Deuterium−Carbon NMR Correlation Spectroscopy in Oriented Materials
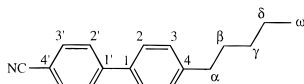
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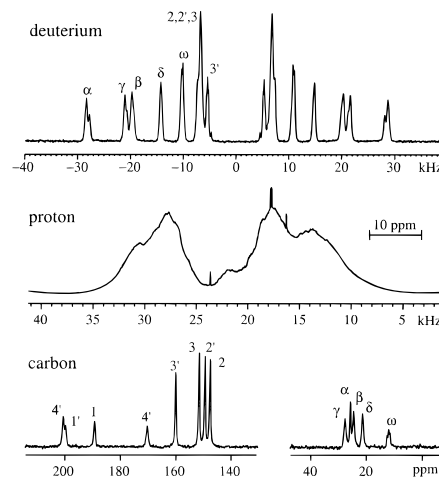2, av. Albert Einstein, 69626 Villeurbanne, France*

Figure 1. 1D deuterium, proton, and carbon NMR spectra of a static sample of the nematic liquid crystal 5CB (**1**). The deuterium spectrum was obtained from a fully deuterated sample of 5CB. Both the 500 MHz proton and the 61.4 MHz deuterium spectra were acquired with a simple one-pulse sequence. The 125 MHz carbon spectrum was obtained with a cross-polarization sequence and proton decoupling.

Deuterium provides a particularly interesting probe nucleus for solid-state NMR studies,[1−4] especially in oriented materials such as liquid crystals or lipids.[5−10] The widespread use of deuterium, in spite of the requirement for chemical isotopic substitution, is largely due to the fact that deuterium spectra are relatively simple, even in fairly large molecules. This is illustrated in Figure 1, where we show the deuterium, proton, and carbon NMR spectra for the nematic liquid crystal 5CB (4-*n*-pentyl-4′-cyanobiphenyl) (**1**).

It is immediately apparent that the proton spectrum is so complex that it cannot be interpreted and that the decoupled carbon spectrum is too simple to provide much information. In the deuterium spectrum, however, the resolved quadrupolar splittings are readily accessible and contain detailed information, especially concerning molecular dynamics. However, it should be noted that since there are essentially no chemical shift differences, it has so far been impossible to assign the deuterium spectrum of a fully enriched material without recourse to prior knowledge or to models. Indeed, no spectroscopic technique exists for the assignment of deuterium NMR spectra.

In this paper, we introduce a two-dimensional short-range deuterium−carbon correlation experiment which allows the assignment and the measurement of quadrupolar couplings in deuterated materials, and we illustrate it with the assignment of all of the quadrupolar couplings in 5CB. Some experiments involving proton to deuterium cross-polarization (CP) have previously been demonstrated for static and spinning samples and for sensitivity enhancement of deuterium spectra,[11−16] and

some results have been presented involving deuterium−carbon REDOR,[17] but no experiments involving deuterium-to-carbon cross-polarization have been reported.

The pulse sequence for the experiment is shown in Figure 2. After evolution of deuterium single-quantum coherence during t_1, a cross-polarization sequence is used to transfer polarization from the deuterium to the attached carbon atom, and carbon evolution is observed during t_2 with continuous-wave deuterium decoupling. The resulting spectrum, after 2D Fourier transform, yields correlation peaks centered at the deuterium frequency in ω_1 and at the carbon frequency in ω_2, thus allowing a simple assignment of the deuterium spectrum based on knowledge of the carbon chemical shifts (which can be assigned using several existing methods).[18] The method relies on two factors. First, the cross-polarization sequence works over a broad range of quadrupolar coupling constants, and second, the polarization transfer step is a mostly one-bond process.

In fact, single-quantum Hartmann−Hahn cross-polarization using constant radio frequency (rf) field amplitudes does work for spin $I = 1$ to $S = \frac{1}{2}$,[11,12] with a sharp match condition of $\omega_{1S} = \sqrt{(2\omega_{1I})}$, when the transmitter frequency is placed at the frequency of one of the two lines in the quadrupolar doublet, $\Omega_{CP} = \pm\omega_Q$. However, this is only valid in the limit $\omega_{1S} \ll \omega_Q$. Figure 2b shows the efficiency of polarization transfer as a function of quadrupolar coupling for a situation where ω_{1S} is comparable to ω_Q. Although the match condition is modified in this regime, it is still only efficient for a limited range of quadrupolar couplings. In order to render the process broad band, we make use of variable amplitude cross-polarization,[15] in which we sweep the amplitude of the deuterium radio frequency field while keeping the carbon field constant. This is a technique which has recently become very popular in proton−carbon cross-polarization experiments to enlarge the match condition in spinning experiments.[19−21] We have inves-

