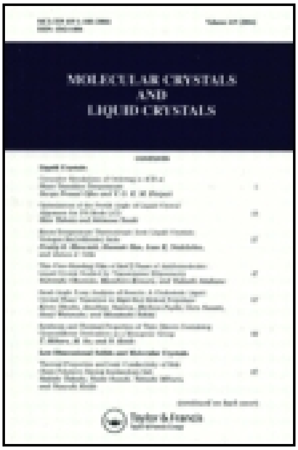

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Two Dimensional NMR Time Evolution Correlation Spectroscopy in Liquid Crystals[†]

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Two dimensional NMR time evolution correlation spectroscopy, where a correlation of NMR relaxation and line-shapes are performed, provides a powerful tool in characterization of systems involving two or more spin groups. This technique is applied to proton NMR study in liquid crystal para-azoxy anisole in the nematic phase at two different frequencies. Two different spin groups corresponding to methyl and phenyl protons are identified, as expected. The methyl proton spin lattice relaxation time shows a greater frequency dependence compared to phenyl protons.

INTRODUCTION

Liquid crystals often have spin groups which reside in different molecular environments. In such systems the transverse magnetization decay or the free induction decay (*FID*), which is a measure of spin-spin interaction,[1] often decays with several time constants. These time constants, or the spin-spin relaxation times (T_2) may be resolved if the T_2's differ by a factor of five or more. If the T_2's differ by less than a factor of five, then the *FID*

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may be partially resolved by using the two dimensional (2*D*) time evolution correlation spectroscopy,[2–4] which allows the reconstruction of an approximate *FID* characteristic of each spin group. In a typical nematic liquid crystal, such as PAA, one might expect nonexponential behavior in both spin-spin relaxation and spin-lattice relaxation, as molecular motions tend to average the dipolar interactions of the protons associated with the end groups while not having any substantial averaging effect on the phenyl protons. These effects give rise to the familiar three line spectrum of PAA, with the central line associated with the end chain protons and the doublet associated with the protons on the benzene rings. Nonexponential relaxation in PAA is rather slight[5] and has been overlooked by many investigators. This indicates that the linewidths of each component are nearly equal (exponential or Gaussian behavior of *FID*) and that cross relaxation between the two spin groups is at least comparable in magnitude to T_1 (exponential behavior of magnetization recovery). In the current work 2*D* time evolution correlation spectroscopy has been applied to resolve the slight nonexponential behavior of PAA.

In 2*D* time evolution correlation spectroscopy, the evolution of magnetization along the t axis (*FID* or of transverse decay) and along the τ axis (the longitudinal recovery) is recorded, producing a measure of the standard spin lattice relaxation time, T_1. However, instead of analyzing the longitudinal recovery at a single time window t at the beginning of the *FID*, analysis is carried out at a number of different t's. Each T_1 recovery is graphically decomposed into components and both the intercepts for $\tau = 0$ and T_1 of the components for different t's are obtained. The $\tau = 0$ intercepts for different t's make up the representative points on the *FID* corresponding to each component. These *FID*'s are then fitted to either exponential or Gaussian functions and the $t = 0$ intercepts corresponding to the true magnitude of each magnetization component is obtained. Thus, not only may each spin group be resolved, but also the important parameters such as T_2, T_1 and equilibrium magnetization for each spin group can be determined.

EXPERIMENTAL DETAILS

NMR measurements were carried out at 122°C on a spectrometer (designed and constructed in our laboratory) controlled by a Nicolet-1180 data system and 293A pulse programmer. T_1 was measured using the standard $90 - \tau - 90$, $180 - \tau - 90$ or saturation burst pulse sequences, at 10 and 30 MHz.

Para-azoxy anisole was synthesized[6] by dissolving 11 g of anisiline and 20.5 g acetonitrile in 200 ml of methanol. The temperature was adjusted to about 35-40°C and the pH to 9.5 (as measured with a glass electrode) by adding 2N sodium hydroxide. 68 ml of 30% hydrogen peroxide was then added slowly drop by drop maintaining the temperature at about 35–40°C and the pH at 9.5. The mixture was then kept aside for 2–4 hours, constantly stirring while maintaining the pH at 9.5. It was then cooled and the solid was filtered and washed with isopropyl alcohol. The solid was recrystallized 2–4 times from isopropyl alcohol and chromatographed over silica gel using chloroform as the mobile phase. The solid was recrystallized once again. The ultra pure PAA thus obtained was filled into a sample tube, which was then evacuated and sealed.

