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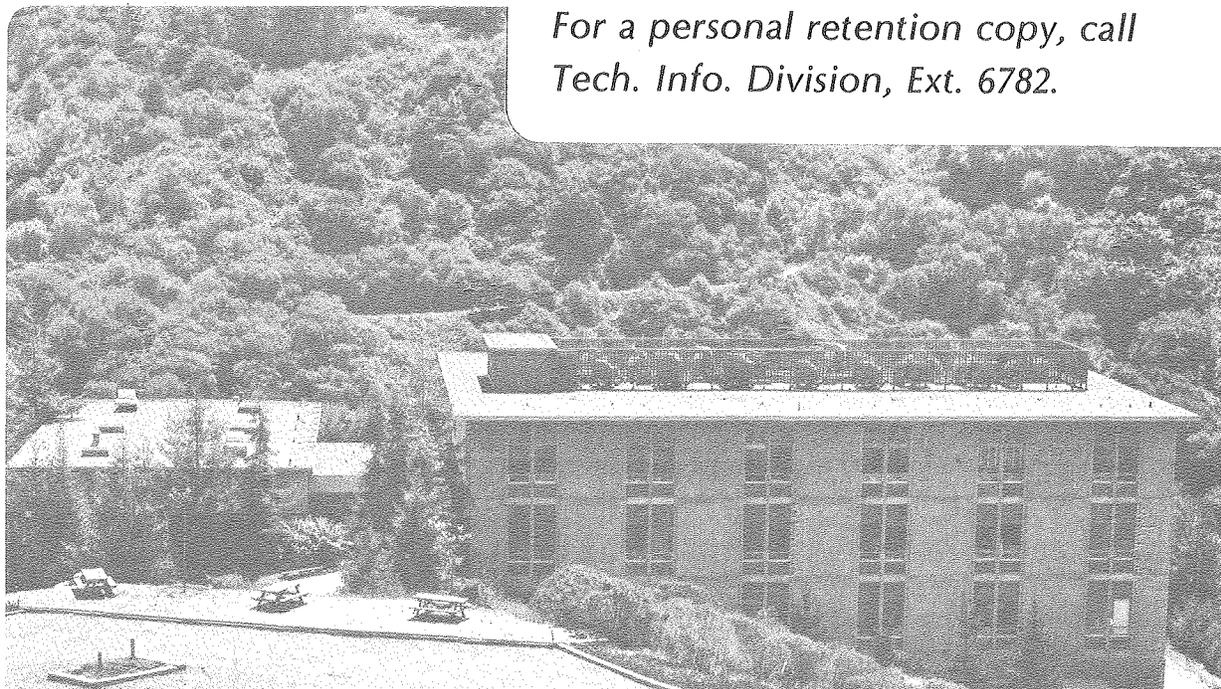
HIGH RESOLUTION NMR IN INHOMOGENEOUS MAGNETIC  
FIELDS: APPLICATION OF TOTAL SPIN COHERENCE  
TRANSFER ECHOES

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TITLE: High Resolution NMR in Inhomogeneous Magnetic Fields:  
Application of Total Spin Coherence Transfer Echoes

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#### ABSTRACT

The method of total spin coherence transfer echo spectroscopy is introduced and shown to give high resolution NMR spectra free of broadening due to magnet inhomogeneity. A single quantum proton spectrum of oriented acetaldehyde demonstrates the technique. Comparison with other spin echo techniques is made and applications to multiple quantum NMR are discussed.

## High Resolution NMR in Inhomogeneous Magnetic Fields: Application of Total Spin Coherence Transfer Echoes

Sirs:

The homogeneity of the static magnetic field is the most common limitation on the resolution of NMR spectra and a variety of spin echo techniques have been devised to extract high resolution information from inhomogeneously broadened samples<sup>1-9</sup>. In this note we demonstrate a novel method for recording high resolution spectra, which for a coupled spin system, gives transitions at the same frequencies and resolution as would be seen with an absolutely homogeneous field. The method uses multiple quantum coherence transfer echoes<sup>5</sup> and is applicable to both single quantum and multiple quantum spectra of coupled systems consisting of one or more spin species in liquids, liquid crystals or solids. Unlike previous methods, it is not restricted by the relative size of the shift differences and the spin-spin couplings<sup>4,7,8</sup>, it does not require two dimensional projections to obtain high resolution<sup>5,9</sup>, and it does not increase the number of transitions nor alter their positions<sup>6</sup>.

(Fig. 1 here)

As an illustrative example, Figure 1 shows single quantum proton spectra of a non-spinning 10 mm sample of acetaldehyde partially oriented in a nematic liquid crystal. Fig. 1(a) is the normal single pulse Fourier transform spectrum and shows the inhomogeneity of the magnetic field to be greater than a ppm. Figure 1(b) is the total spin coherence transfer echo spectrum and gives linewidths of  $\sim 4$  Hz ( $\sim 0.02$  ppm). The line positions are governed by both direct and indirect spin-spin couplings and a chemical shift difference and the spectral simulation in Fig. 1(c) shows that all are preserved. The linewidths obtained are independent of magnetic field homogeneity in the limit of negligible diffusion<sup>1,2</sup>.

