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Two-Dimensional Deuterium Double-Quantum NMR in Partially Ordered Systems*

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The NMR spectra of solute molecules in the anisotropic environment of liquid crystal solvents contain information about molecular structure and motion (*1, 2*). For complex molecules, the number of allowed transitions in conventional proton NMR spectra is very large, and results in extensive spectral overlaps. To reduce this, protons may be replaced by deuterons, thereby minimizing the network of spin–spin interactions, and the systems analyzed by means of deuterium high-field Fourier-transform NMR (*3*). Deuterium NMR spectra are dominated by residual quadrupolar interactions, each chemically shifted deuteron contributing a quadrupolar doublet to the spectrum, and the utility of high-field ^{2}H NMR to characterize molecular ordering in such systems has been well demonstrated recently by Prestegard *et al.* (*4*).

While such nuclear quadrupole coupling constants are important parameters (*5*), dipolar couplings between nuclei are potentially even more important sources of structural information. Unfortunately, however, ^{2}H NMR line widths in ordered systems (arising mainly from the distribution in quadrupolar splittings) are on the order of 20–50 Hz, and often such large line widths preclude the possibilities of resolving smaller dipolar splittings. In addition, overlaps between different quadrupolar-split doublets may often preclude ready interpretation of dipolar structure in complex systems. In this Communication we thus report a two-dimensional (*6*) NMR technique which facilitates measurement of both dipolar and quadrupolar splittings in partially deuterated systems, by displaying quadrupolar splittings along one frequency (ω_2) axis, while both homo- *and* heteronuclear interactions are resolved along the second axis (ω_1). For simplicity, we have chosen to demonstrate the utility of the technique on partially oriented CD_2HI.

Our method is based on the multiple-quantum spin-echo technique of Bodenhausen *et al.* (*7, 8*) and involves the excitation and detection of deuterium double-quantum coherence. Of the several methods available for the creation of multiple-quantum coherence in heteronuclear spin systems (*9*), we have used the method of offset-independent excitation by means of nonselective strong pulses ($\pi/2$–$\tau/2$–π–$\tau/2$–$\pi/2$) as shown in Fig. 1. Heteronuclear decoupling during the double-quantum

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preparation period facilitates the setting up of the optimal value for τ (for maximal creation of the double-quantum coherence of interest) and eliminates ^1H–^2H dipolar interactions during t_2. The evolution of the double-quantum (DQ) coherence is studied for a period t_1. The simultaneous application of $^1H(S)$ and $^2H(I)$ π pulses at the midpoint of the period t_1 serves to refocus the effects of I spin resonance offset without affecting DQ evolution due to dipolar couplings. Conversion of the DQ coherence into an observable deuterium signal is effected by the last deuterium $\pi/2$ pulse. By applying suitable transmitter and receiver phase (ϕ_i) cycling schemes (*9*), signals arising solely from the transfer of DQ coherence into the single-quantum manifold are obtained. Repeating the experiment for various values of t_1 and subjecting the data matrix, $S(t_1, t_2)$, to a double Fourier transformation results in a two-dimensional spectrum reflecting only the homo- and heteronuclear dipolar couplings on the ω_1 axis, and essentially the residual quadrupolar couplings and chemical shift on the ω_2 axis.

To demonstrate the utility of this technique we used a 9 wt% solution of CD_2HI dissolved in Merck Phase IV liquid crystal, and the resulting double-quantum spectrum is shown in Fig. 2. The spectrum can be analyzed by considering the static spin Hamiltonian:

$$\mathscr{H}_0 = -\omega_0(I_{z1} + I_{z2}) + (\omega_Q/3)[3(I_{z1}^2 + I_{z2}^2) - I_1^2 - I_2^2] + D[3I_{z1}I_{z2} - I_1 \cdot I_2] + 2D_{IS}[I_{z1} + I_{z2}]S_z \quad [1]$$

where the terms have the usual meanings (*1, 2*). A symmetrically equivalent and axially symmetric quadrupole coupling tensor has been assumed for the two deuterium nuclei, and the scalar couplings are neglected. In the eigenstates of the I_2S spin system, characterized by 18 product functions of the form $|I, S\rangle = |\psi_I\rangle|\psi_S\rangle$, the time evolution of the spin density matrix, $\sigma(t)$, can be conveniently studied by straightforward matrix algebra (*7*). It can be shown that under the pulse sequence shown in Fig. 1, with $\phi_1 = \phi_2 = \phi_3 = 0$, no zero or triple-quantum coherences are excited. For the conditions $\omega_Q \gg D$ and $\omega_Q\tau = \pi/2$, the stimulation of six double-quantum coherences, with precessional frequencies $-4D \pm 2D_{IS}$, $\pm 2D_{IS}$ and $4D \pm 2D_{IS}$ is maximized, whereas double-quantum terms with precessional frequen-

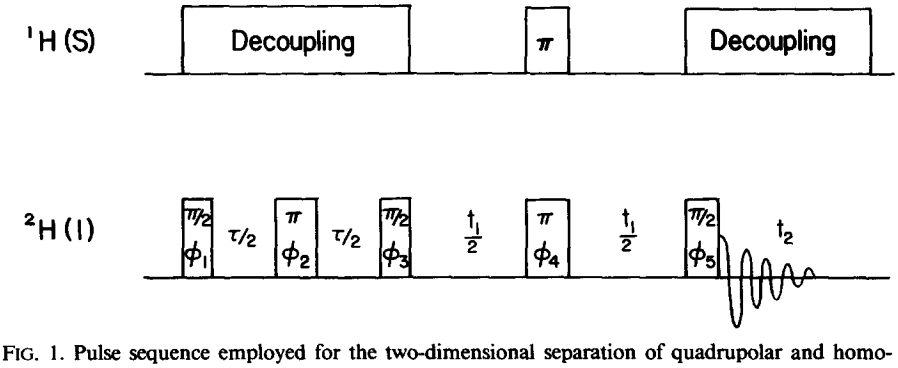

FIG. 1. Pulse sequence employed for the two-dimensional separation of quadrupolar and homo- and heteronuclear dipolar splittings in partially deuterated spin systems in ordered media.

