

# Deuteron NMR Lineshapes in the Antiferroelectric Liquid Crystalline Phase of MHPOBC

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The deuteron NMR lineshapes in the tilted antiferroelectric smectic liquid crystalline phases are evaluated for: i) the case of a discrete short pitch modulation  $P_1 = N \cdot d$  where  $N = 2, 3, 4$ , ii) for a superposition of two modulations  $p_1$  and  $p_0$  where  $p_0 \gg p_1$  as well as iii) for the case where in addition rapid molecular exchange between adjacent layers takes place due to translational diffusion. The results are compared with the experimental deuteron NMR spectra of  $\alpha$ -CD<sub>2</sub> deuterated MHPOBC in the Sm C<sub>A</sub><sup>\*</sup> phase measured at different angles between the magnetic field direction and the normals to the smectic layers. The alternating tilt structure of the Sm C<sub>A</sub><sup>\*</sup> phase is confirmed.

**Key words:** Liquid Crystals; NMR; Diffusion.

In chiral ferroelectric smectic liquid crystals the directions of the average molecular tilt and the in-plane polarization slowly vary on going from one smectic layer to another in the direction of the ferroelectric helix. The molecules in adjacent layers tilt in the

same direction and we speak of synclinc ordering. Recently, however, a number of tilted smectic phases have been discovered [1] where the tilt direction alternates from layer to layer thus exhibiting anticlinic ordering (Figure 1). The directions of the in-plane polarization as well alternate so that these phases are antiferroelectric.

The microscopic mechanisms favoring anticlinic respectively sinclinc ordering are still poorly understood. To get some additional insight into the structure of these phases and the nature of the inter-layer tilt coupling we decided to evaluate the theoretical deuteron NMR lineshapes of the Sm C<sub>A</sub><sup>\*</sup> phase and compare them with those measured in chiral  $\alpha$ -CD<sub>2</sub> deuterated MHPOBC for a general direction of the magnetic field with respect to the smectic layer normals.

The molecular structure and the phase diagram of MHPOBC are shown in Figure 2. The NMR measurements were performed in a superconducting magnet of 9 T. A newly developed sample orientation switching technique [2] has been used to measure the spectra as a function of the angle between the direction of the magnetic field and the normal to the smectic layers.

In view of the fast rotation around the long molecular axis, the time averaged electric field gradient

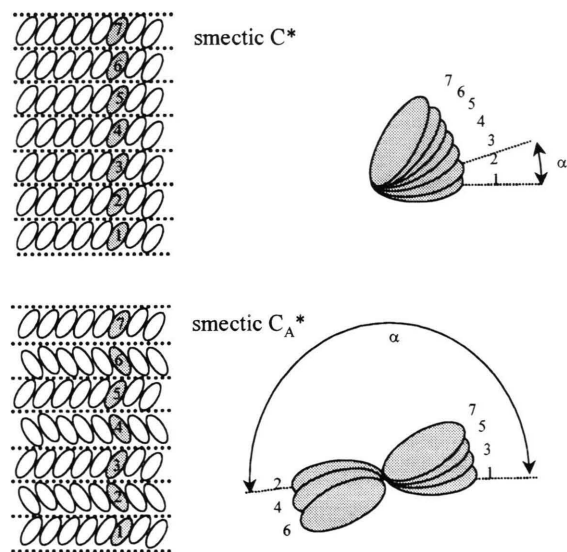


Fig. 1. Synclinc (Sm C<sup>\*</sup> phase) and anticlinic (Sm C<sub>A</sub><sup>\*</sup> phase) ordering in tilted smectic phases.

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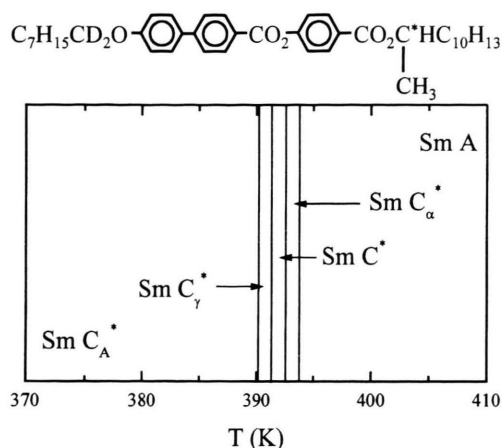


Fig. 2. Molecular structure and phase diagram of MHPOBC.

(EFG) tensor at the deuteron site will be cylindrically symmetric with the largest principal axis  $V_{zz}$  pointing along the molecular director.

The quadrupole perturbed deuteron NMR frequency in a given smectic layer is in this case obtained as

$$\nu = \nu_L \pm \frac{3}{8} \nu_Q S [3(\sin \theta_0 \sin \theta \sin \phi + \cos \theta_0 \cos \theta)^2 - 1], \quad (1)$$

where  $\nu_Q = \frac{3}{2} eqQ/h$  is the deuteron quadrupole coupling constant  $q = V_{zz}$ ,  $S$  the nematic order parameter,  $\theta$  the angle between the magnetic field  $\mathbf{H}$  and the normal to the smectic layers,  $\phi$  the azimuthal angle and  $\theta_0$  the tilt angle. Let us now assume that the incremental change in the azimuthal angles  $\Delta\phi_i$  between the directors in two adjacent smectic layers is

$$\Delta\phi_i = \frac{2\pi}{N}, \quad (2)$$

where  $N = 2, 3, 4, \dots$  designates the number of smectic layers forming the antiferroelectric unit cell. In the  $\text{Sm } C_A^*$  phase, in particular, one should have  $N = 2$  so that the average molecular tilt alternates as one goes from one layer to another.

