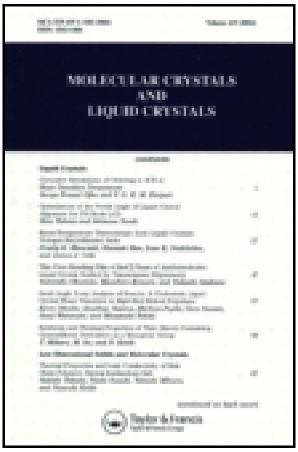

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FREQUENCY DEPENDENT NMR SPIN RELAXATION STUDIES OF DEUTERONS AND PROTONS IN NEMATIC LIQUID CRYSTALS

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Abstract. As first discussed by Pincus and Blinc, order fluctuations of the director in a nematic liquid crystal should lead to a characteristic square-root dependence of the nuclear magnetic relaxation times T_1 of the considered atoms on the Larmor frequency ν, i.e. $T_1 \sim \nu^{1/2}$. The significance of this process is violently disputed in the literature, essentially because standard NMR spectrometers do not allow a broad frequency variation sufficient to separate different dispersion laws reliably. Using a newly developed field-cycling NMR spectrometer with a fast switchable 1.2 T detection field and fast Fourier transform data processing capabilities, it became possible to extend previous proton relaxation studies to selective frequency dependent deuteron T_1 measurements in the range between 500 Hz and 7 MHz for various deuterated nematogens (PAA-d6, PAA-d8, PAA-d14, MBBA-d6). Compared with previous proton results in the same frequency range, the relaxation dispersion of the deuterons at identical sites is relatively small in all studied samples, and unlike the proton T_1 the deuteron T_1 does not show a fully developed square-root regime. However, the process is clearly detectable at medium and low Larmor frequencies between about 5 kHz and 500 kHz, where the Pincus-Blinc model dominates the proton spin relaxation. Thus the first deuteron field-cycling measurements support the previous proton results that nematic order fluctuations are not visible by T_1 at standard high Larmor frequencies in the megahertz range.

Keywords: spin relaxation, liquid crystal, frequency dependence, field-cycling, order fluctuations, Pincus-Blinc-Model

1. INTRODUCTION

One of the most disputed problems of NMR in liquid crystals has been for many years the question about the significance of collective molecular reorientations to the nuclear spin relaxation times of protons or deuterons, and thus the question about it s observability. In 1969 Pincus [1] and Blinc et al. [2] independently predicted on the basis of estimations by de Gennes [3] that a special kind of such collective modes in liquid crystals, namely *cooperative small angle rotations about the short axis* of elongated nematic molecules now called "order fluctuations of the director" (OFD or OFN), should lead to characteristic square-root dependence of the longitudinal proton relaxation time T_1 on the Larmor frequency $\nu \equiv \omega/2\pi$ or the related Zeeman field B. This famous Pincus-Blinc model

$$T_{1OFD} \sim \nu^{1/2} \sim B^{1/2} \tag{1}$$

and later refinements or extensions [4-7] of the form

$$T_{1OFD} = A\ f(\nu/\nu_L, \nu/\nu_H)\ \nu^{1/2} \tag{2}$$

have initiated countless experimental studies [e.g. 4-10] to verify the unusual relaxation mechanism, and in this way to analyse the properties of the involved motional spectrum. In Eq. (2), the model paramater A depends on the molecular geometry of the spin positions, on macroscopic material parameters which determine the director modes, and on the inclination of the director respective to the applied Zeeman field. The function $f(\nu/\nu_L, \nu/\nu_H)$ takes into account that there exists a lower bound (ν_L) and an upper bound (ν_H) of the square-root profile, because the OFD modes should be restricted by a longest and a shortest possible wavelength, respectively.