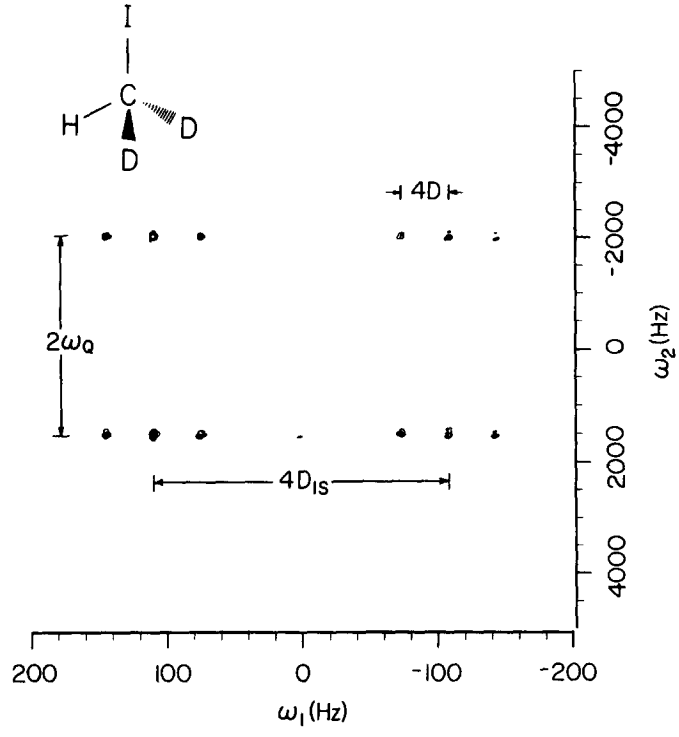

FIG. 2. Two-dimensional deuterium double-quantum NMR spectrum (absolute value mode), of a 9 wt% solution of CD_2HI dissolved in Merck Phase IV liquid crystal, recorded at 76.750 MHz (11.7 T), at room temperature. The pulse sequence shown in Fig. 1 was employed (with appropriate phase cycling to suppress unwanted signals) with 128 and 512 points in the t_1 and t_2 dimensions, respectively. The $\tau/2$ delay was 80 μs, and t_1 was incremented in 2.5 ms intervals. "Zero filling" in the t_1 dimension was used to improve resolution. The deuterium $\pi/2$ and π pulse widths were 35 and 80 μs, while the proton π pulse width was 80 μs. The experimental recycle time was 300 ms, and on-resonance proton decoupling was employed.

cies essentially dependent on the quadrupolar couplings, and four-quantum coherences, are not excited appreciably. Thus, in the 2D plot, measurement of double-quantum peak separations in the ω_1 dimension provides information concerning the dipolar couplings, and line separations in the ω_2 dimension give the residual quadrupolar couplings.

The deuterium DQ spectrum shown in Fig. 2 was recorded at 76.753 MHz using a "home-built" 11.7 T NMR spectrometer. The 2D data matrix was generated with 128 points in the t_1 domain and 512 points in the t_2 domain. A total of 272 scans per t_1 value (incremented by 2.5 ms) were employed. Zero-filling in the t_1 domain was used to improve spectral appearance. From the DQ spectrum we obtain D_{IS} = 54.7 Hz, D = 8.6 Hz and ω_Q = 1778 Hz. The deuteron–deuteron and deuteron–proton dipolar couplings are consistent with the gyromagnetic ratios. For a C_{3v} molecular symmetry, using $\langle$HCH = 107.35° and $r_{C\text{-}H} = r_{C\text{-}D}$ ranging from 1.088 to 1.14 Å (*11*) the deuterium quadrupole coupling constant (for zero asymmetry parameter) in CD_2HI is found to be 163–187 kHz which is in reasonable

agreement with earlier measurements (159.3–184.6 kHz) on other deuterated iodomethanes (*12*).

The results presented above thus indicate that it is possible to resolve both homo- *and* heteronuclear dipolar splittings by eliminating difficulties associated with line broadening (in the ω_1 dimension) arising from distributions in quadrupolar splitting and field inhomogeneities. Such resolved dipolar couplings, besides providing structural information, may also facilitate proper pairing of deuterium quadrupolar doublets in complex systems, and should be a better alternative than methods based on chemical shift differences (*4*). Although, of course, a study of partially deuterated systems in ordered media can be carried out by means of proton NMR (*9, 13, 14*), such investigations either do not provide information about deuterium quadrupolar couplings, or may require deuterium double-quantum decoupling for spectral simplification. Deuterium DQ decoupling (*13, 15*), besides requiring more rf power, critically depends on the carrier offset for efficient decoupling; therefore, in complex molecules with several chemically shifted deuterium nuclei, such decoupling is unlikely to be very efficient. Application of high-power deuterium decoupling will lead to temperature fluctuations in the sample, inducing a large variation in the measured quadrupole splittings. Proton decoupling using composite pulse sequences (*16, 17*), by contrast, should cause only minimal difficulties.

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