^\lambda_{2m} D^{(2)}_{mn}(\Omega^\lambda_{\text{PC}}) D^{(2)}_{n0}(\Omega_{\text{CL}}) , \tag{2}$$

where, for the respective coupling λ, C^λ is a constant, T^λ_{20} is a component of the spin dependent second rank irreducible spherical tensor operator, and ϱ^λ_{2m} are the irreducible spherical components of the coupling tensor in its PAS frame. $D^{(2)}_{ij}$ are elements of the second order Wigner rotation matrix $\boldsymbol{D}^{(2)}$ as functions of the sets of Eulerian angles Ω by which the rotational transformations between the coordinate frames denoted by the indices on Ω are accomplished.

In the following the $\boldsymbol{q}$ and $\boldsymbol{S}$ tensors are both taken to be axially symmetric. The axial or at least nearly axial symmetry of the EFG tensor at the deuteron site in carbon-hydrogen bonds is a matter of experience [11, 12]. Surface electric field gradients such as are claimed to exist above the basal planes of graphite [13] are, in general, very low as compared to the intramolecular field gradients, and can therefore be neglected [14]. The axial symmetry of the shielding tensor is a matter of crystallography. For graphite with a sufficiently large basal plane exposed the axial symmetry of $\boldsymbol{S}$ is a consequence of the axial symmetry of the susceptibility tensor $\boldsymbol{\chi}$. In such cases the distinct principle axis (z-axis) of $\boldsymbol{S}$ is naturally perpendicular to the surface. Hence, the PAS frame of $\boldsymbol{S}$, and the C frame can be chosen to be the same.

With axially symmetric coupling tensors, (2) may be simplified to

$$\mathscr{H}_\lambda = C^\lambda T^\lambda_{20} \varrho^\lambda_{20} \sum_{n=-2}^{2} D^{(2)}_{0n}(\Omega^\lambda_{\text{PC}}) D^\lambda_{n0}(\Omega_{\text{CL}}) . \tag{3}$$

Writing explicitly the relevant Eulerian angles as $\Omega^{\text{S}}_{\text{PC}} = (0, 0, 0)$, $\Omega^{\text{Q}}_{\text{PC}} = (0, \theta, \varphi)$ and $\Omega_{\text{CL}} (\alpha, \beta, 0)$, and introducing into (3) the known expressions for C^λ, T^λ_{20}, ϱ^λ_{20}, $D^{(2)}_{0n}$, and $D^{(2)}_{n0}$ [9] the following relations are obtained:

$$\mathscr{H}_{\text{Q}} = a_{\text{Q}} (3 I_z^2 - 2) , \tag{4}$$

$$\mathscr{H}_{\text{s}} = a_{\text{s}} I_z \tag{5}$$

with

$$\begin{aligned} a_{\text{Q}} = \tfrac{1}{16} \cdot \text{DQCC} \cdot [&(3\cos^2\theta - 1)(3\cos^2\beta - 1) \\ &+ 3\sin^2\theta \cos 2(\alpha + \varphi) \sin^2\beta \\ &- 3 \sin 2\theta \cos(\alpha + \varphi) \sin 2\beta], \end{aligned} \tag{6}$$

$$a_{\text{s}} = \tfrac{1}{3} \nu_0 \Delta s (3\cos^2\beta - 1) . \tag{7}$$

In (6) and (7) $\text{DQCC} = e^2 q Q/h$ is the quadrupole coupling constant, and $\Delta s = s_\parallel - s_\perp$ is the shielding anisotropy.

Introducing (4) and (5) into (1), the energy eigenvalues of the stationary states are easily calculated from which the resonance frequencies $\nu_{\text{A}}(|1\rangle \rightarrow |0\rangle)$

and $\nu_B(|0\rangle \rightarrow |-1\rangle)$ are obtained as

$$\begin{aligned} \nu_A &= \nu_0(1-s_{iso}) - 3a_Q - a_S\,, \\ \nu_B &= \nu_0(1-s_{iso}) + 3a_Q - a_S\,. \end{aligned} \tag{8}$$