Since almost any relaxation model contains a small range where one approximately gets [4,11,12] $T_1 = \text{const}_1 + \text{const}_2\ \nu^{1/2}$, the Pincus-Blinc relation is indeed hard to separate from other potential contributions to the experimentally observed total relaxation rate, which can include reorientations of whole individual molecules or of individual segments. Therefore, a reliable direct confirmation of the OFD model requires measurements over a sufficiently broad and properly positioned Larmor frequency range. However, conventional NMR spectrometers only work in the megahertz regime within relatively narrow limits, and hence have to be supplemented by methods allowing frequency variations by many orders of magnitude for a critical separation of superimposed relaxation dispersion profiles. The most powerful, yet still unfamiliar approach to study $T_1(\nu)$ profiles is provided by fast field-cycling NMR (FC) [8,13]. It s basic idea is to separate in the NMR experiment periods of high magnetic fields for signal detection, and periods of low fields to make visible effects due to low Larmor frequencies.

Up to the present, the field-cycling technique could only be applied to proton spins (^1H) in liquid crystalline phases because of difficulties due to the unfavourably smaller gyromagnetic ratios of other, in many respects more informative nuclei like e.g. deuterons (D, ^2H) or carbons (^{13}C). The detection field strengths of available fast field-cycling instruments were still too low to give a satisfactory signal quality for such spins in solid-like states, and this circumstance has caused additional conflicting conclusions about the importance of the Pincus-Blinc model. Though all known FC *proton* studies on nematic liquid crystals clearly demonstrate that the $T_1(\nu)$ square-root dispersion dominates the relaxation process only at rather low frequencies, which are inaccessible to standard high-field spectrometers, this aspect is generally overlooked in the numerous work on conventional high-field *deuteron* NMR of liquid crystals. A big problem for comparing proton with deuteron results is that deuterons, in contrast to protons, separate individual atomic sites on the molecules by a generally well-resolved ^2H-spectrum, whereas ^1H-spectra usually show a more or less unresolved broad line [16]. Therefore the comparison needs assumptions on how to relate the site dependent deuteron relaxation times to one single, average proton T_1, which are hard to prove without the knowledge of the deuteron relaxation dispersion over a similarly broad frequency interval as for the protons.

In order to determine directly where order fluctuations eventually dominate the deuteron spin relaxation dispersion in nematic liquid crystals, we have developed a more powerful field-cycling spectrometer that can produce a switchable Zeeman field of 1.2 T with cycle transits of less than 1 ms, and that provides Fourier transform data processing to separate individual NMR lines. It allows us to perform selective deuteron $T_1(\nu)$ measurements on deuterated mesogens in the Larmor frequency range between 100 Hz and 7.5 MHz, and proton studies between 100 Hz and 50 MHz. This paper describes some of our first results for various selectively or fully deuterated samples of para-azoxyanisole (PAA-d6, PAA-d8, PAA-d14) and para-methoxybenzylidene-butylaniline (MBBA-d6). A preliminary report was recently given at the 22nd Congress AMPERE in Stuttgart [14,15].

2. EXPERIMENTAL TECHNIQUES

The performance of fast field-cycling techniques to determine the frequency dependence of relaxation times by suitable Zeeman field-cycles and radiofrequency pulse sequences has been explained in the literature [8,13]. However, numerous refinements were necessary to apply the method to solid-state signals of nuclear spins with low gyromagnetic ratio as in the present case to deuterons in liquid crystals. To measure the deuteron relaxation dispersion of liquid crystalline materials, it was essential to improve the instruments used for previous proton FC studies [e.g. 8-10] considerably by implementing several more efficient apparatus concepts [15]. A new air-cored low-inductance 1.2 T copper coil magnet was designed by means of a special optimization formalism of the conductor geometry, which provides the strongest field for a given electric power with selectable constraints on the field homogeneity. The new switching network and current regulation makes use of novel high-power semiconductor devices like MOSFETs and GTOs to obtain switching times of the order of milliseconds. Both the field stability and homogeneity could be improved considerably, and the NMR signal aquisition and processing have been fully automated. More details on these manifold instrumental developments and methodical progress are given in Schweikert's thesis [15], and will also be reported elsewhere. A typical measurement of T_1 for one deuteron position on a selectively deuterated molecule takes about 1/2 to 1 h at one selected Larmor frequency and temperature. Hence the data aquisition and processing for a full dispersion plot with 50 to 100 frequency points at several sample temperatures lasts almost one week, provided everything goes well.