To understand the essence of the technique consider a system of  $N$  coupled proton spins. The idea is to exploit the properties of the

unique N-quantum coherence, the total spin coherence, which connects the extreme eigenstates of the coupled spin system. In the resonant rotating frame (defined so that the sum of the chemical shifts is zero), this coherence evolves only under the inhomogeneous Zeeman term and independently of chemical shift differences and spin-spin couplings. By having the spins evolve for a period in this N-quantum coherence and then in any other n-quantum coherence, the inhomogeneous term can be completely removed from the n-quantum spectrum.

(Fig. 2 here)

Figure 2 is a general schematic diagram of pulse sequences for total spin coherence transfer echo spectroscopy. The total spin coherence is prepared by a propagator U acting on the equilibrium density operator. Evolution proceeds in the inhomogeneous field for a time  $nt_1/N$  where  $n = \Delta M$  (difference in Zeeman quantum numbers) is the order of the coherence we wish to observe. At this time a coherence transfer to the lines of order n takes place under the action of the homogeneous propagator W and evolution proceeds for the time  $t_1$ , at the frequencies of interest. At the end of  $t_1$  only that part of the coherence which spent period  $nt_1/N$  as  $nN$  quantum coherence and period  $t_1$  as  $n$  quantum coherence has amplitude independent of magnet inhomogeneity. The only modulation of the amplitude of this echo is due to the internal Hamiltonian acting during  $t_1$ . This modulation is monitored by mixing the coherence back to observable magnetization with the propagator V and detecting during  $t_2$ . Fourier transformation of  $S(t_1, t_2)$  gives the homogeneous spectrum along the  $\omega_1$  axis. No 2D data manipulation is necessary and in fact the spectrum of Fig. 1(b) was taken with sampling at  $t_2 = 0$  only. The multidimensional analog of total spin coherence transfer echo spectroscopy would correspond to a projection<sup>5</sup> of cross peaks which correlate the total spin transition with other totally symmetric transitions. When  $n \neq 1$  this would involve collecting data over two variable time dimensions in addition to  $t_2$ . The sequence presented here shows that this or any other projection is unnecessary.

The propagator  $U$  may be as simple as the sequence  $\pi/2-\tau/2-\pi-\tau/2-\pi/2$  or may be a selective excitation sequence<sup>10</sup>. The other propagators may be single pulses or more elaborate and selective pulse sequences. For the single quantum case ( $n = 1$ ), no mixing is necessary between  $t_1$  and  $t_2$  and Figure 1(b) was obtained with  $V = 1$ . When  $n \neq 1$  an advantage of more elaborate mixing propagators is that properly phased lines of known relative amplitude and homogeneous width may be obtained for multiple quantum transitions. Modulation of the relative rf phases of the propagators allows complete separation of the desired transitions of different orders and eliminates artifacts arising from nonidealities of the pulse sequence<sup>8</sup>. Quantitative aspects of line intensities, phases, widths, separation techniques and the role of diffusion will be presented in a full paper.

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## Captions:

Fig. 1 Removal of inhomogeneous broadening by total spin coherence transfer echo spectroscopy. (a) The single quantum Fourier transform proton spectrum of acetaldehyde in a nematic liquid crystal was taken in an inhomogeneous field and then (b) with the pulse sequence of Fig. 2. The simulation of this  $AB_3$  system is shown in (c) with parameters  $J_{AB} = 2.8$  Hz,  $\nu_{AB} = 1360.9$  Hz,  $D_{AB} = -179.0$  Hz,  $D_{BB} = 458.6$  Hz. The lines of E symmetry are absent because they do not correlate with the total spin transition.

Fig. 2 General sequence to use total spin coherence transfer echoes to produce multiple quantum spectra without inhomogeneous broadening. U is a preparation sequence for N-quantum (total spin) coherence. This evolves for a time  $nt_1/N$  at which time a pulse or sequence of pulses W transfers the total spin coherence to other n quantum coherence. At time  $t_1$  echoes are observed through transfer by V to single quantum coherence. Fourier transformation with respect to  $t_1$  gives a homogeneous n-quantum spectrum. For the spectrum in Figure 1(b), U was the sequence  $\pi/2-\tau/2-\pi-\tau/2-\pi/2$ , W was a  $\frac{\pi}{2}$  pulse, V was omitted,  $N = 4$  and  $n = 1$ .

