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NMR Measurement of Transient Phenomena in Liquid Crystals†

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A method for measuring the time dependence of molecular orientation is presented. The molecular orientation is obtained from the nuclear free induction decay using the method of moments. This technique is useful for measuring a variety of transient phenomena with several applications to liquid crystals.

1 INTRODUCTION

In this paper we present a method of measuring a variety of transient phenomena with several applications to liquid crystals. The method uses pulsed NMR techniques to monitor molecular orientation as a function of time. Such techniques have proved to be extremely valuable in the study of liquid crystal systems. For example, the second moment of a proton magnetic resonance absorption line provides a measure of the degree of molecular order in a liquid crystal. This information may be used to determine the order parameter and its variation with temperature, etc. In the method discussed here, we do not determine the order parameter itself, but rather use the measured second moments to determine the time dependence of molecular orientation. It is this orientational dependence which is the interesting variable in many problems such as in the cholesteric-nematic transition in a nematic-cholesteric mixture. While the technique has much broader application, in what follows we shall use the example of an electric field induced cholesteric-nematic transition to clarify the discussion.

In many systems the response time of molecular order to the sudden change of an applied field is on the order of a few seconds, and, therefore,

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one can not use conventional NMR techniques. In our technique, we perform a pulsed NMR experiment in which the free induction decay (FID) is sampled many times during the change in molecular orientation. It should be noted that the free induction decay is not itself a direct measure of molecular orientation, and that it is necessary to use numerical analysis techniques to derive the second moment from the FID.

2 EXPERIMENTAL TECHNIQUES

Figure 1 shows a block diagram of the apparatus. The pulsed NMR spectrometer is free running so that the magnetization is sampled every t seconds, where t is slightly greater than the spin-spin relaxation time T_2 and much shorter than the spin-lattice relaxation time T_1. The resulting FID signal is phase-sensitively detected, and the output of the phase sensitive detector is sampled by a boxcar integrator operating in the delayed gate mode. The boxcar width (usually one or two microseconds) is much less than the duration of the FID. The output of the boxcar integrator is digitized and recorded on a signal averaging computer whose memory sweep period is greater than the total time of the transient phenomenon to be studied.

The timing of the experiment is controlled by the signal averager. In the work discussed here, a Nicolet model 1074[1] signal averaging computer was used. This instrument provides an output pulse at a fixed delay following the initiation of the sweep, and a second pulse which occurs when a selected memory address is reached in the measurement. These two cursor pulses are used to control the applied perturbing field (in our example, an ac electric field) for the experiment.

As an example, let us suppose that the boxcar gate width is set for one microsecond, the boxcar delay for 20 microseconds, and that the signal

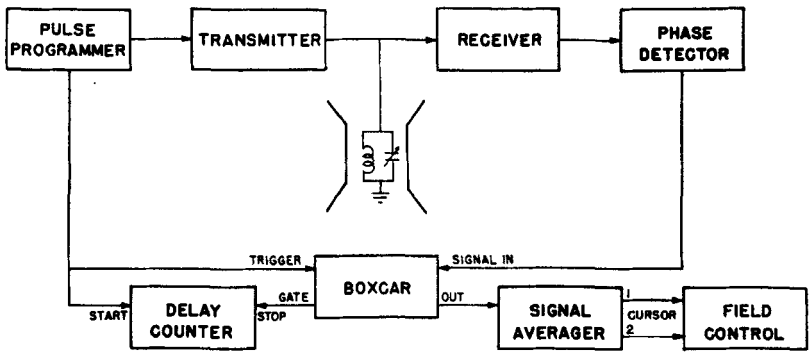

FIGURE 1 Block diagram of apparatus.

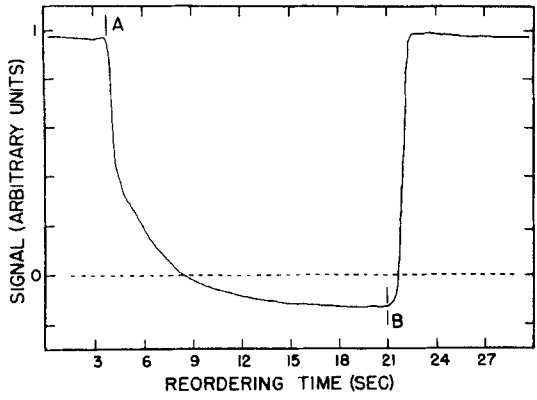

FIGURE 2 Typical signal averaging computer recording for one position along the free induction decay.

averaging computer is adjusted to record 1024 addresses with a dwell time of 30 milliseconds per address. Further, let us suppose that the first cursor pulse turns on the perturbing field, that the second cursor pulse turns off the perturbing field, and that the signal averaging computer is set to record 16 complete sweeps. For these parameters, the signal stored in the averaging computer will be the time response of a 1 microsecond interval of the FID 20 microseconds from the beginning of the FID in 30 millisecond intervals with a total time duration of approximately 30 seconds. After the series of 16 sweeps is completed the signal averager stops with the perturbing field turned off. At this time the signal averager memory is recorded (in our case, on a digital magnetic tape recorder), the memory cleared and the experiment repeated for a different boxcar delay time. In this manner, the time response of a number of points along the FID is recorded. Finally, a base line signal is recorded by adjusting the boxcar gate delay to a time long in comparison to T_2. Because the boxcar delay must be accurately set in order to correctly determine the second moments, the delay is adjusted using a digital period counter as shown in Figure 1.