Getting the necessary amount (1 cm^3) of deuterated crystalline materials proved a more delicate task than expected. Originally, we assumed fully deuterated molecules to be the best choice, because they should give the maximum information on the site-dependent ^2H relaxation processes. However, it turned out that the magnetizations of individual spin positions are coupled that the relaxation functions of separate lines became nonexponential under FC conditions. We therefore decided to consider for the beginning selectively deuterated molecules, where such couplings are absent or negligible. An ideal sample, i.e. a liquid crystal with only one single deuterated site, was not (yet) available to us; but we could obtain samples deuterated in special groups, namely in phenyl- or methyl-positions, where the different sites are approximately equivalent to exclude non-exponential cross-relaxation effects. For that reason this paper is restricted to T_1 measurements of ring- and chain-deuterated para-azoxyanisole (PAA-d8, PAA-d6) and methyl-deuterated para-methoxybenzylidene-butylaniline (MBBA-d6). These samples were either synthesized in cooperation with the Chemistry Department of the University of Stuttgart or purchased from MSD, Canada.

3. EXPERIMENTAL RESULTS

Figs. 1 and 2 show the experimental T_1 relaxation dispersion profiles of the deuteron spins in PAA-d8 (CH_3O-$C_6D_4N_2OC_6D_4$-OCH_3), PAA-d6 (CD_3O-$C_6H_4N_2OC_6H_4$-OCD_3) and MBBA-d6 (CD_3O-$C_6H_4N_2HC_6H_4$-$(CH_2)_4CD_3$), respectively, at temperatures in the nematic phase. The spectral resolution of our apparatus and Fourier transform processing is illustrated by Fig. 3 using PAA-d14 as example, where the distinction between the narrow inner methyl group doublet and the broader outer phenyl group lines (three overlapping doublets due to slightly different bonding angles of the eight ring deuterons) are easily seen[16]. Both selectively deuterated PAA's, on which the measurements of Fig. 1 were performed, reveal only one type of line doublet, because the fine structure is smeared out by the proton deuteron coupling, and accordingly give one single (average) T_1 relaxation decay for all the deuterons of the respective group. This was no longer the case for MBBA-d6, where the two unequivalent methyl groups on the two unlike chains separate into two doublets, one resolved and one not resolved, and thus allow to determine two distinct relaxation rates for the methoxy- and butyl-deuterons, respectively (Fig. 2). Problems with cross-relaxation were not observed, probably because the two time constants are rather similar; the $T_1(\nu)$ plots even have a crossing point!

At present, the new spectrometer covers a deuteron Larmor frequency range from 100 Hz to 7.5 MHz, i.e. about 5 orders of magnitude. For a typical plot the frequency steps were adjusted to give 30 to 50 $T_1(\nu)$ points, and signal averaging up to 500 times was needed to obtain satisfactory signals (see e.g. Fig. 3). Some additional 15 MHz measurements could be performed by conventional methods with a 2T Bruker iron magnet. As a rule, data reported in the literature [17,18] for the megahertz regime between 4 and 60 MHz are essentially in accordance with our results, though an exact comparison is somewhat problematical because deuterated materials seem very sensitive to degradation [15].

