NOTES

Study of anisotropic diffusion of oriented molecules by multiple quantum spin echoes

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A variety of methods have been used to analyze the diffusive motion of molecules. In this note we report on the application of multiple quantum NMR to the problem of high sensitivity measurements of diffusion in anisotropic systems. The multiple quantum diffusion experiment is related to the standard NMR spin echo diffusion experiment[1] and is a generalization of the two-quantum experiments of Martin et al.[2] to arbitrary dipolar coupled proton systems. Like the standard experiment, it measures diffusion in a system at equilibrium without the need to introduce any external probes or labels. Individual molecules, instead, are labeled by their position in a magnetic field gradient after an initial radio frequency (rf) pulse, and the motion is followed by monitoring the amplitude of the spin echo following a second rf pulse some time later, as depicted in Fig. 1(a). Those nuclear spins which have moved little contribute more to the bulk echo signal than those which have strayed far from the field in which they were labeled.

While the NMR spin echo diffusion experiment is routinely performed on isotropic systems, the interesting case of anisotropic diffusion, as is found in liquid crystals, bilayers, membranes, or solids, is studied less frequently.[3] Though the same conceptually simple method is applicable, it is complicated by two factors: First, the diffusion tends to be slower (which necessitates larger field gradients) and second, the dipolar interactions, which are absent in isotropic systems, interfere with the formation of a spin echo at times long compared to the inverse of the dipolar spectral width.

The multiple quantum spin echo diffusion experiment substantially alleviates both these problems. Normal Fourier transform NMR techniques involve the excitation and detection of coherences where the difference in Zeeman quantum numbers Δm is ± 1. Multiple quantum NMR utilizes a sequence of rf pulses to prepare and detect coherences where $n = \Delta m$ is arbitrary.[4] We exploit the fact that an n quantum coherence dephases in a field gradient n times faster than does a single quantum coherence.[5] This effect is obviously of considerable advantage in diffusion studies and has previously been demonstrated by Martin et al.[2] for the two-quantum co-

herence of CH_2Cl_2 dissolved in various liquid crystals. For N coupled protons, the N-quantum transition is both free of dipolar couplings and most sensitive to dephasing by the field gradient. This approach eliminates the need for those line narrowing techniques typically employed for diffusion measurements in dipolar coupled systems.[6] Our generalization of the NMR spin echo diffusion experiment to multiple quantum echoes is shown in Fig. 1(b).

Gradients of up to 15 G/cm (calibrated against H_2O) were applied through a quadrupole coil and homemade current pulser capable of switching 2 A in 10 μs. The gradient coil was rotated to produce gradients either parallel or perpendicular to the main magnetic field.
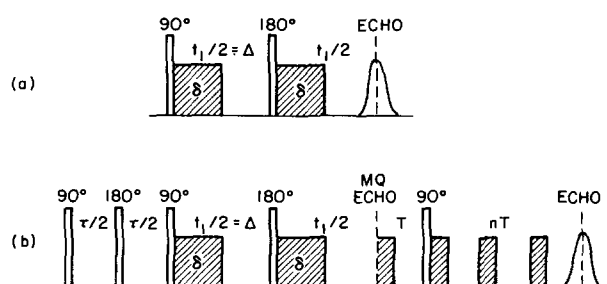

FIG. 1. NMR pulsed gradient diffusion experiment. Cross-hatched areas indicate gradient pulses. The experiment is typically performed with Δ fixed and δ regularly incremented. This eliminates transverse relaxation as an experimental parameter. Only the peak height of the single quantum echo is digitized. The results are fitted to Eq. (1) and the diffusion constant D extracted. (a) The single quantum version. (b) The multiple quantum version. This sequence prepares multiple quantum orders nonselectively. Orders are detected selectively by the use of an additional short gradient pulse and delay during multiple quantum evolution followed by n identical gradient-delay periods in the mixing period. The subsequent echo arises solely from magnetization which evolved during t_1 as n quantum [Ref. 5(b) and 7]. Preparation and mixing times (τ and T) were optimized for the multiple quantum order of interest using parameter proportional phase incrementation (PPPI) (Ref. 8). The fixed multiple quantum evolution time t_1 was similarly chosen to maximize the amplitude of the observed coherence transfer echo.
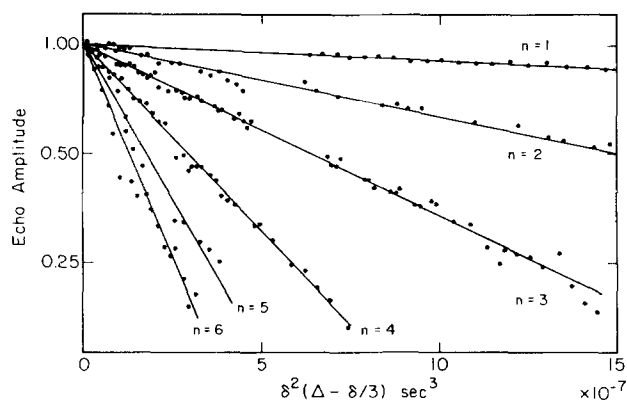
FIG. 2. Results of the NMR diffusion experiment for all n-quantum orders of benzene (25 mol%) dissolved in Eastman liquid crystal No. 15320. The plots show the normalized echo amplitude vs the gradient pulse timing parameter of Eq. (1). The straight lines are linear least-squares fits to the accumulated data whose slopes vary as n^2. This illustrates the vastly increased sensitivity of the multiple quantum diffusion experiment. Accumulation times varied from 15 min for the one quantum measurement to 200 min for the six quantum measurement.

Multiple quantum diffusion experiments, performed on nematic phase samples of benzene and 2-butyne dissolved in Eastman liquid crystal No. 15320, demonstrate the increasing sensitivity of the n-quantum echoes. The natural linewidths are expected to vary much less with order. Figure 2 shows the order dependence of the echo amplitude decay in benzene. The straight lines represent fits to the Stejskal—Tanner equation modified for n-quantum echoes:

$$\ln \frac{A(t_1)}{A_0(t_1)} = -\gamma^2 n^2 g^2 D[\,\delta^2(\Delta - \delta/3)]\;,$$

where $A(t_1)$ is the observed echo amplitude, $A_0(t_1)$ is the amplitude in the absence of any gradient, γ is the magnetogyric ratio, n is the multiple quantum order, D is the diffusion constant, and δ and Δ are as defined in Fig. 1. Results for these two systems are summarized in Table I.

It is clear that the high n-quantum echoes form much more sensitive measures of diffusion. The technique is likely to find its greatest applicability in the measurement of slow self-diffusion of oriented molecules where current methods fail either due to short T_2's or the need

TABLE I. Results of the multiple quantum spin echo diffusion experiment for solute molecules dissolved in Eastman No. 1532(The data represent an average over all n-quantum orders. No order gave results outside the error limits. The primary uncertainty arises from the gradient calibration. Experiments performed in a time-dependent gradient and corrected for T_2 relaxation gave essentially identical results.

	$D_{\perp}$ (cm^2/s)	$D_{\parallel}$ (cm^2/s)	$D_{\parallel}/D_{\perp}$
Benzene	$(0.9\pm0.1)\times10^{-6}$	$(1.1\pm0.1)\times10^{-6}$	1.25 ± 0.05
2-Butyne	$(3.1\pm0.2)\times10^{-6}$	$(3.5\pm0.2)\times10^{-6}$	1.1 ± 0.05

for unrealistically large field gradients. The combination of heightened sensitivity and narrowed lines achievable in the multiple quantum spin echo diffusion experiment seems the ideal solution to current experimental limitations.

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