Molecular Crystals and Liquid Crystals

Improved Calculation of Diffusion Effects in NMR Spectra of Cholesteric Liquid Crystals

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Version of record first published: 20 Apr 2011.

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Improved Calculation of Diffusion Effects in NMR Spectra of Cholesteric Liquid Crystals

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We give an improved model for the calculation of NMR spectra in the cholesteric phase. It is compared to an earlier model that starts with simplifying assumptions. Our method gives better coincidence between experimental and calculated spectra and diffusion constants, and activation energies are found with greater accuracy.

INTRODUCTION

NMR methods have been widely used for the calculation of self-diffusion constants D in the cholesteric phase.[1-5] The dependence of D on temperature and pitch length gives information about activation energies of the diffusion process and the phase structure. We regard nematic liquid crystals twisted by addition of some wt.% of a chiral compound. The director $\vec{n}$ changes its orientation along a pitch axis x periodically: $\vec{n} = \vec{e}_z \cos \theta + \vec{e}_y \sin \theta$; with $\vec{e}_x, \vec{e}_y, \vec{e}_z$ being orthogonal unit vectors, $\theta = 2\pi x/p_o$, and p_o is the pitch length. As the magnetic susceptibility anisotropy of the regarded mixtures is positive the helical axes are arranged perpendicularly to the magnetic field $\vec{B}$ of the spectrometer. A translational diffusion of the molecules along $\vec{e}_x$ changes the average molecular orientation to $\vec{B}$ and is thus detectable by NMR, where diffusion effects are strong for pitch lengths of the order of about 1 μm. Corresponding methods for ^{2}H NMR spectra have been proposed by Luz et al.[1] and Chidichimo et al.[2-5] We use a slightly different model to calculate spectra of ^{13}C and ^{2}H NMR.

THEORY

The resonance frequency ω^i of one single ^{13}C NMR line i in the spectrum is given by

$$\omega^i = 2\pi[\nu^i - \nu^i_{iso} - (1 - \eta)\nu^i_a/4]$$

$$= \omega^i_o \cos 2\theta \quad \text{with} \quad \omega^i_o = 2\pi(3 + \eta)\nu^i_a/4 \quad (1)$$

η is the asymmetry parameter, the field $\vec{B}$ is taken to be in $\vec{e}_z$ direction, ν^i_{iso} is the resonance frequency in the isotropic phase and ν^i_a is the anisotropy of chemical shift frequency. The index i be omitted in the following and we describe the behaviour of only one ^{13}C site. The total spectrum is a superposition of these single lines. In the case of ^2H NMR ν_a has to be replaced by the frequency $3\nu_Q/4$, and $\nu_{iso} \approx$ 0. We assume the helices to be undistorted by the field, i.e. the angles θ of the molecules are equally distributed. A molecule being situated at $\theta = \theta_a$ at time $t_a = 0$ to be carried to the new orientation θ at time t by a Markovian diffusion process with the probability density

$$p(\theta|\theta_a,t) = (\pi t/\tau_c)^{-1/2} \exp[-(\theta - \theta_a)^2\tau_c/t] \quad (2)$$

τ_c is related to the diffusion constant D by $\tau_c = p_o^2/(16\pi^2 D)$. It is obvious that after the time t the resonance frequencies $\omega(\theta_a,t)$ of the molecules starting at θ_a are distributed due to the diffusion. Since their individual paths of motion are different the frequencies during the time t and hence the phases $\varphi(\theta_a,t) = \int_o^t \omega(\theta_a,t')dt'$ must be distributed as well. The first and second moments of the distribution of $\varphi(\theta_a,t)$ can be calculated according to:[6,7]

$$\overline{\varphi}(\theta_a,t) = 1!\int_o^t dt_1 \int_{-\infty}^{\infty} d\theta_1 \, p(\theta_1|\theta_a,t_1) \, \omega(\theta_1)$$

$$\overline{\varphi^2(\theta_a,t)} = 2!\int_o^t dt_2 \int_2^t dt_1 \int_{-\infty}^{\infty} d\theta_2 \int_{-\infty}^{\infty} d\theta_2 \times p(\theta_2|\theta_1,t_2 - t_1) \quad (3)$$

$$\times \, p(\theta_1|\theta_a,t_1)\omega(\theta_2)\omega(\theta_1)$$

For simplicity we use the approximation of a Gaussian distribution of the phases

$$P[\varphi(\theta_a,t)] = (2\pi\Delta^2)^{-1/2}\exp[-(\varphi - \overline{\varphi})^2/(2\Delta^2)], \Delta^2 = \overline{\varphi^2} - \overline{\varphi}^2,$$

giving the correct first and second moments of Eq. (3). Using Eq. (1) and (2) we obtain

$$\Delta^2 = \omega_o^2[t\tau_c - 4\tau\tau_c/3 + \tau_c^2(1 - \exp(-4t/\tau_c))/12 + \cos^2 2\theta_a\,(2\tau\tau_c/3$$
$$- \tau^2 - \tau_c^2(1 - \exp(-4t/\tau_c))/6)] \quad \tau = \tau_c[1 - \exp(-t/\tau_c)]$$

and the Free Induction Decay (FID) is given by

$$G(t) = G_o \int_0^{\pi/2} d\theta_a \int_{-\infty}^{\infty} \cos\varphi\, P(\varphi)\, d\varphi\, R(t)$$

$$= G_o \int_0^{\pi/2} d\theta_a \cos\overline{\varphi}\, \exp(-\Delta^2/2)\, R(t) \qquad (4)\cdot$$