These first deuteron FC relaxation dispersion results in liquid crystals over a really significant frequency range and not shown temperature shifts indicate some general lines, most of which are surprising and also in conflict with suggestions derived in the literature from high-field NMR experiments. Some details:

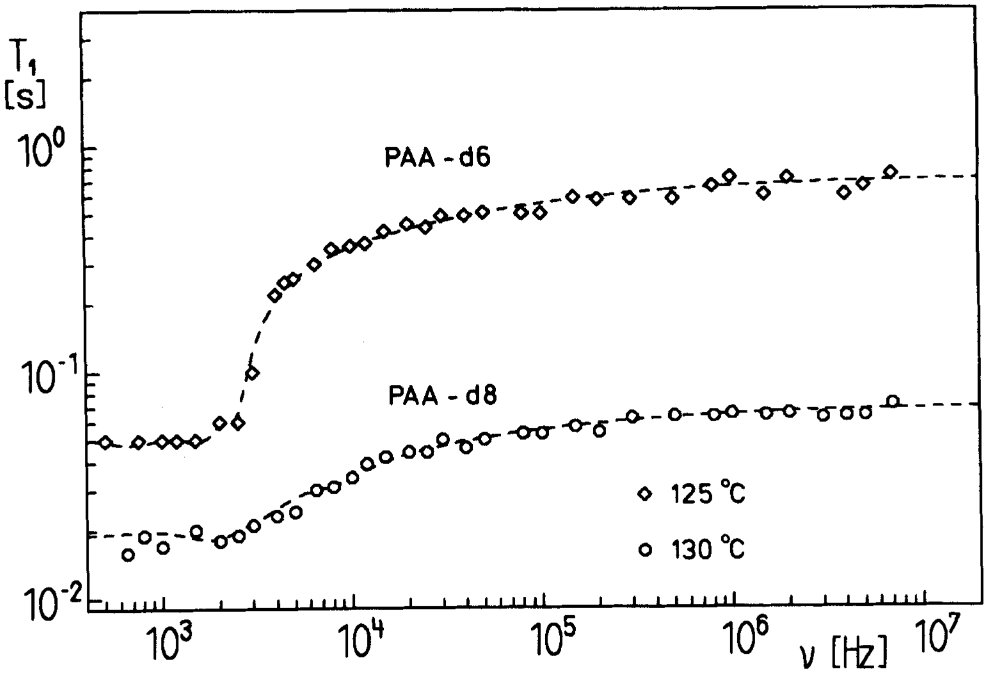

Fig. 1. Deuteron relaxation dispersion in PAA-d6 and PAA-d8

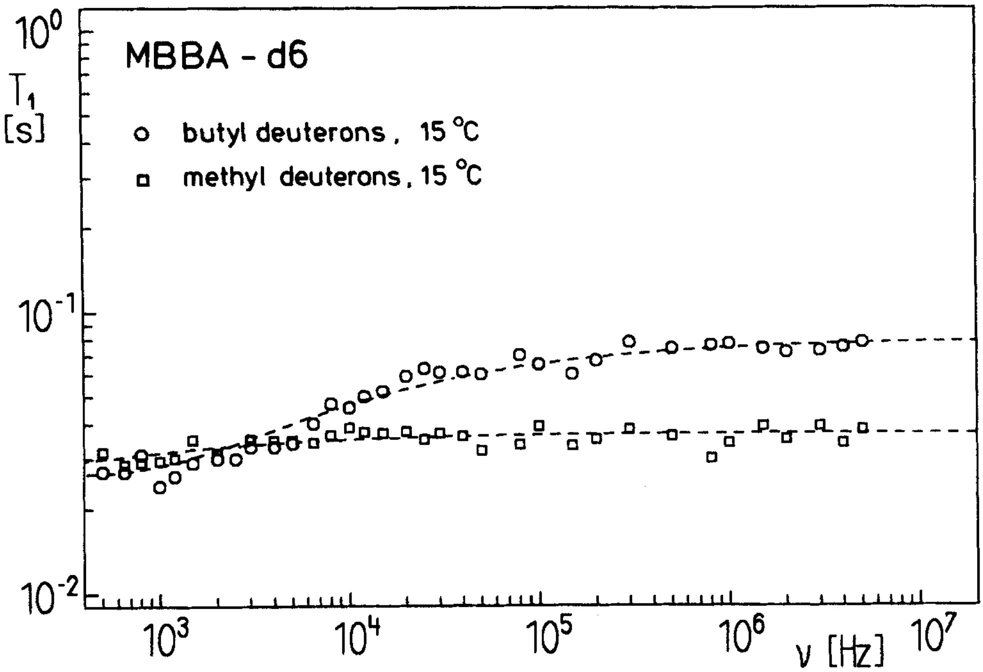

Fig. 2. Deuteron relaxation dispersion in MBBA-d 6

(1) All samples studied so far reveal frequency dependent T_1's. However, the variations are small if contrasted with corresponding proton data.

