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NUCLEAR SPIN-LATTICE RELAXATION MEASUREMENTS BY TONE-BURST MODULATION

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The purpose of this Letter is to explain a method of accurately measuring both long and short nuclear spin-lattice relaxation times (T_1) in liquids and solids using cw NMR spectroscopy. Cw NMR is used primarily for line-shape studies although relaxation investigations are sometimes carried out, usually by one of three methods¹: (a) a direct method in which the recovery of the signal is observed in a weak rf field H_1 , after saturation in a strong H_1 ; (a) a progressive-saturation method in which the steady-state signal is measured as a function of rf field strength; (3) a transient method, in which the spin system is saturated at resonance, quickly moved off resonance for a time τ , and then swept back through the resonance to observe the magnetization recovered in time τ . Method (1) has the disadvantage that the relaxation is occurring in the presence of H_1 , requiring a correction factor; also H_1 must be switched from a high to a low value. Method (2) requires an accurate measurement of H_1 and is only useful for simple line shapes, either Lorentzian or Gaussian. Method (3) is excellent for long relaxation times (10 sec or greater) where the spin system is easily saturated, but it is not readily adaptable to measure short-er times.

The one existing method which gives reliable results for both long and short relaxation times is the pulsed-NMR technique. This method does, however, require a different spectrometer and usually is less sensitive to weak-signal spin systems.

The new method we propose for the measurement of T_1 is easily incorporated into a standard cw spectrometer at relatively small expense, and gives results independent of rf field strength, modulation field strength, or modulation frequency. In situations where signal enhancement is needed, automatic, unattended operation is possible with time-averaging computers, waveform editors, or repetitive-scan storage oscilloscopes.

The heat of the instrumentation needed, and the only device not common to most laboratories, is a tone-burst generator, which essentially gates an oscillator on and off for a preset number of cycles. We use a General Radio Model 1396 tone-burst generator, while our basic wide-

line NMR spectrometer is a Varian Model 4200B. The input to the tone-burst generator is an audio-frequency triangle wave (a sine wave also works), provided by a Wavetek Model 111 oscillator, while the tone-burst signal is fed to the NMR probe's modulation coils through an amplifier which gives an output current proportional to the input voltage. The spin signal, after rf detection, may be displayed on an oscilloscope and photographed, or added repetitively in a signal enhancement device, triggered at the beginning of each tone burst. Also, a second modulation signal may be added through our amplifier if phase detection is desired.

The adjustable parameters in the experiment are set as follows: The tone-burst gate is set closed for three or four T_1 's (i.e. until the magnetization is essentially fully recovered); the modulation field strength H_m is made much larger than the linewidth; and the combination of rf field strength H_1 and modulation frequency ν_m are adjusted to lead to a nonadiabatic signal response (the adiabatic case will be discussed later). These requirements may be written² as

$$\nu_m H_m \gg \gamma H_1^2, \quad H_m \gg \delta H, \quad \nu_m \gg (T_1)^{-1}, \quad (1)$$

where δH is the linewidth and γ is the nuclear gyromagnetic ratio. Finally, the dc magnetic field is adjusted such that the signal amplitude peaks are equally spaced in time ($\frac{1}{2}\nu_m$ between any two peaks).

Designating the sequence of amplitude peaks by $M_0, M_1, M_2, \dots, M_n, \dots$, the value of the $(n+1)$ st peak just before sweeping through, M_{n+1}^- , is related to the n th peak just after sweeping through, M_n^+ , by

$$M_{n+1}^- = M_n^+ + (M_0 - M_n^+)(1 - e^{-\tau/T_1}), \quad (2)$$

where $\tau = \frac{1}{2}\nu_m$, the time between two peaks. We will define the reduction in signal amplitude immediately after a sweep by

$$M_n^+ = M_n^- (1 - X). \quad (3)$$

If Eq. (1) holds, and the spin transition probability is proportional to M_n^- , then we can apply standard first-order time-dependent perturba-

tion theory³ to find, for spin $\frac{1}{2}$,

$$X = \frac{\pi}{4} \frac{\gamma H_1^2}{\nu_m H_m} \quad (4)$$

The line-shape function does not enter Eq. (4) because X is essentially a ratio of magnetizations. By manipulation of finite series we can combine Eqs. (2) and (3) to get

$$M_n = M_0 \frac{1 - e^{-\tau/T_1} \{1 - X(1-X)^n e^{-n\tau/T_1}\}}{1 - (1-X)e^{-\tau/T_1}}, \quad (5)$$

where we have replaced M_n^- by M_n , the measured signal amplitude. After many modulation cycles the amplitude reaches a constant value M_∞ , given from Eq. (5) by

$$M_\infty = M_0 (1 - e^{-\tau/T_1}) / [1 - (1-X)e^{-\tau/T_1}]. \quad (6)$$

For computation purposes we combine Eqs. (5) and (6) to get

$$\ln(M_n - M_\infty) = \ln(M_0 - M_\infty) + n \ln[1 - (M_0/M_\infty)(1 - e^{-\tau/T_1})], \quad (7)$$

so that a plot of $\ln(M_n - M_\infty)$ vs n has an intercept $I = \ln(M_0 - M_\infty)$ and a slope $S = \ln[1 - (M_0/M_\infty)(1 - e^{-\tau/T_1})]$. Then, combining the equations for S and I , the relaxation time T_1 is given by

$$\frac{\tau}{T_1} = \ln \left\{ \frac{1 + M_\infty e^{-I}}{1 + M_\infty e^{-I} S} \right\}. \quad (8)$$

