1.10: Relaxation Effects on NMR Signals

It should be emphasized that relaxation begins as soon as the nuclei absorb energy from the rotating field vector. Obviously, if T1 and T2 are both extremely short, the signal strength at a given field value will be very small because both longitudinal and transverse relaxation destroy the component of magnetization in the X, Y directions. On the other hand, if the relaxation times are long, other effects are noted. For example, if T_1 is very long, a "saturation" effect may be noted with respect to the signal strength because the energy absorbed by the nuclei from the oscillator is not readily dissipated to the surroundings. In this situation, the nuclei reach an equilibrium distribution between their magnetic quantum states which is determined by the relaxation time T_1. When T_1 is short, the nuclei remain more or less at thermal equilibrium with their surroundings and the absorption of energy then depends primarily on T_2.

It should be clear that if one were suddenly to turn off the oscillator in the middle of a resonance signal, the signal would not cease at once because the rate of loss of magnetization in the X, Y directions depends on both T_1 and T_2. This sort of effect leads to pronounced differences in the appearance of NMR signals, depending on the rate of sweep, as illustrated in Fig. 1-8. A fast sweep produces a signal peak followed by a succession of diminishing peaks, which are often called "relaxation wiggles." A slow sweep gives a more symmetrical peak with perhaps only a trace of the relaxation wiggles. The "envelope" of relaxation wiggles arises in the following way. The first peak of a plot of signal vs. magnetic field represents the point at which the precession frequency of the nuclei is equal to the oscillator frequency. As the field sweep continues from this point, the precession frequency increases and, hence, the precessing macroscopic resultant goes out of phase with the oscillator while the X, Y magnetization diminishes by longitudinal and transverse relaxation. Whenever the precessing macroscopic vector gains 360" on the rotating field vector, it comes into phase again with that vector and picks up an increment of X, Y magnetization which produces an increase in the signal strength. Repetitions of this process give a series of signal pulsations which finally cease when transverse relaxation is complete. Obviously, the slope of the decay envelope of the relaxation wiggles[4] is a measure of T_2. It has been shown by comparison of the decay envelopes of their relaxation wiggles that hydrogens in different chemical environments (as the methyl and phenyl groups of toluene) have quite different T_2 values.

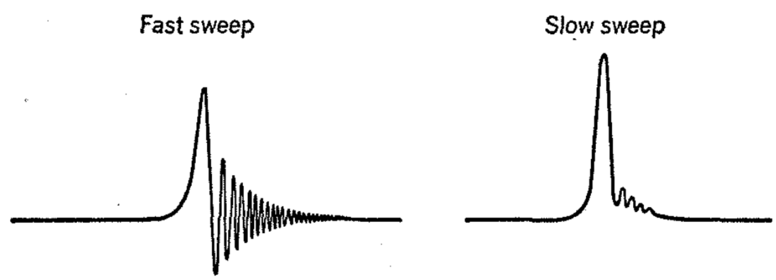

Fig. 1-8. Relaxation effects in fast and slow sweeps through the benzene resonance. Fast sweep displays "relaxation wiggles."

4 G. W. Nederbrogt and C. A. Reilly, J. Chem. Phys., 24, 1110 (1956); C. A. Reilly and R. L. Strombotne, J. Chem. Phys., 26, 1338 (1957).