If by some molecular motion the deuteron considered is moved in space the Hamiltonians $\mathscr{H}_Q$ and $\mathscr{H}_S$, in general, become time dependent. In that case the spectral frequencies in (8) are affected if a characteristic time τ of the motion becomes the order of the NMR time scale, vide infra, or less. For the present discussion it is assumed that (i) the characteristic time τ of translational motion during which the spin remains on a surface plane of definite orientation in space is long on the NMR time scale; (ii) the $\boldsymbol{S}$ tensor at the deuteron site is the same in all positions taken on in the course of rotational and in plane translational molecular motions. Under these circumstances, the Hamiltonian $\mathscr{H}_S$ is time independent, and $\mathscr{H}_Q$ becomes time dependent only by the action of rotational types of motions through the Eulerian angles θ and φ defined above. The NMR time scale is then $1/\nu_Q$, where $\nu_Q = \frac{3}{2}\frac{e^2qQ}{h}$ is the quadrupole frequency. Typically, $1/\nu_Q$ amounts to several microseconds.

If the rotational motion considered is fast on the NMR time scale the Hamiltonian $\mathscr{H}_Q$ has simply to be replaced [9] by its average over the motion, i.e. $\overline{\mathscr{H}_Q} = \overline{a_Q}(3I_Z^2 - 2)$ where $\overline{a_Q}$ is obtained by averaging in (6) the terms containing the angles θ and φ. The resonance frequencies are then calculated from (8) by replacing a_Q by $\overline{a_Q}$.

We consider now the case where the rotational motion occurs about an axis which is fixed with respect to both the molecular frame to which the deuteron is attached and the crystal frame C. Transformation of the EFG tensor by the set of Eulerian angles $(0, \Delta, \Phi)$ from its PAS to a coordinate frame which is fixed with respect to the C frame and has its z-axis oriented parallel to the axis of rotation, and performing the average over the motion yields for the irreducible components $\bar{\varrho}^Q_{2q}$ of the motionally averaged tensor [9]:

$$\bar{\varrho}^Q_{2q} = \varrho^Q_{20}\,\overline{D^{(2)}_{0q}(0, \Delta, \Phi)}\,, \tag{9}$$

where Δ is the constant angle between the distinct EFG PAS tensor axis and the rotation axis. If the molecular rotation is of the Brownian motion type or consists of movements in a potential wells structure of at least threefold symmetry the averaged Wigner rotation matrix elements $\overline{D_{0q}(0, \Delta, \Phi)}$ $(q \neq 0)$ in (9) can easily be shown to be zero, leaving

$$\bar{\varrho}^Q_{20} = \tfrac{1}{2}(3\cos^2\Delta - 1)\,\varrho^Q_{20}\,, \tag{10}$$

i.e. the motionally averaged tensor is axially symmetric with its distinct principle axis aligned along the molecular rotation axis.

Under these circumstances, the previously developed formalism leading to (8) may be taken over merely by replacing in (3) ϱ^Q_{20} by $\bar{\varrho}^Q_{20}$ given in (10) and redefining the angles θ and φ. Consequently, in order to cover the two cases of slow rotational motion and rapid single axis rotation within a unified theoretical framework, (6) may be used, where the deuterium quadrupole coupling constant DQCC is e^2qQ/h and $(e^2qQ/h)\,\frac{1}{2}(3\cos^2\Delta - 1)$ for slow rotational motion and fast single axis rotation, respectively, and the set (θ, φ) denotes the angles

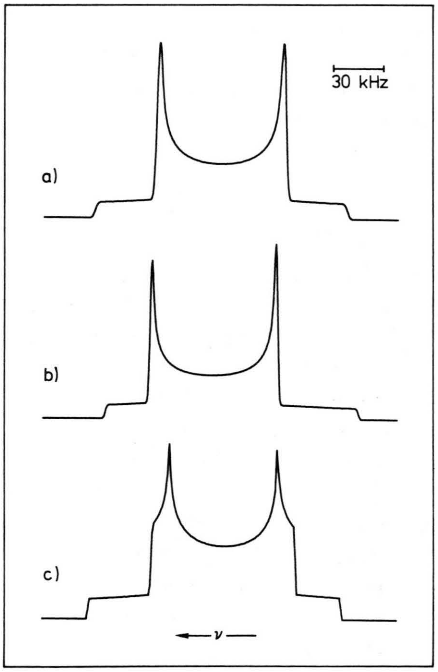

Fig. 1. Theoretical ^{2}H solid state NMR powder spectra at resonance frequency $\nu_0 = 52.7$ MHz. The deuteron is assumed to be acted on by an axially symmetric EFG tensor only (a), by axially symmetric EFG and shielding tensors which are parallel (b) and orthogonal (c) to each other. Deuterium quadrupole coupling constant: DQCC = 100 kHz; shielding anisotropy: $\Delta s = +200$ ppm, isotropic shielding constant $s_{iso} = 0$.

between the crystal frame z-axis (the normal to the surface) and the distinct principle axis of the rigid EFG tensor in the first, of the motionally averaged EFG tensor in the second case.