(2) The main dispersion effects occur at very low Larmor frequencies, i.e. for $\nu \leq 20$ kHz within one decade, whereas for $\nu \geq 20$ kHz a frequency increase by 3 orders of magnitude only leads to a T_1 change of typically less than a factor of 2. This means that the broad $T_1 \sim \nu^{1/2}$ range familiar from proton experiments is hidden or absent.

(3) Inspite of the strong site dependence of the relaxation times, the form of the dispersion profile for $\nu \geq 20$ kHz is very similar in all cases.

(4) In contrast to the minor differences at high ν's, the dispersion steps at low ν's show strong differences between the samples. The height of the step varies from neglibly small (MBBA-d6, methoxy site) to a factor of 10 (PAA-d6) and even involves crossings.

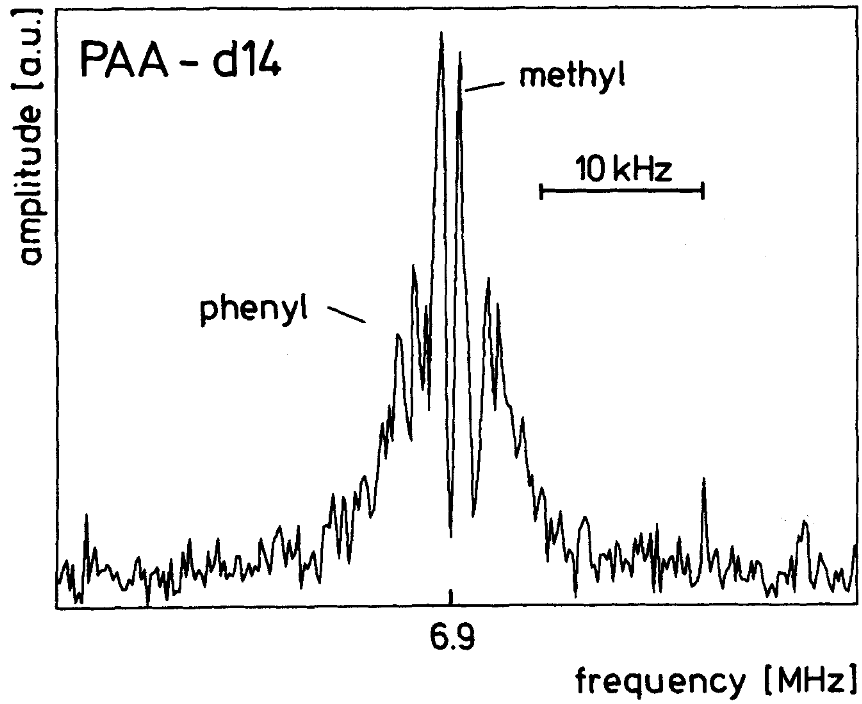

Fig. 3. FC Deuteron line spectrum of PAA-d14 at 7 MHz

With the exception of the PAA-d6 data, the deuteron measurements can in principle be roughly described by a superposition of two relaxation contributions, one responsible for the low-field dispersion and the second for the high-field plateau. However, such an approach

