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Measurement of Spin Relaxation in Complex Systems

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A complete exploitation of NMR in the study of molecular dynamics would require an analysis of the fluctuating local fields at every spin in the molecule. One would like, for example, to measure the longitudinal relaxation rate of each species. When the spins are coupled together, one cannot identify each line in the NMR spectrum with a particular spin, but studies of the longitudinal relaxation behavior of each line can still yield the desired information.

Various experimental methods[1-7] have been used to measure longitudinal relaxation of individual lines, but they all suffer to some extent from either or both of two major defects: a) the initial state from which the spins relax is complicated or not well characterized, b) the spin system is perturbed by measurement of the recovery to equilibrium. In this letter we describe a new method which avoids both of these problems entirely.[8]

The initial state of the spins is established by a non-selective[9] 180° pulse of the type used in standard T_1 measurements. After a time τ, a non-selective 90° pulse is applied and the entire free induction decay following this pulse is recorded. From the Fourier transform of this decay,[10] according to a well known theorem,[11] one obtains the partly relaxed spectrum. The history of this spectrum as a function of τ gives the full unperturbed relaxation behavior.

Figure 1 is a superposition of such Fourier transformed free induction decays from a 1.5×10^{-3}M solution of $FeCl_3$ in equal volumes of acetone and water, as a function of τ. The spectra have been displaced isometrically proportional to the logarithm of the pulse spacing to display the characteristic recovery functions. The induction decays were obtained with an extensively modified Varian HR 60 spectrometer operating at 60 MHz in conjunction with a modified Northern Scientific 544 signal averaging computer. The 90° pulse duration was 50 μsec. The Fourier transforms of the digitally accumulated decays were performed on the LRL 6600 computers. As expected, the water protons relax more rapidly than the acetone protons. Similar results are obtained for other systems, e.g. the protons of ethyl alcohol.

The limiting factor on frequency resolution in this experiment is the static field inhomogeneity, exactly as for ordinary slow passage field sweep experiments. However, a problem arises if the longitudinal relaxation rates are comparable to the inhomogeneity broadening, $1/T_2^*$. In this case, errors in setting the initial pulse produce an initial transverse magnetization which persists long enough to interfere with the induction decay following the 90° pulse. In our experiments, the interfering transverse magnetization was destroyed by producing a temporary, large static field gradient between the 180° and 90° pulses.

Apart from its main purpose, this experiment could be useful in the analysis of equilibrium spectra containing overlapping lines. For example, an exact accidental superposition of two transitions cannot be recognized in the equilibrium spectrum but becomes evident in our experiment through the time development of intensity of the two transitions.

The procedure demonstrated above may be applied to measure differential transverse relaxation times and differential diffusion coefficients. A Carr-Purcell[12] pulse sequence, as routinely employed for the measurement of transverse relaxation times, produces spin echoes, each of which may be Fourier transformed to reveal the partially relaxed spectra. The well known method of determining diffusion coefficients by performing spin echo experiments in the presence of a pulsed field gradient[13] may be combined with the Fourier transform method to permit the simultaneous measurement of diffusion coefficients of chemically shifted species.

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Figure Caption

Figure 1. Longitudinal proton relaxation surface for 1.5×10^{-3} M $FeCl_3$ in a 1:1 acetone-water mixture. Each spectrum results from the Fourier transform of the free induction decay following the second pulse of a 180°-90° pulse sequence. The time interval between pulses is indicated on the right-hand edge of the spectrum. The spectra are displaced isometrically on a logarithmic scale.

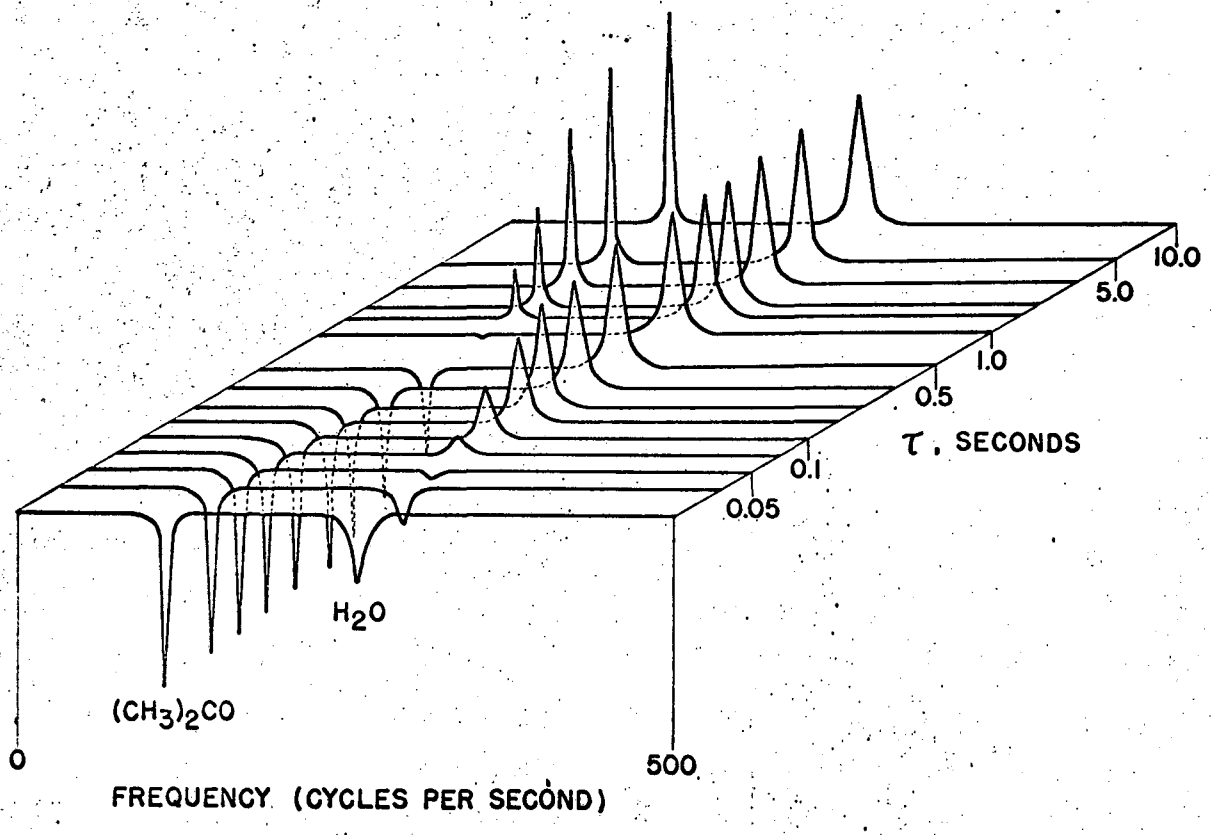

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Fig. 1

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