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September 1982

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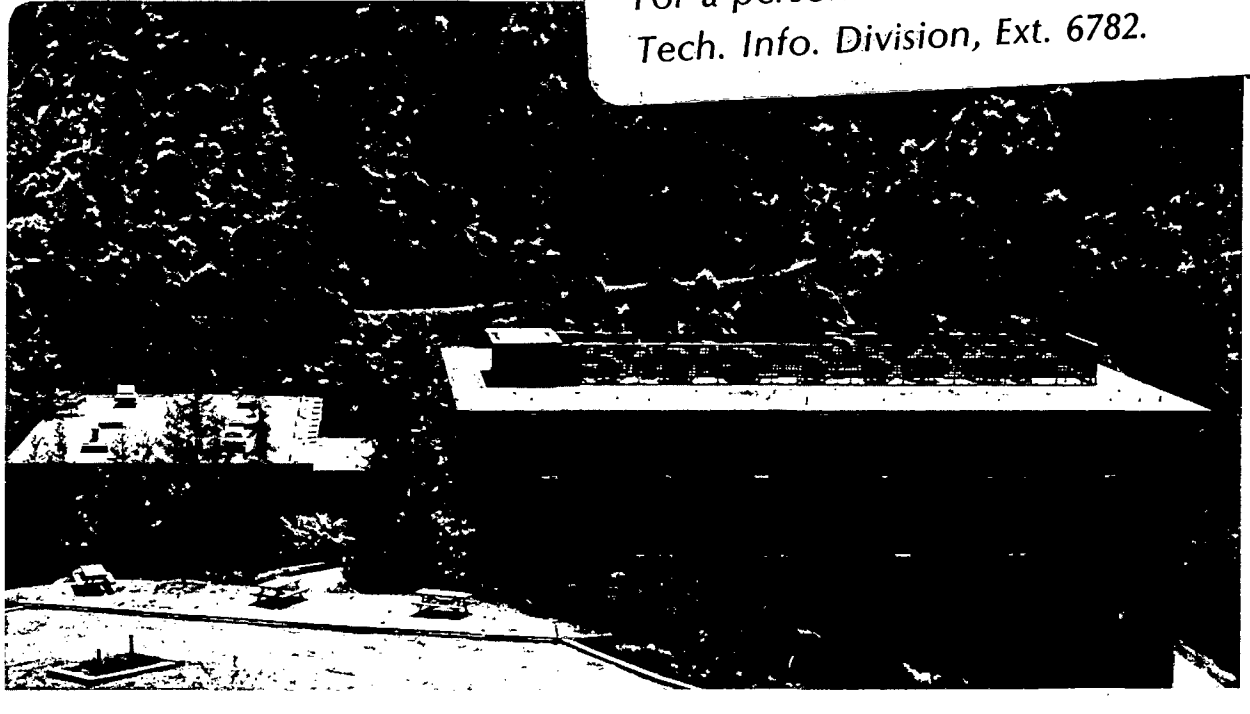

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STUDY OF ANISOTROPIC DIFFUSION OF ORIENTED MOLECULES BY MULTIPLE QUANTUM SPIN ECHOES

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Abstract

Experiments have been completed which demonstrate the greatly enhanced sensitivity of the multiple quantum version of the NMR spin echo diffusion experiment. These experiments are particularly well-suited to studies of anisotropic diffusion where the presence of dipolar couplings may make the standard experiment technically infeasible.

A variety of methods have been used to analyze the diffusive motion of molecules. In this communication 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 2-quantum experiments of Morton et al.[2] to arbitrary dipolar coupled proton systems. It shares those qualities which have made the NMR diffusion experiment a favorite method of measuring diffusion constants. 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 (r.f.) pulse, and the motion is followed by monitoring the amplitude of the spin echo following a second r.f. pulse some time later, as depicted in Figure 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. Though the same conceptually simple method is applicable, it is complicated by two factors: firstly, the diffusion tends to be slower (which necessitates larger field gradients) and secondly, 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 r.f. pulses to prepare and detect coherences where $n = \Delta m$ is arbitrary[3]. We exploit the fact that an n quantum coherence dephases in a field gradient n times faster than does a single quantum coherence[4]. This effect is obviously of considerable advantage in diffusion studies and has previously been demonstrated by Morton et al.[2] for the 2 quantum coherence 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.[5] Our generalization of the NMR spin echo diffusion experiment to multiple quantum echoes is shown in Figure 1(b).

Gradients of up to 15 gauss/cm (calibrated against H_2O) were applied through a quadrupole coil and homemade current pulser capable of switching 2 amp in 10 μsec. The gradient coil was rotated to produce gradients either parallel or perpendicular to the main magnetic field. Multiple quantum diffusion experiments have been performed on samples of benzene and 2-butyne dissolved in Eastman liquid crystal #15320, forming a nematic phase, which demonstrate the increasing sensitivity of n quantum echoes as n increases. Figure 2 shows the order dependence of the decay of the echo amplitude for all orders of benzene. The straight lines represent best fits to the Stejskal-Tanner equation modified for n quantum echoes:

$$\ln \frac{A(t_1)}{A_0(t_1)} = -\gamma^2 n^2 g^2 D(\delta^2(\Delta - \frac{\delta}{3}) \qquad (1)$$

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 Figure 1.