$$T_1^{-1} = A\,(\nu + \nu_L)^{\alpha} + B \qquad (3)$$

with $\alpha \approx 1/2$, where A and B measure the strengths of the two terms and ν_L takes into account the existence of a low-field plateau, is hard to relate to the Pincus-Blinc model: As illustrated by Figs. 4 and 5, the comparison with previous proton results [9,10] for the same atomic site, e.g. the protons of PAA-d6 with the deuterons of PAA-d8 or the protons of PAA-d8 with the deuterons of PAA-d6, clearly demonstrates that the proton $T_1 \sim \nu^{1/2}$ dispersion is important at much higher Larmor frequencies than the related square-root range for the deuterons on the basis of Eq. (3). Furthermore, Eq. (3) overlooks the minor, yet non-vanishing frequency dependence of the deuteron T_1 above $\nu \approx 50$ kHz. Therefore a reasonable model fit has to consider both the deuteron and proton FC studies in a consistent way.

4. DISCUSSION AND CONCLUSIONS

The relaxation rates of nuclear spins on a molecule are determined by the couplings of the spins between each other and with their surroundings (lattice), and these interactions reflect the motions of the nuclei and molecules [19]. Different types of motions can lead to characteristic relaxation processes, which allow to study the reorientations, provided they can be separated properly. For liquid crystals, i.e. anisotropic systems, this separation is particularly inconvenient because the anisotropic mechanisms complicate the analysis, and more experimental data are needed to examine theoretical models reliably than in the case of isotropic liquids. If for this purpose one considers both the deuteron and proton relaxation times at equivalent sites of a molecule, it is obvious that the underlying motion should be the same (neglecting isotopic effects). However, due to the completely different couplings of proton (mainly dipolar) and deuteron spins (mainly quadrupolar), respectively, the dominating relaxation mechanism at a selected frequency, and thus the relaxation dispersion, is not necessarily the same in both cases. For instance, the dipolar coupling is sensitive to intermolecular reorientations, wheres the quadrupolar is not. This circumstance allows us to interpret both the parallels and the distinctions between the two sets of data