Because of the inherent low sensitivity of NMR methods no single crystal surface studies can be carried out, but powders must be used. Since the resonance frequencies in (8) depend on the microcrystallite surface orientations in space through the Eulerian angles α and β the spectrum of the powder is obtained by summing up the contributions from all orientations occurring. Assuming random distribution of surface orientations in space the calculation of the powder spectrum may be carried out by known procedures [8, 9].

Figure 1 shows the results of sample calculations of powder spectra if the quadrupole coupling alone ($a_s = 0$) or in combination with the shielding anisotropy coupling ($a_S \neq 0$) is operative. Equations (6) to (8) were employed with $\nu_0 = 52.7$ MHz, DQCC = 100 kHz, and $\Delta s = +200$ ppm. The tensors were assumed to be either parallel ($\theta = 0$) or orthogonal ($\theta = 90°$) to each other, the isotropic shielding was set to zero. The figure demonstrates clearly the effect of shift anisotropy to render the spectra unsymmetrical with respect to their centers.

3. Experimental

The adsorbents used for the present investigation were the graphitized carbon blacks Graphon (Cabot, Boston, Mass., USA) and Sterling MT (a gift from Prof. Dr. D. H. Everett, Bristol, England), and a microcrystalline boron nitride powder (325 mesh, Alfa-Ventron, Danvers, Mass., USA) having nitrogen BET specific surface areas of 80, 8, and 15 m^2/g, respectively.

Graphon consists of agglomerated primary particles of mean diameter of about 25 nm. The agglomerates are almost completely bounded by layers of graphite like sheaths parallel to the surface. From spatially resolved TEM pictures the linear dimensions of the graphite stacks of well defined orientation parallel and perpendicular to the basal planes exposed were determined [14] to be about 4 and 8 nm, respectively, in agreement with literature data [15].

The polyhedrally shaped Sterling MT particles have mean diameter of about 400 nm [15] and are bounded by the basal plane faces of graphite [13, 15].

The boron nitride powder used consists of terraced platelets with mean diameter of about 3000 nm and diameter to thickness ratio of about 10 [16].

The adsorbents were put into 10 mm outer diameter NMR tubes, evacuated at slowly increasing temperatures and finally baked at 450 °C under high vacuum ($p \lesssim 10^{-4}$ Pa) for 12 hrs. Subsequently, such amounts of benzene-d_6 (Merck, Sharp and Dohme, Montreal, Canada) were chilled onto the samples to give a coverage of approximately one monolayer based on the N_2-BET surface areas of the adsorbents and a benzene molecule area of 0.40 nm^2.

The NMR measurements were carried out with the aid of a high power NMR spectrometer (CXP 100, Bruker Physik, Karlsruhe, Germany) operating at 52.7 MHz in conjunction with a nominal 8.5 T cryogenic magnet system (Oxford Instruments, Oxford, England). The ^2H spectra were obtained by Fourier transformation of solid state quadrupole echoes after applying $(\pi/2)_y - \tau - (\pi/2)_x$-pulse sequences [17] with delays τ between 30 and 40 μs using the quadrature detection mode.

4. Results and Discussion

Figure 2 shows the 52.7 MHz deuteron NMR spectra of benzene adsorbed on boron nitride, Graphon and Sterling MT at the temperatures 75, 90 and 85 K, respectively. In all cases, no dependence on temperature in the range 75 to 110 K was observed. The spectrum of the boron nitride sample exhibits the typical Pake powder pattern whereas with the graphitized carbon blacks marked asymmetries of the type shown in Fig. 1b are to be seen. The distinct edges are separated by $\Delta\nu = 70 \pm 2$ kHz in each case but are more inclined with respect to the vertical for the carbons as compared with boron nitride.