Figure 2 shows the contents of the signal averaging computer for one point along the FID. These data are for an ac electric field induced cholesteric-nematic transition in a nematic-cholesteric mixture.

3 RECONSTRUCTION OF THE FID

The free induction decay signals are computer reconstructed from the signal averager recordings. The signal averager recordings are read into a matrix array in which the matrix row index is successive boxcar gate delay times,

and the column index is the signal averager memory location. In our example, if we had made measurements at 100 points along the free induction decay, we would then have a 100 by 1024 matrix. Denoting a typical element of this matrix by $Y(i, j)$, each element represents the amplitude of the free induction decay at the ith position along the free induction decay at the jth interval of time following the beginning of a signal averager sweep. The FID's are then reconstructed by holding j constant and indexing i. In this manner one obtains the amplitude of the free induction decay at successive positions i for a fixed time interval j. Thus, in our example we obtain 1024 100 point FID signals at 30 millisecond intervals.

The reconstruction of the FID data must be done with some care. Improper determination of the base line or of the boxcar gate delay has very strong effects upon the values of the second moment. The base line is determined by recording the signal amplitude with a boxcar gate delay much larger than T_2. This signal is then subtracted from each reconstructed FID signal to restore the base line. Several typical reconstructed FID's for the cholesteric-nematic example are shown in Figure 3.

The second moments are then extracted from the reconstructed FID signals using the power series expansion of Lowe and Norberg.[2] Because of the relatively small number of points along the FID that are sampled this is the appropriate method of determining the second moment, rather than a direct numerical Fourier transform to obtain the resonance absorption line shape. These numerical methods have been discussed in some detail elsewhere.[3]

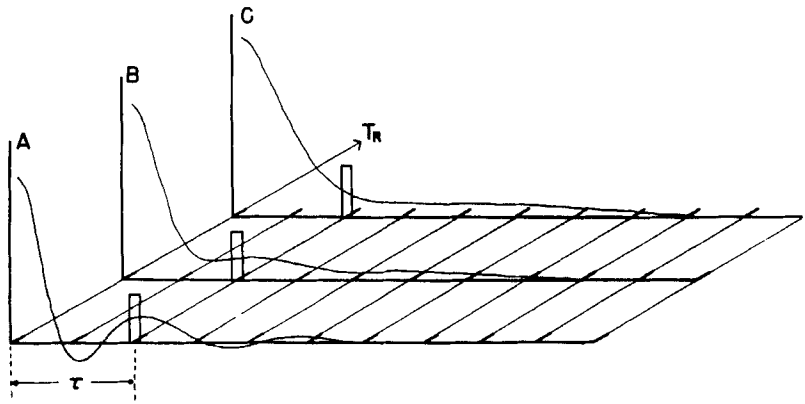

FIGURE 3 Typical reconstructed FID's showing time evolution in a cholesteric-nematic transition. These data are for the case of turning off an a.c. electric field at time $T_R = 0$ (curve A). The molecular reorientation then progresses as indicated by curves B and C. The boxcar gate delay is indicated by τ.

4 EXPERIMENTAL LIMITATIONS

There are several limitations which must be considered in an experiment of this kind. In particular, the time constants of the transient phenomenon which can be studied are limited by both T_1 and T_2. First, the time constant can not be so long as to introduce systematic errors due to electronic instabilities or magnetic field drift. Second, the free induction decay must be sampled very rapidly during the transient process with a sampling period longer than T_2. If T_2 is too long one has not only the problem of obtaining very few data points in the region of interest, but also, the effective integration time constant of the boxcar will be greatly increased by the low duty factor. Further, in some systems there are also orientationally dependent T_1's. This leads to a distortion of the FID if there is significant orientational averaging in the experiment. Fortunately, for many liquid crystal systems this is not a significant problem.

5 CONCLUSION

The technique outlined above provides a simple method of monitoring molecular orientation in a variety of systems. In subsequent papers we shall discuss applications of this technique to nematic-cholesteric mixtures and to molecular reorientation of a nematic liquid crystal in the presence of competing magnetic and electric fields.

References

1. Nicolet Instrument Corp., Madison, Wisc. Note: A 9-bit model SD-72A digitizer and a model SW-71B sweep control unit were used in this work.
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3. A. M. Fuller and C. E. Tarr, *Mol. Cryst. Liq. Cryst.*, **25**, 5 (1974).