Results are shown in Table 1, and represent an average over all n quantum orders. None of the orders gave results outside of the error bars listed. The primary uncertainty remains the gradient calibration. Experiments performed in a time-independent gradient and corrected for T_2 relaxation gave essentially identical results.

TABLE 1

	$D_\perp$ (cm^2/sec)	$D_\parallel$ (cm^2/sec)	$D_\parallel / D_\perp$
Benzene	$.9 \times 10^{-6} \pm .1$	$1.1 \times 10^{-6} \pm .1$	$1.25 \pm .05$
2-Butyne	$3.1 \times 10^{-6} \pm .2$	$3.5 \times 10^{-6} \pm .2$	$1.1 \pm .05$

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 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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Figure 1. NMR pulsed gradient diffusion experiment. Cross hatched areas indicate gradient pulses. The experiment is typically performed with Δ fixed and δ regularly incremented. Only the peak height of the single quantum echo is digitized. The results are fitted to Equation 1 and the diffusion constant, D, extracted. (a) The single quantum version. (b) The multiple quantum version. This sequence prepares multiple quantum orders nonselectively and detects selectively only magnetization which evolved during t_1 as n quantum.[6]. Preparation and mixing times (τ and T) were optimized for the multiple quantum order of interest using parameter proportional phase incrementation (PPPI).[7] The fixed multiple quantum evolution time, t_1, was similarly chosen to maximize the amplitude of the observed coherence transfer echo.

Figure 2. Results of the NMR diffusion experiment for all n quantum orders of benzene (25 mol %) dissolved in Eastman liquid crystal #15320. The applied gradient is parallel to the magnetic field axis. The plots show the normalized echo amplitude vs. the gradient pulse timing parameter of equation 1. Straight lines are linear least-squares fits to the accumulated data. The slopes of these lines vary as n^2, as is predicted by theory. This illustrates the vastly increased sensitivity of the multiple quantum diffusion experiment.

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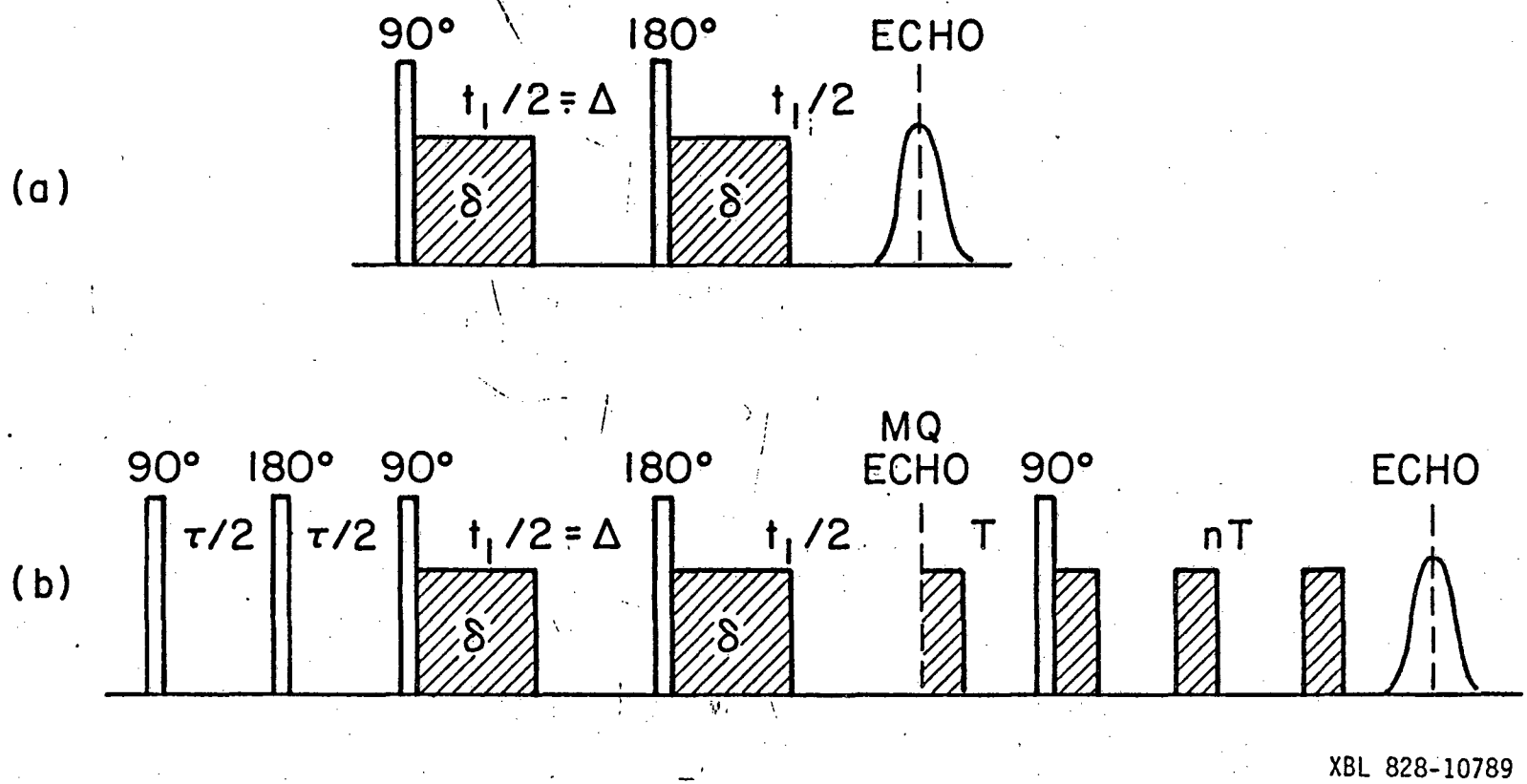