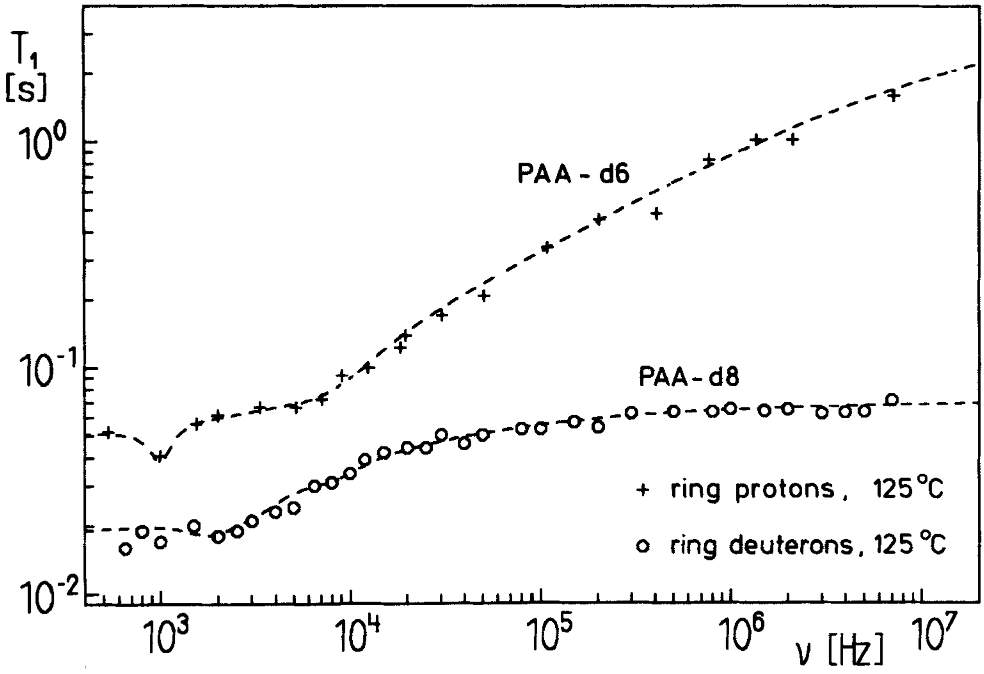

Fig. 4. Proton and deuteron relaxation dispersion of the PAA ring-sites

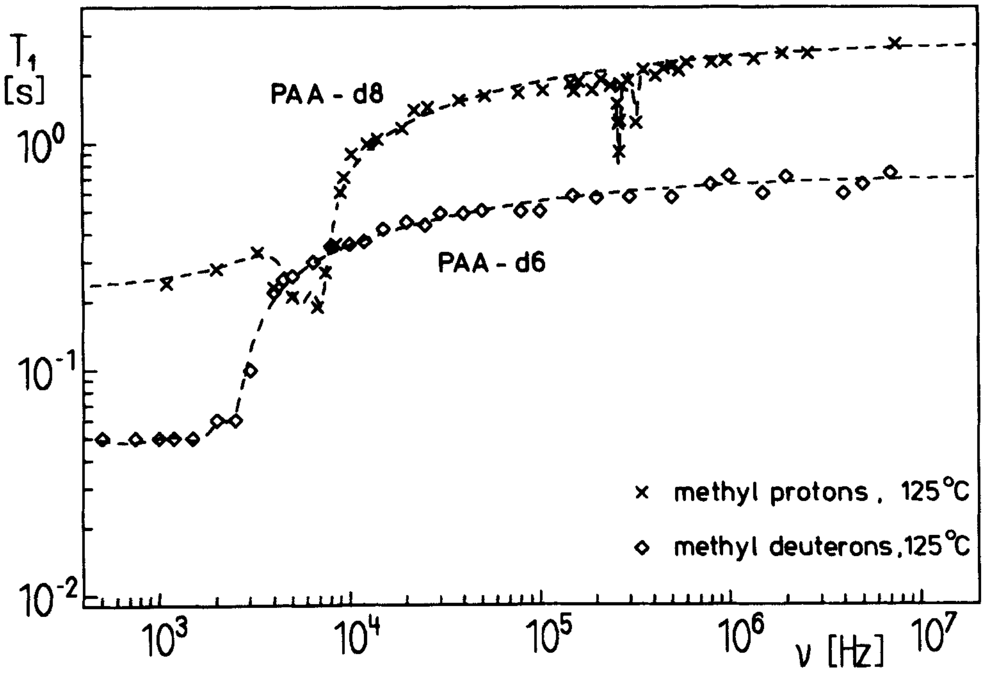

Fig. 5. Proton and deuteron relaxation dispersion of the PAA chain-sites

illustrated in Figs. 4 and 5.

To analyse the shown dispersion profiles for deuterons and protons, one has to consider extensions of the familiar relaxation formalism, since FC experiments include low Larmor frequencies where the standard Redfield limit is no longer valid [19,20] without modifications for the dipolar or quadrupolar order. A detailed description of the employed formalism will be reported elsewhere. Essentially, the concept is based (i) on previous observations that the proton $T_1(\nu)$ is dominated at low ν's by order fluctuations (T_{1OFD}) and at high ν's by molecular self-diffusion (T_{1SD}), but also reveal minor contributions due to molecular rotations about the short axis (T_{1RT}) and due to cross-relaxation between proton and nitrogen spins (T_{1CR}); (ii) on the facts that the quadrupolar deuteron relaxation is not affected by self-diffusion, and reflect rotations of the molecular axis in a different way than protons because of the dissimilar orientations of C-D bonds and H-H pairs at the same position. This concept is expressed [15] by the established proton $T_1(\nu)$ dispersion model function

$$T_{1(H)}^{-1} = A\,\nu^{-1/2}\,f_{OFD}(\nu,\nu_c) + B\,f_{SD}(\nu,\tau_{SD}) + C\,f_{RT}(\nu,\tau_{RT}) + D\,f_{CR}(\nu,\tau_{CR}), \qquad (4)$$

and the related deuteron model [15]