If desired, X may be calculated from

$$X = (1 - e^S) / (1 + M_\infty e^{-I} e^S) \quad (9)$$

and allows calibration of the rf field H_1 by Eq. (4). If desirable for accuracy, M_∞ may be quickly measured separately by leaving the modulation free-running (tone-burst gate open continuously).

We have applied this method and analysis to a wide variety of liquids and solids, with T_1 's ranging from 0.01 to 40 sec and linewidths from several milligauss to several gauss. There appears to be no dependence of T_1 upon H_m , ν_m , or H_1 as long as Eq. (1) is satisfied. However, there is a time constant associated with the decay of the field in a standard metal NMR probe which distorts the field for fast sweeps and practically limits measurements of T_1 to the region greater than a few milliseconds. This is not a

fundamental problem; a probe constructed largely of dielectric materials would remove this limitation.

An important feature of this method is that all necessary information may be obtained in one sequence of amplitude peaks, and many sequences may be added together if necessary to improve the signal-to-noise ratio. Since the opening of the tone-burst gate will trigger an oscilloscope or time-averaging computer, the apparatus may be left unattended, perhaps overnight, while data are being collected.

In Figs. 1(a)-1(c) are shown M_n sequences in liquid H_2O , powdered CdO , and Ho^{3+} -doped single-crystal CaF_2 , respectively. The linewidths of these substances span a range of a few milligauss to about 5 G. The CdO data (Cd^{113} spins) are the result of 7000 scans added on a time-averaging computer. The computer was used in the other cases, also, for recording purposes. However, for strong signals the data may be displayed on an oscilloscope and photographed.

For completeness, we give the results for the adiabatic case also, i.e., the case in which

$$\gamma H_1^2 \gg \nu_m H_m \gg \delta H / T_1. \quad (10)$$

For n odd,

$$M_n^{ad} = M_0^{ad} \frac{1 - e^{-\tau/T_1} (1 + 2e^{-n\tau/T_1})}{1 + e^{-\tau/T_1}}, \quad (11)$$

and for n even,

$$M_n^{ad} = M_0^{ad} \frac{1 - e^{-\tau/T_1} (1 - 2e^{-n\tau/T_1})}{1 + e^{-\tau/T_1}}. \quad (12)$$

Here the magnetization after many cycles is seen to be

$$M_\infty^{ad} = M_0^{ad} (1 - e^{-\tau/T_1}) / (1 + e^{-\tau/T_1}), \quad (13)$$

a result already known and used.^{4,5} For the adiabatic case, a plot of $\ln(M_n^{ad} - M_\infty^{ad})$ vs n for even or odd n gives the slope as $-\tau/T_1$. Experimentally, this case is more difficult to achieve than the nonadiabatic one, especially in solids, because of the high rf field required and the uncertainty of complete adiabaticity.

Finally, it should be mentioned that the methods described in this paper are not limited to NMR but, with minor modifications, are applicable to EPR; such experiments are in progress.

We would like to acknowledge the generosity of

FIG. 1. Actual recorder tracings of data for M_n vs n from time-averaging computer. The adjustable parameters are given in each part. (a) 50 sequences added; $\nu_0 = 4$ MHz; $H_1 = 0.040$ G; $H_m = 3.5$ G; $\nu_m = 7.0$ cps. (b) 7000 sequences; $\nu_0 = 4$ MHz; $H_1 = 0.14$ G; $H_m = 17$ G; $\nu_m = 30$ cps. (c) 150 sequences; $\nu_0 = 10$ MHz; $H_1 = 0.30$ G; $H_m = 50$ G; $\nu_m = 30$ cps. See text for further details.

Dr. Carl Verber of Battelle Memorial Institute for lending the water and CaF_2 samples after measuring their relaxation times by pulsed NMR. Our results for these samples agree with pulsed-NMR results within experimental error. The only other check of our method is for Cd^{113} in CdO at $4.2^\circ K$, which has a T_1 long enough to also measure by the transient method (3) mentioned earlier; the results agree within 10%.

¹For a discussion of these methods, see E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, London, England, 1958), p. 107ff.

²For a discussion of adiabatic passage, see A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, England, 1961), pp. 34 ff and 65 ff.

³Ref. 2, pp. 27 ff.

⁴L. E. Drain, Proc. Phys. Soc (London) **A62**, 301 (1949).

⁵A. G. Redfield, Phys. Rev. **101**, 67 (1956).