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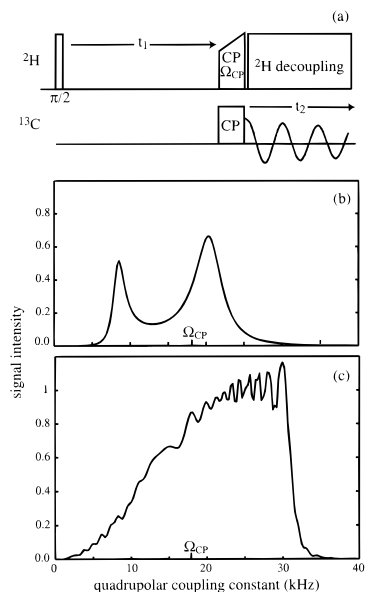
Figure 2. (a) Pulse sequence for the DECOR experiment. (b) The simulated maximum (quasi-equilibrium) ^{13}C polarization following Hartmann−Hahn CP calculated as a function of the quadrupolar coupling. In the calculations, the dipolar and quadrupolar couplings scale together (with the order parameter), corresponding to the situation in a liquid crystalline sample. The parameters are such that a quadrupolar coupling of 30 kHz corresponds to a heteronuclear coupling of 800 Hz (i.e., $\omega_Q/\omega_D = 37.5$). The RF field strengths were 19.5 kHz for carbon and 13.8 kHz for deuterium with the offset of the deuterium transmitter frequency set to 17.8 kHz. (c) The simulated signal intensity after CP using a linear ramp of duration 5 ms as a function of quadrupolar coupling. The rf was ramped linearly between 13.8 ± 4.6 kHz. The use of ramped CP effectively broadens the match condition.

tigated a number of functional forms for the sweep and details will be presented elsewhere, but we find that good overall performance is offered by a linear sweep, as illustrated in Figure 2c, yielding transfer which is broad band with respect to the quadrupolar interaction.

We can justify that the deuterium−carbon transfer process is dominated by one-bond correlations (in contrast to proton−carbon cross-polarization) if we consider that the magnetogyric ratio of the deuterons is 6 times smaller than that of protons. As a result, deuterium homonuclear dipolar couplings are relatively small and homonuclear spin diffusion processes should be slow. For the same reasons, if cross-polarization is observed at all, it should be much more rapid for the one-bond interaction than for two-bond and longer range interactions.

The above considerations are verified by experiment, and in Figure 3 we present a deuterium−carbon correlation spectrum obtained using the sequence in Figure 2 for a sample of uniformly deuterated 5CB. The experimental conditions are given in the figure caption. All of the expected correlations are clearly visible, and this spectrum makes the assignment of the deuterium spectrum almost trivial. The resulting assignment, given in Figure 1, agrees with previously published assignments based on model dependent arguments.[22] We remark that no correlations are observed to the quaternary carbons, as expected if one-bond processes dominate. It is interesting to note that for some of the aliphatic peaks, which have the largest quadrupolar (and dipolar) coupling constants, we can also observe splitting of the deuterium resonances due to the sum of the heteronuclear dipolar and scalar couplings. These splittings may contain useful structural information, but if
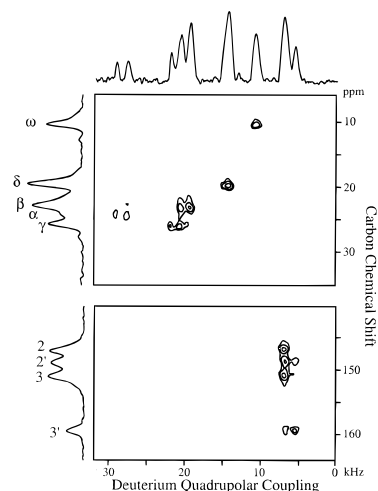
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Figure 3. 2D DECOR spectrum of uniformly deuterated 5CB. The spectrum was obtained at room temperature on a Bruker DSX400 wide-bore spectrometer using a 7 mm triple-resonance CP-MAS probe without sample rotation. A total of 128 t_1 increments with 96 scans each were collected. The contact time for cross-polarization was set to 5 ms using a radio frequency field strength of 13.8 kHz at the center of the ramp for deuterium and 19.5 kHz for carbon. The rf was ramped linearly between 13.8 ± 4.6 kHz. During the CP step, the deuterium frequency was moved 17.8 kHz off resonance to allow single-quantum cross-polarization. The deuterium decoupling field strength during t_2 was $\omega_1 = 23$ kHz (on-resonance continuous-wave decoupling). Quadrature detection in ω_1 was achieved using the TPPI method. A 4 s recycle delay was used between scans (to avoid sample heating problems).

necessary they could be removed by an 180° deuterium pulse at the center of the evolution period t_1. Note that the 2′ and 3′ deuterons show, in addition to the one-bond correlation, a second correlation to the next-nearest neighbor. This is expected from considerations of the (well-known) geometry and dynamics of the molecule, which lead to the average dipolar couplings being very similar for the one-bond and for the next-nearest neighbor interactions.[23] Polarization transfer is, as expected, largely confined to the half of the spectrum in which the transmitter offset is placed; it is not possible in general to spin-lock both single-quantum transitions simultaneously.

Note that not only does this technique provide a method for assigning deuterium spectra but it also allows the measurement of couplings which are not resolved from each other in the one-dimensional spectrum. This is, for example, the case of the aromatic deuterons in 5CB which are not resolved in the one-dimensional spectrum, but which give rise to resolved correlations in the two-dimensional experiment.

In conclusion, we have provided the first spectroscopic method for assigning deuterium NMR spectra. The method (which we refer to as DECOR for deuterium correlation) uses deuterium-to-carbon cross-polarization and thereby allows the assignment of deuterons on the basis of the chemical shift of the attached carbon. We have demonstrated the method on a nematic liquid crystal. It should also be useful in other oriented materials such as lipid and membrane samples.

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