RESULTS

Transverse magnetization decay

The transverse magnetization decay is seen to be nonGaussian, as shown in Figure 1 for the 30 MHz data. The magnetization is a superposition of

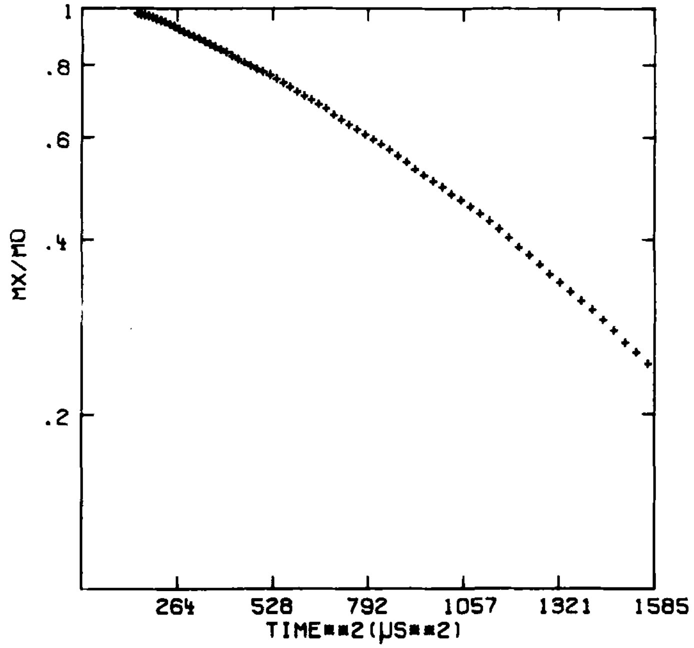

FIGURE 1 Free induction decay at 30 MHz.

the Fourier transform of the central line with that of the doublet, and the latter is modulated by a sinusoidal function whose frequency is determined by the line splitting. Thus, it is not possible to express this magnetization decay as a linear combination of exponential or Gaussian functions. The initial portion of the FID's were fitted to a Gaussian with T_2's equal to 26.7 ±0.2 μs ($M_2 = 2.72 \pm 0.1$ G^2) and 30.0 ±0.2 μs ($M_2 = 2.16 \pm 0.1$ G^2) for 10 MHz and 30 MHz respectively (see Table I).

Spin lattice relaxation in the laboratory frame

The recovery of the longitudinal magnetization in the laboratory frame was recorded at 20 different t values, with t's measured from the beginning of the *FID*. Each magnetization recovery was graphically resolved into two components (Figure 2) and T_1's as a function of t at 30 MHz are shown in Figure 3. Neither the shorter nor the longer T_1's are dependent on the window position; however, a considerable amount of scatter was present at both frequencies. The $\tau = 0$ intercepts obtained while decomposing the composite recovery are shown in Figure 4.

The above primary analysis of the magnetization recovery resolved the magnetization corresponding to two different spin groups with different T_1's rather well at 30 MHz. The resolution at 10 MHz was poorer. This resolution could be improved by an iterative procedure, referred to as secondary analysis.

TABLE 1

Proton Relaxation in PAA

				2D Time Evolution	
Expt.	Spin Group	Magnetization Fraction (%)	T_2 (μs) or T_1 (ms) (M_2^1 [G^2]	T_2 (μs) M_2 (G^2)	Magnetization Fraction
			$\underline{f = 30 \text{ MHz}}$		
FID (or T_2)	—	100	30.0 ±0.2 ($M_2 = 2.16 \pm 1$)		
T_1	Phenyl	—	1904 ±55	29.9 ±0.4 ($M_2 = 2.16 \pm .1$)	69.8 ±1
	Methyl	—	1223 ±7	27.2 ±1.0 ($M_2 = 2.6 \pm .2$)	30.2 ±1
			$\underline{f = 10 \text{ MHz}}$		
FID (or T_2)	—	100	26.7 ±0.2 ($M_2 = 2.72 \pm .1$)		
T_1	Phenyl	—	1795 ±45	27.5 ±0.5 ($M_2 = 2.57 \pm 1$)	66.8 ±2
	Methyl	—	797 ±59	27.2 ±1.0 ($M_2 = 2.60 \pm .3$)	33.2 ±3