On the basis of the previously developed theory the appearances of the spectra suggest that in contrast to boron nitride the graphitized carbon supports provide magnetic fields which give rise to anisotropy shieldings at the deuteron sites of the benzene molecules adsorbed thereon. This notion is substantiated by recognizing the highly different

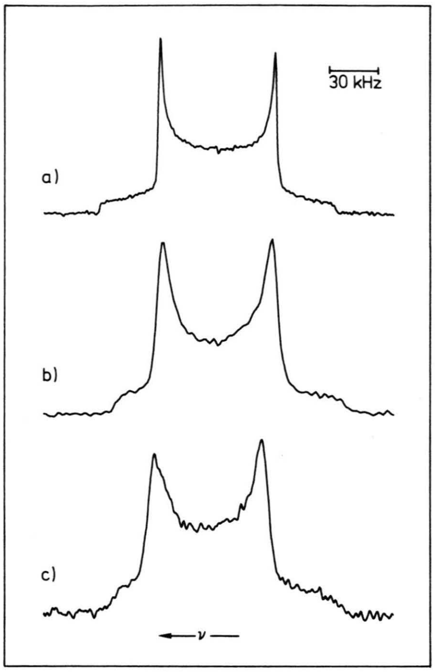

Fig. 2. ^{2}H NMR spectra of benzene adsorbed on boron nitride and graphitized carbon black. a) Boron nitride: $T = 75$ K, 4000 scans, 0.5 s cycle time. b) Graphon: $T = 90$ K, 2000 scans, 0.2 s cycle time. c) Sterling MT: $T = 85$ K, 20000 scans, 0.2 s cycle time.

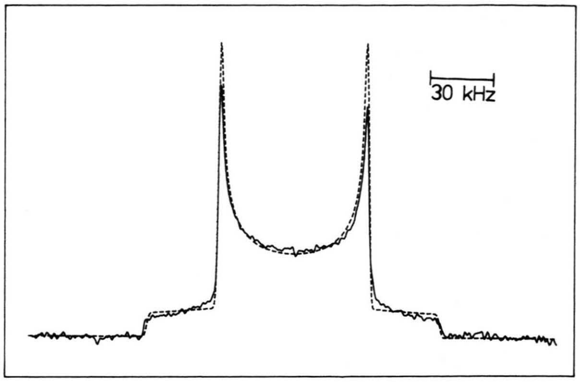

Fig. 3. Experimental and theoretical ^{2}H NMR spectra of benzene adsorbed on boron nitride, $T = 75$ K. The fitted curve was calculated with DQCC = 93 kHz.

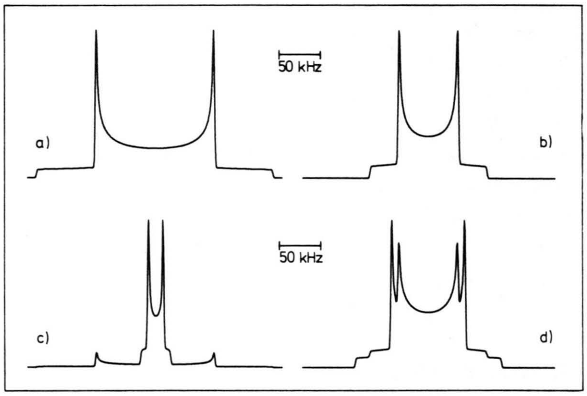

Fig. 4. Theoretical ^{2}H NMR spectra of benzene for various rotational models. a) All rotations proceed slowly on the NMR time scale. b) Rapid hexad axis rotation. c) Rapid rotation about diad axis passing through opposite C atoms. d) Rapid rotation about diad axis bisecting opposite C–C-bonds.

values of the diamagnetic susceptibility anisotropies $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ of $-0.2 \cdot 10^{-6}$ and $-22.4 \cdot 10^{-6}$ cgs/g (293 K) for boron nitride [18] and graphite [19], respectively. In addition, with decreasing temperature $\Delta\chi$ of graphite increases by a factor of about 1.5 [20] between 300 K and the temperatures of the measurements.