$$T_{1(D)}^{-1} = A^*\,\nu^{-1/2}\,f_{OFD}(\nu,\nu_c) + C^* + D^*\,f_{CR}(\nu,\tau_{CR}), \qquad (5)$$

with a potential square-root term ($A^* = ?$) down to a frequency cutoff ν_c (not necessarily caused by ν_L), a frequency independent rotational term (attributed mainly to the fast rotation about the long axis), and one or more resonant cross-relaxation terms (caused by deuteron-proton and deuteron-nitogen energy level crossings). Details about the meaning of the numerous model parameters (A, B, C, D, ν_c, τ_{SD}, τ_{RT}, τ_{CR}, A^*, etc.) and spectral functions (f_{OFD}, f_{SD}, f_{RR}, f_{CR}) should be looked up in previous works [8-10,15]. The dashed lines in the diagrams, which were obtained by computer assisted optimization procedures, demonstrate that both model functions not only allow satisfactory, but also self-consistent fits to the experimental data.

We learn from such curve fits that at high Larmor frequencies, typically above $\cong 10^5$ Hz, the deuteron relaxation times are dominated by the rotational contribution. The frequency independence of T_{1RT} implies that the related reorientation time is short on the scale of the Larmor period. Both other processes cannot explain a plateau over the broad ν range seen by the experiment. The surprising, yet reasonable new finding comes from the comparison of the C and C* terms, because for the deuterons $1/T_{1RT}$ is much too large to be explained by the same type of motion as for by the proton spins! This can be attributed to the unlike C-D bond and spin pair orientations of comparable sites, which enhances the relaxation by rotations about the short axis for the deuterons. At medium frequencies, typically between 10^4 Hz and 10^5 Hz, the deuteron data reveal in addition to the C* term a square-root law contribution characteristic of nematic director fluctuations. The rather narrow interval of this range compared with the proton results for the ring positions (Fig. 4), which came unexpected because the absent T_{1SD} mechanism should entail the opposite effect, is obviously a consequence of the large differences between C and C*. It means that the OFD process is indeed also effective for the deuteron spins, but almost hidden by the rotational C*-term. This conclusion is supported by the measurements on the more mobile methyl positions (Fig. 5), where both A and A* are small, which impliesthat the deuteron and proton dispersion profiles look similar. More than that: If one expresses A* explicitly by the line splitting $\Delta\nu$, viscosity η, average Frank constant K and temperature ϑ, the calculated ratio A*(PAA-d8)/A*(PAA-d6) is the same (11) as the result from the model fits (10.7), and even the calculated absolute values of the two model parameters A* prove to be in good agreement with the experiment (e.g. at 125 °C, A*(PAA-d8) = 1400 $s^{-3/2}$, A*(PAA-d6) = 130 $s^{-3/2}$). So there exist numerous evidences that our assignment of the Pincus-Blinc model is reasonable.

The complex behaviour at low frequencies ($\nu \leq 10^4$ Hz) is not yet quantitatively understood. For PAA-d6, but slightly also for PAA-d8, the rotational and the order fluctuation terms are insufficient to interpret the deuteron T_1 dispersion, essentially because of the steep slope and the height of the steps; also the inclusion of local order effects like quadrupolar and dipolar relaxation [19,20] does not solve the problem. Since the unusual $T_1(\nu)$ occurs at frequencies where the proton relaxation dispersion shows sharp "dips" due to possible resonant energy level crossings between Zeeman proton and quadrupolar nitrogen niveaus [21], we presently favour a similar model for the deuterons [15]. E.g. in Fig. 5, the proton $T_1(\nu)$ clearly shows three such resonances, which essentially reflect the symmetry of the nitrogen bonds, and the low-field deuteron behaviour can be related to the left one. However, there should exist more and it is not yet clear why they are not observed. It should be emphasized that these not clear details , which will be discussed elsewhere, do not significantly affect the evaluation of the

Pincus-Blinc model parameters A and A*.

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