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FIGURE 1

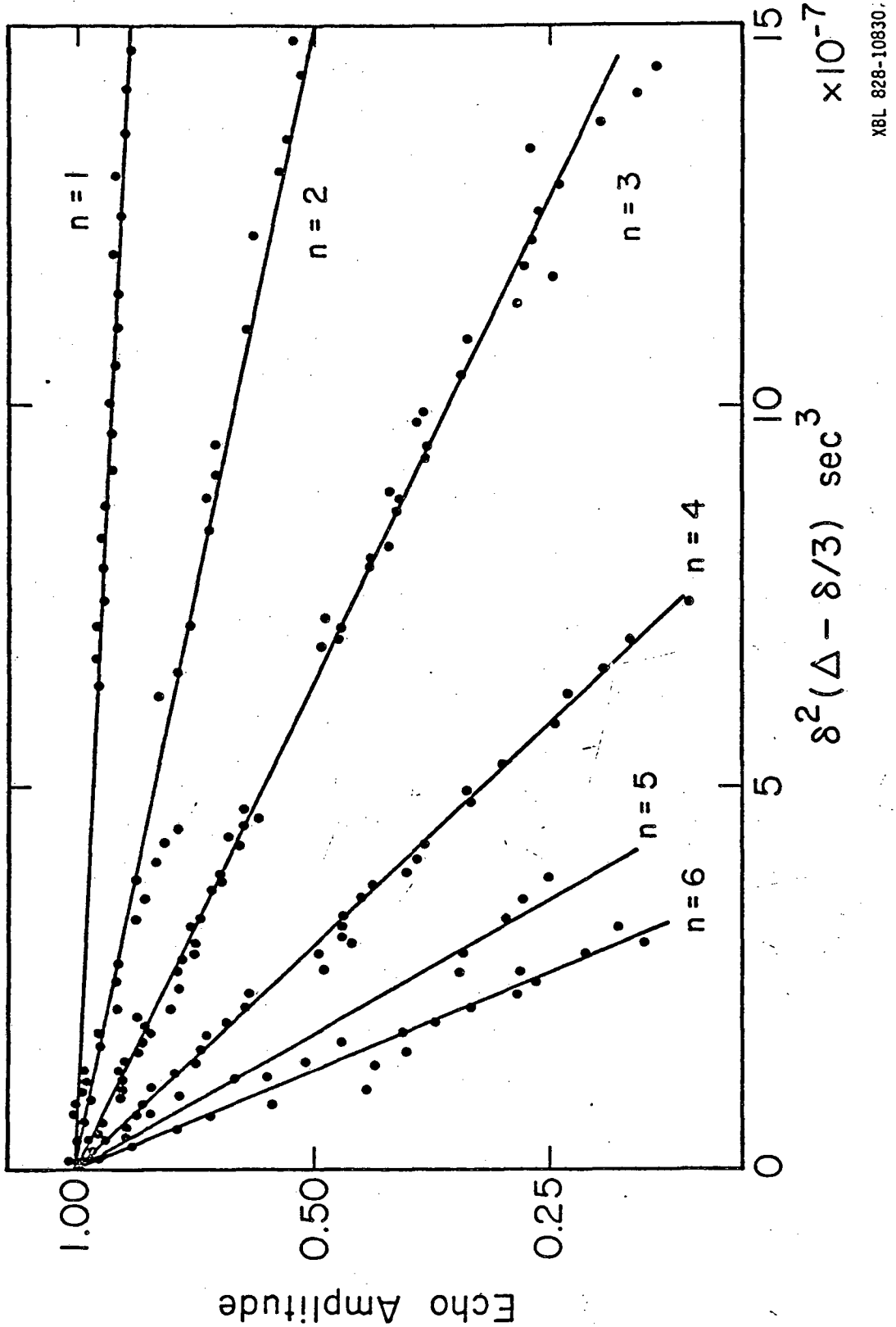
Echo Amplitude
1.00
0.50
0.25
0
5
10
15
$\delta^2(\Delta - \delta/3)$ sec^3
$\times 10^{-7}$
n = 1
n = 2
n = 3
n = 4
n = 5
n = 6
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FIGURE 2

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