Considering the benzene/boron nitride spectrum first the quadrupole coupling constant DQCC is immediately obtained from the relation [11]

$$\Delta\nu = \tfrac{3}{4}\,|\mathrm{DQCC}| \tag{11}$$

to be DQCC = ± 93 ± 3 kHz which besides the sign is just one half of the rigid value $e^{2}qQ/h = 186.6$ kHz [21]. This result can only be explained by rapid hexad axis rotation being operative since according to the previously introduced relation

$$\mathrm{DQCC} = \tfrac{1}{2}(3\cos^{2}\Delta - 1)\,e^{2}qQ/h \tag{12}$$

the angle Δ between the distinct EFG PAS tensor axis (C–D bond direction) and the molecular rotation axis is $\pi/2$. Figure 3 shows the nearly perfect agreement between experiment and the calculation on the basis of this theoretical model. For the calculations a Gaussian type individual line broadening of halfwidth $\delta\nu = 2$ kHz was applied.

In order to demonstrate the uniqueness of the above result in Fig. 4 are shown the calculated spectra of benzene molecules rotating either slowly or rapidly on the NMR time scale about the various molecular symmetry axes. Obviously, only the rapid hexad axis rotation model is suited to explain the spectra. Taking not into account the asymmetries of the benzene on graphitized carbon spectra it is evident that the model of rapid diad axis reorientation (Fig. 4d) of benzene on Graphon as deduced from

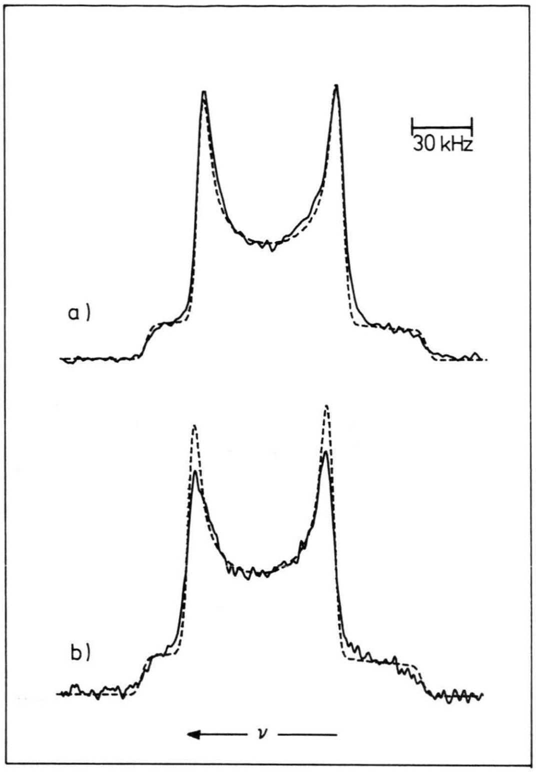

Fig. 5. Theoretical ^{2}H NMR spectra (dashed lines) of benzene adsorbed on the graphitized carbon blacks superimposed on experimental spectra of Figure 2. a) Graphon: DQCC = 93 kHz; $\Delta s = +150$ ppm. b) Sterling MT: DQCC = 93 kHz; $\Delta s = +200$ ppm.

the analysis of ^{1}H relaxation data [1] has to be rejected.

The ^{2}H spectrum of benzene on boron nitride provides no means to determine the orientation of the adsorbed molecule with respect to the surface. However, with rapid hexad axis rotation the parallel orientation of the molecular plane relative to the surface is the most reasonable assumption [22]. The ^{2}H spectra of benzene on the graphitized carbon blacks, on the other hand, offer the possibility to determine the molecular orientation since the spectrum shape depends on the relative orientation of the EFG and shielding tensors which are fixed in the molecular frame and in the crystal frame, respectively.

Figure 5 shows the calculated ^{2}H NMR of benzene on Graphon and Sterling MT (dashed lines) superimposed on the experimental spectra. Equations (6) to (8) were employed with DQCC = 93 kHz, i.e. rapid hexad axis rotation, and the shift anisotropy set to +150 and +200 ppm for Graphon and Sterling MT, respectively. The motionally averaged EFG tensor and the shielding tensor were assumed to be parallel to each other, i.e. the axis of sixfold symmetry of the benzene molecule is oriented parallel to the surface normal. For the calculations Gaussian type broadening functions for the individual lines with halfwidths $\delta\nu = 6$ kHz were used in both cases. Obviously, excellent agreement with experiment is obtained. The notion of parallel orientation of the hexad axis with respect to the surface plane [13] can be discarded since in this case the theoretical line shape (Fig. 1 c) is rather different from experiment. In fact, the flat orientation is predicted by theoretical models to be the energetically most favoured configuration [23–25].