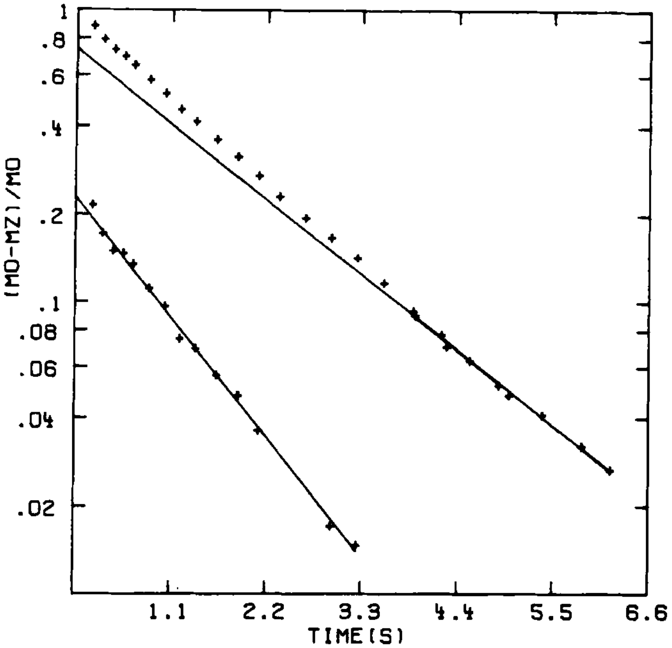

FIGURE 2 Typical decomposition of magnetization recovery (t = 14.6 μs, f = 30 MHz).

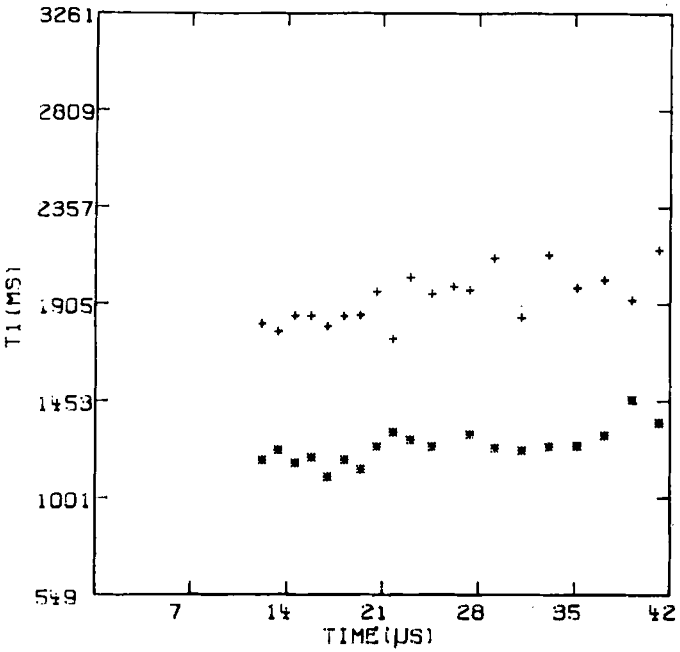

FIGURE 3 Proton T_1's versus t at 30 MHz.