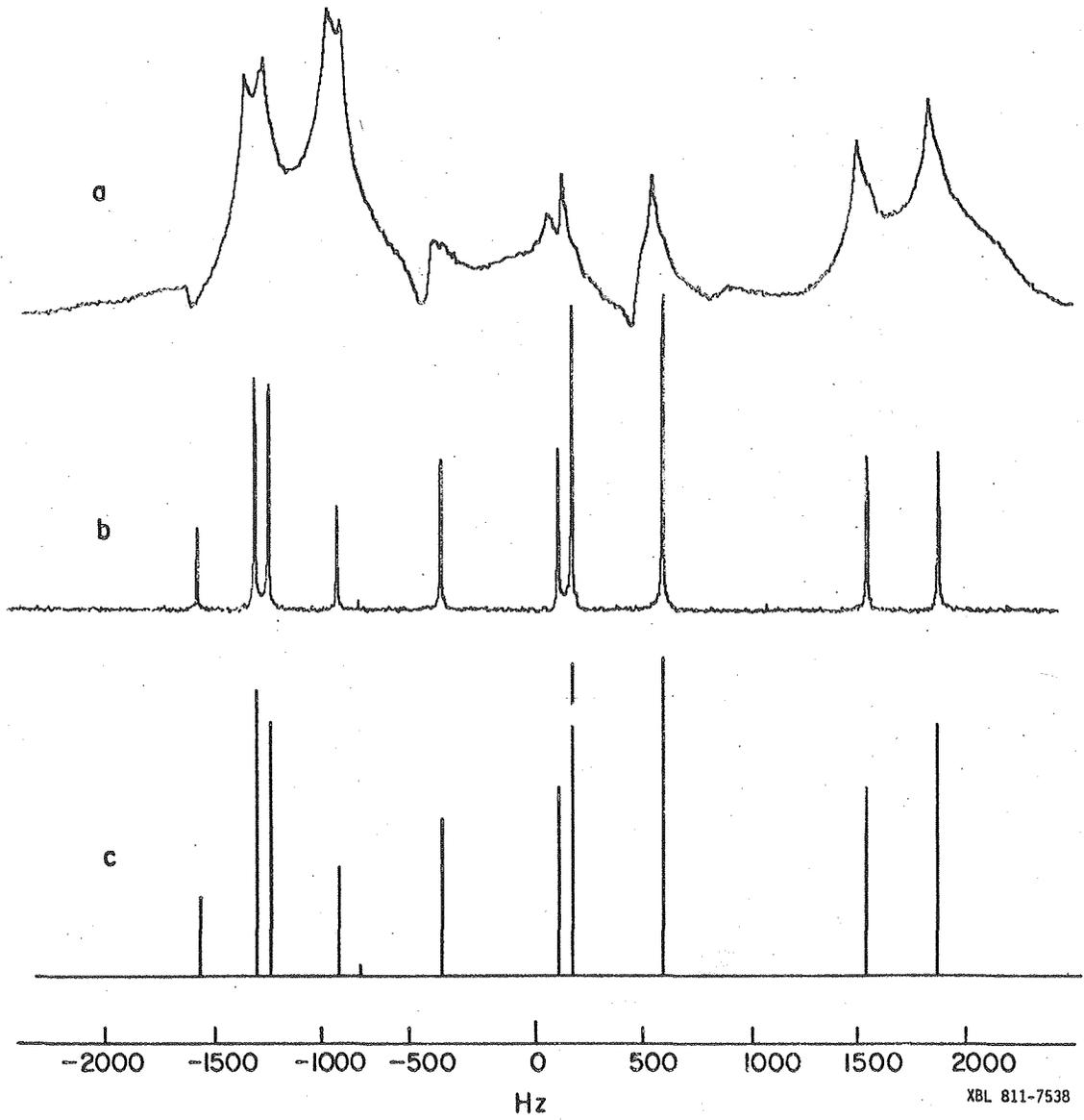
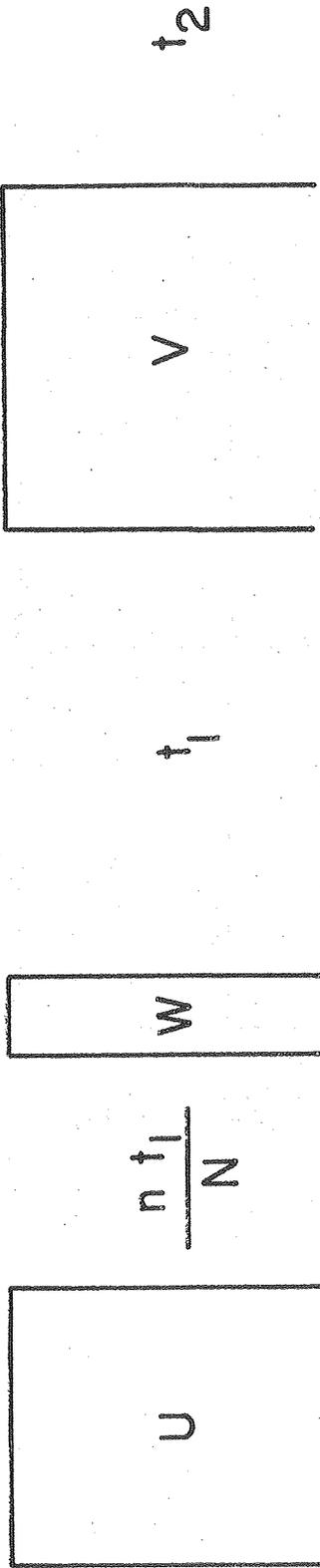


Figure 1



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Figure 2