The most striking results of the previous discussion are the very large shift anisotropy values which have to be introduced in order to fit the spectra. The positive sign clearly indicates that the molecules are adsorbed above the graphite basal planes. Since the microcrystalline regions of the Sterling black particles are larger in size than of Graphon the greater value of the shielding anisotropy of the former substrate is thus readily explained.

The unusual large shielding anisotropy of graphitized carbon blacks found in this work should give rise to noticeable ^{1}H spin lattice relaxation in analogy to relaxation by chemical shift anisotropy [26] if the adsorbate exhibits 2D fluid like behaviour allowing the molecules to sample rapidly the variously oriented crystal faces of the microcrystallites. In fact, a recent work on butane adsorbed on Graphon [14] has revealed this effect. A shift anisotropy of $\Delta s = 200$ ppm was estimated which is in excellent agreement with the present findings.

The comparatively large line broadening (≈ 6 kHz) of the graphitized black samples mentioned previously may have several reasons. Most probably, this line broadening is due to the finite sizes of the graphite like crystallites both parallel and perpendicular to the faces exposed. Thus, some distribution function of the shift anisotropy must be assumed which consequently leads to line broadening. It must be kept in mind that the theory which the interpretation of the spectra is based on assumes sufficiently (ideally infinitely) large crystal faces.

A most interesting problem concerns the mechanism of hexad axis rotation of benzene molecules adsorbed on graphite. By the present study it has unequivocally been proven that this motion proceeds fast on the NMR (μs) time scale down to temperatures as low as 75 K. Most probably it proceeds with frequencies in the several hundred MHz range [1], i.e. on the ns time scale. The LEED method, on the other hand, operating on the fs time scale provides a practically static picture of the benzene layer with well defined orientational positions of the benzene molecules with respect to the underlying graphite lattice and well defined long range order with close packing of the molecules [6]. The same picture holds true for benzene adsorbed on Grafoil [3] and graphitized carbon blacks [3, 4] as deduced from neutron diffraction experiments.

From these results the most important conclusion must be drawn that the mechanism of molecular rotation consists of reorientational jumps in a sixfold equal wells potential which is determined predominantly by the molecule/substrate interaction since otherwise the static LEED and the dynamic NMR view could not be reconciled. Other mechanisms of rotational motion that were mentioned previously to yield the same motionally averaged ^{2}H NMR spectrum, e.g. Brownian rotational diffusion, have to be rejected. A direct proof of this notion by NMR should be possible through an analysis of partially relaxed patterns since T_1 relaxation allows to discriminate between jump and diffusive types of motion [10]. Such a study is being undertaken.

The reasons for drawing conclusions on the rotational dynamics and the orientation of the benzene molecules with respect to the surface from proton NMR relaxation times [1] which are at variance with the present deuteron NMR results are not clear as yet. Presumably, the simplified treatment of proton relaxation of the rather complicated multispin system in terms of the pairwise additive interaction approximation as well as not taking proper account of the very subtle electronic structure of the graphitized carbon black surface [14] have caused mainly the misinterpretation of the proton NMR results. Efforts are being undertaken at present to clear up these points which seems especially worthwhile since through the analysis of the intermolecular proton-proton dipolar interaction contribution to relaxation informations can be obtained about the structure of the 2D solid layer which are not accessible by deuteron NMR.

5. Conclusions

The present investigation has shown that deuteron solid state NMR spectroscopy is well suited not only to study the rotational dynamics of molecules adsorbed on microcrystalline solid substrates but also to determine the orientation of molecules relative to the surface if the diamagnetic susceptibility anisotropy of the solid is sufficiently large to produce shielding effects to the order of 100 ppm as in the case of the graphitized carbon blacks. Of course, high static magnetic fields of the order of 8 T as in the present study are a prerequisite for the detection of the shielding anisotropy with the ^{2}H nucleus probe.

The comparison of the spectra for benzene adsorbed on Graphon and on Sterling MT proves the Graphon material, which because of its rather high specific surface area offers less experimental difficulties than Sterling is well suited for the study of gas/graphite surface interactions.

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