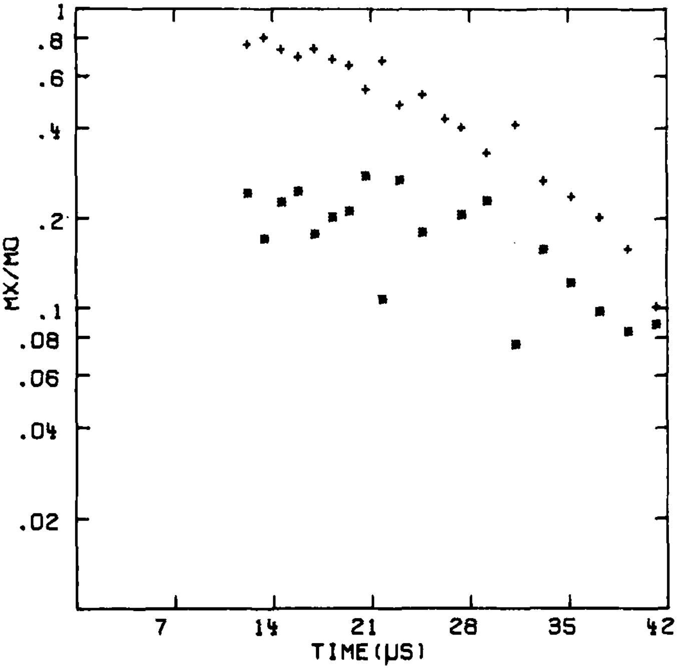

FIGURE 4 Reconstructed *FID*'s at 30 MHz.

In the secondary analysis the longer T_1's are averaged ($T_{1\,\mathrm{AVRG}}$ = 1795 ±45 ms at 10 MHz and 1904 ±55 ms at 30 MHz) and this $T_{1\,\mathrm{AVRG}}$ is used as the representative value of T_1 for the spin group with longer spin-lattice relaxation time. The graphical fitting was then repeated holding longer T_1 fixed to the average value. This procedure did reduce the scatter appreciably at both frequencies. The reconstructed *FID* after secondary analysis for 30 MHz is shown in Figure 5. Further iteration or tertiary analysis was carried out by averaging the shorter T_1 also, but this did not reduce the scatter any further for the data at either frequency.

Reconstruction of the FID from 2D NMR

In the reconstructed *FID* ($\tau = 0$ intercepts at different t's) analysis of both the *FID*'s were fitted to a Gaussian and the $t = 0$ intercepts were obtained. The $t = 0$ intercepts after normalization correspond to the fractions of the magnetization of each spin group.

Because PAA contains 8 phenyl protons and 6 methyl protons it would be reasonable to expect contributions to the magnetization corresponding to

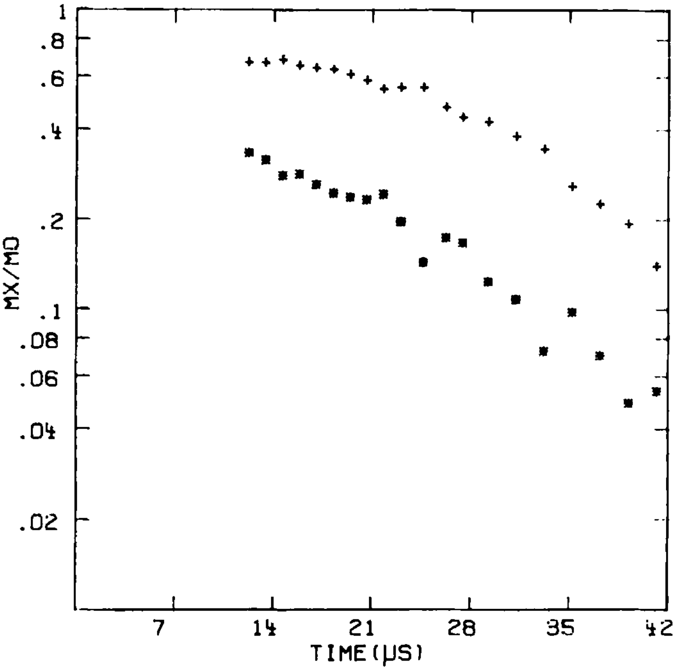

FIGURE 5 Reconstructed *FID*'s after secondary analysis at 30 MHz.

57% and 43% respectively. However, cross relaxation and other effects may give rise to further non-exponential recovery. The results of the present study are summarized in Table 1. The 2D analysis used here yields spin populations of 68% and 32% corresponding to phenyl and methyl protons respectively, which are reasonably close to the expected values. The phenyl proton T_1 is more or less independent of frequency, whereas the methyl proton T_1 shows rather significant increase with increase in frequency (see Table I).

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