$R(t) = \exp(-t/T_2)$ is a relaxation function which accounts for magnetic field inhomogeneity in ^{13}C spectra. We regard R to be independent of θ_a. This is correct for ^{13}C NMR but an approximation for ^2H spectra where angular dependent dipole-dipole interactions are present, too.

The term $\exp(-\Delta^2/2)$ represents an additional convolution due to the diffusion which broadens the spectrum. As the line shape is influenced mainly by the convolution of the singularities we can set $\Delta^2 = \Delta^2(\theta_a = 0) = \Delta_{min}^2$ independent of θ_a to perform the integration in Eq. (4) analytically. It gives

$$G(t) = G_o J_o(\omega_o\tau)\, \exp(-\Delta_{min}^2/2)\, R(t) \qquad (5)$$

where J_o is the Bessel function of order zero. The first moment of $P(\varphi)$, $\overline{\varphi}(\theta_a,t) = \omega_o\tau\cos 2\theta_a$ is exact, and the approximation for Δ could be avoided by a numerical integration in Eq. (4). Comparing our result with the formula given by Chidichimo et al.[2] we find that the convolution factor $\exp(-\Delta^2/2)$ is absent there because the authors have neglected the distribution of phases and assume a coherent diffusion of all molecules starting at one distinct θ_a. In the case of ^2H NMR the neglection of Δ may be justified partially since broad dipole-dipole interactions (which are included in R) mask its effect. The ^{13}C NMR line shape, however, is crucially influenced by the factor $\exp(-\Delta_{min}^2/2)$. Figure 2 shows simulated ^2H spectra. The line shapes

a-d were computed according to Eq. (5). For comparison we show spectra calculated by:

$$G(t) = G_o \int_o^{\pi/2} d\theta_a \cos[t\Omega(\theta_a,t_m)]R(t) \quad \text{with}$$

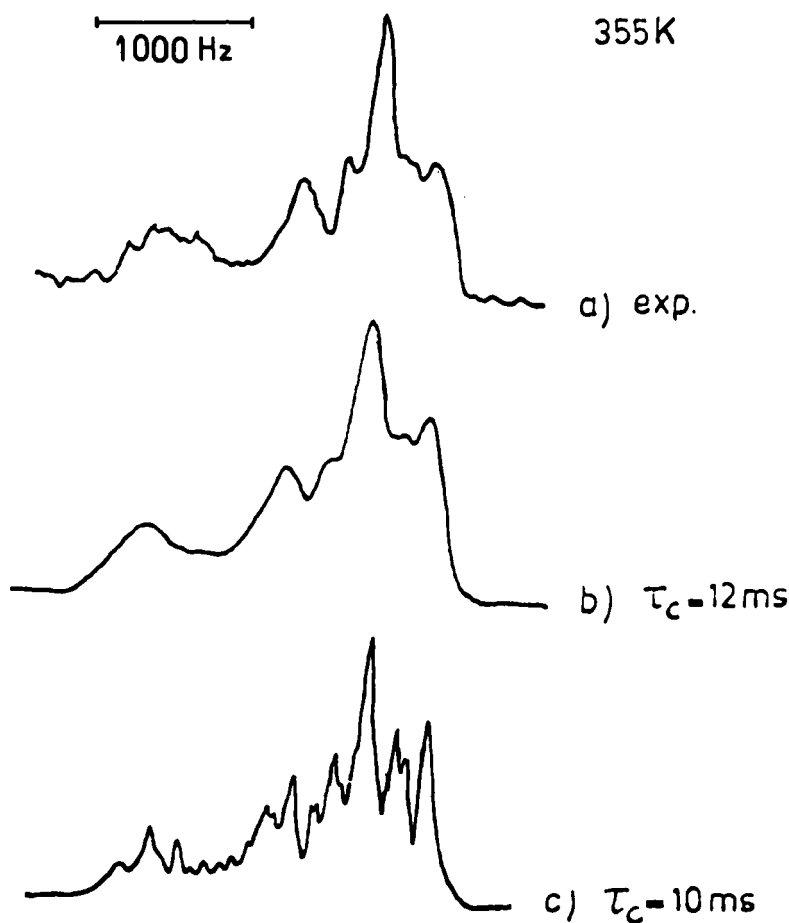$$\Omega(\theta_a,t_m) = \varphi_o\cos 2\theta_a[1 - \exp(-t_m/\tau_c)]\tau_c/t_m \qquad (6)$$