The theoretical deuteron NMR spectra between  $\theta = 0^\circ - 90^\circ$  for  $N = 2, 3$  and 4 are shown in Figure 3. The experimental spectra in the  $\text{Sm } C_A^*$  phase cannot be described by any of these models. If we now add to the discrete short pitch modulation

$$p_1 = N \cdot d, \quad (3)$$

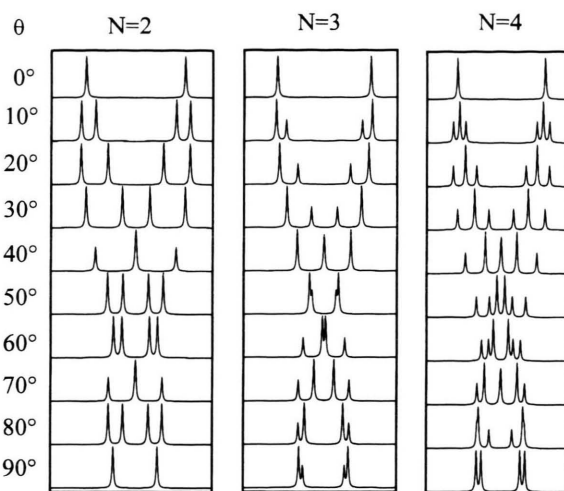


Fig. 3. Theoretical deuteron NMR spectra for tilted smectics with two layer unit cells,  $N = 2$  ( $\Delta\phi = 180^\circ$ ), three layer unit cells,  $N = 3$  ( $\Delta\phi = 120^\circ$ ) and four layer unit cells,  $N = 4$  ( $\Delta\phi = 90^\circ$ ). This is the case of a discrete modulation with a pitch  $p_1 = N \cdot d$ , where  $d$  is the inter-layer distance.

where  $d$  is the inter-layer spacing, a long pitch continuous modulation similar to the one in the chiral ferroelectric smectic  $C^*$  phase,  $p_0 \gg p_1$ , we get a continuous variation of  $\phi = \phi(z)$  and  $\nu = \nu(z)$ . The resulting inhomogeneous frequency distribution [2]

$$f(\nu) = \frac{\text{const}}{\left| \frac{d\nu}{d\phi} \right| \cdot \left| \frac{d\phi}{dz} \right|} \quad (4)$$

has intensity singularities [2], where  $d\nu/d\phi = 0$ , at

$$\nu_{I,II} = \nu_L \pm \frac{3}{8} \nu_Q S [3 \cos^2(\theta_0 \pm \theta) - 1] \quad (5a)$$

and

$$\nu_0 = \nu_L \pm \frac{3}{8} \nu_Q S. \quad (5b)$$

The last singularities appears only if  $\tan(\theta_0) > \cot(\theta)$ . The resulting spectra for  $N = 2$  are shown in Figure 4. They as well do not describe the experimental data.

A good agreement between the theoretical and the experimental spectra in the  $\text{Sm } C_A^*$  phase (Fig. 5) is however obtained if one takes in addition to the  $p_1$  and  $p_0$  modulations also rapid molecular exchange between adjacent layers followed by a reorientation  $\phi_i \rightarrow \phi_i + \pi$  into account. In this case the nuclear

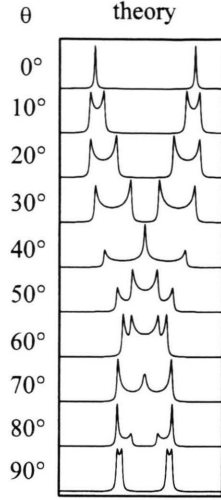


Fig. 4. Theoretical deuteron NMR spectra for the case of a superposition of a discrete  $p_1 = 2d$  and quasi-continuous ( $p_0 \gg p_1$ ) modulations.

spins “feel” only the time averaged EFG tensors of the two neighboring smectic layers:

$$\langle \underline{V} \rangle = \frac{1}{2} [\underline{V}_i + \underline{V}_{i+1}]. \quad (6)$$

The resulting frequency distribution  $f(\nu)$  has here only two intensity singularities at

$$\nu_I = \nu_L \pm \frac{3}{8} \nu_Q S [3 \cos^2 \theta_0 \cos^2 \theta - 1] \quad (7a)$$

and

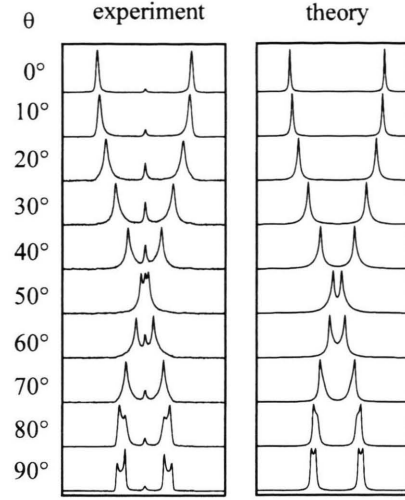


Fig. 5. Comparison between the experimental deuteron NMR spectra of  $\alpha$ -CD<sub>2</sub> deuterated MHPOBC in the Sm C<sub>A</sub><sup>\*</sup> phase and theoretical lineshapes for a superposition of discrete ( $N = 2$ ) and quasi-continuous modulations where rapid molecular exchange between adjacent layers has been taken into account.

$$\nu_{II} = \nu_L \pm \frac{3}{8} \nu_Q S [3(\cos^2 \theta_0 \cos^2 \theta + \sin^2 \theta_0 \sin^2 \theta) - 1], \quad (7b)$$

which are well separated only at relatively large  $\theta$  and  $\theta_0$  values. The angular dependence of the positions of the singularities is as well radically different from the ones predicted by (5a, b) or (1) and perfectly agrees with the experimental data.

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