FIGURE 1 ^{13}C NMR spectra of the benzene ring carbons of 4n-octyloxyphenyl-4′n-pentyloxy-benzoate twisted by addition of 4.2 wt.% of chiral cholesterylundecyl-carbonate at 355 K a) experimental, b) calculated according to Eq. (5), c) calculated according to /2/ (with neglection of Δ).
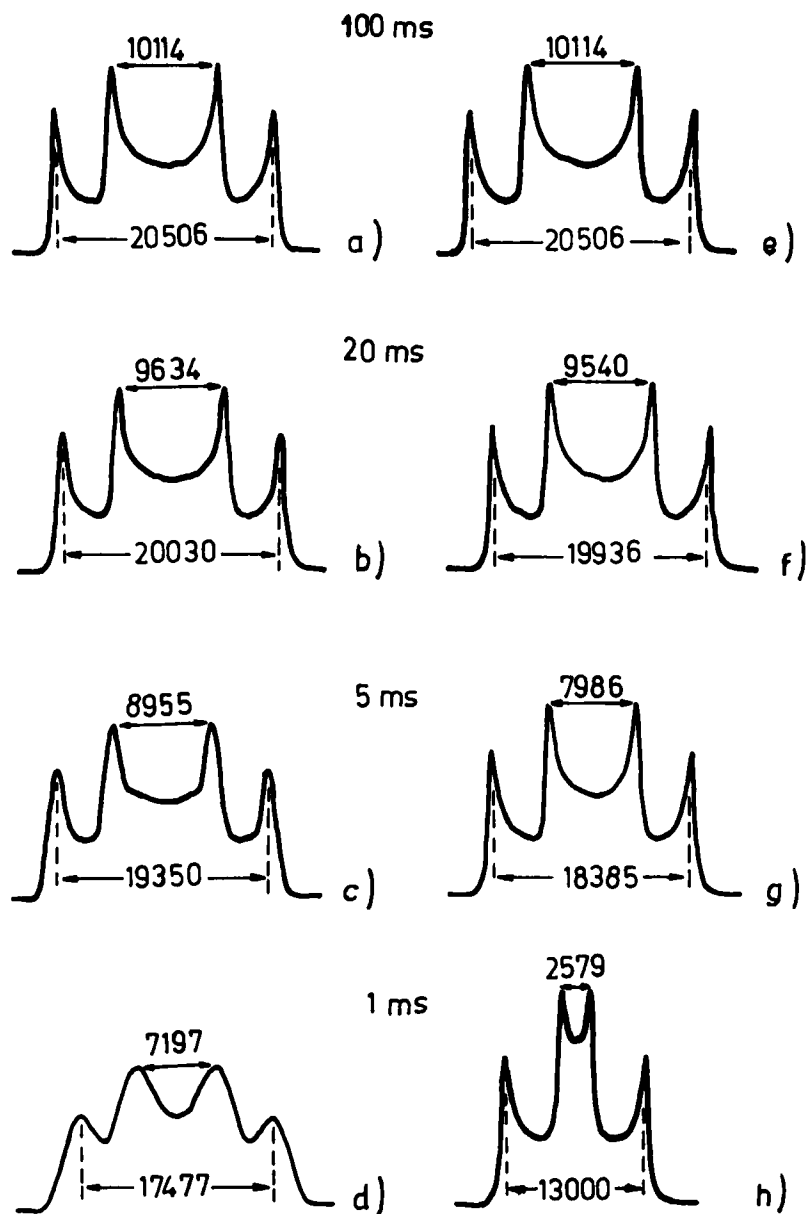
FIGURE 2   Calculated ^{2}H NMR spectra of one single deuterium position with $3\nu_q/4 = 10.4$ kHz ($\omega_p \approx 49000/s$), $t_m = 1.5$ ms and $T_2 = 0.7$ ms, for different τ_c. The splitting frequencies which are characteristic for the fitting procedure are given in s^{-1}, τ_c are given in ms. a–d) calculated according to Eq. (5), e–h) calculated according to Eq. (6).

This formula was used by Vaz et al.[3] for undistorted helices. t_m is an average FID length. The chosen values for τ_c, t_m and τ_2 are typical for ^{2}H NMR spectra. Only for small diffusion constants (high τ_c) both methods give similar results. For strong diffusion the line shapes differ remarkably. We note that the spectral shapes of Figure (2a-d) seem to be consistent with those calculated by Luz et al.[1] with a different algorithm.

CONCLUSIONS

The proposed model for the calculation of NMR spectra in the cholesteric phase gives line shapes which are consistent with the measured ones. Results of ^{13}C-NMR will be published elsewhere. We argue that spectra which are simulated with the assumptions of a coherent diffusion (and constant FID length) may lead to an overestimation of the line narrowing due to diffusion (see Figure 2). The neglection of Δ_{min} influences the values of the calculated diffusion constants as well as the activation energies of the diffusion process. Moreover, as the ^{2}H FID is much shorter than that of ^{13}C, and the influence of Δ_{min} is smaller, the fitting might give different D values for both methods.

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