Title

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Authors

Markley, John L.
Horsley, William J.
Klein, Melvin P.

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LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

SPIN LATTICE RELAXATION MEASUREMENTS IN SLOWLY RELAXING COMPLEX SPECTRA

John L. Markley*, William J. Horsley, and Melvin P. Klein

Laboratory of Chemical Biodynamics
Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

Recently, it was demonstrated that the longitudinal relaxation rates of all lines in a high-resolution NMR spectrum could be measured simultaneously.[1] This method (I) employs a non-selective 180° pulse which inverts the entire spin system; at a variable time t_1 later, a non-selective 90° pulse samples the magnetization. The Fourier transform[2] of the following induction decay gives the partially relaxed spectrum. A field gradient pulse between the rf pulses suppresses echo formation. A time t_r equal to 5 T_1's must intervene between each pulse pair to assure a (99%) return to thermal equilibrium. Such measurements on weak samples with long T_1's require frustratingly long times. (Furthermore, one generally must overestimate t_r for unknown samples to ensure complete relaxation.)

An alternative method (II) which permits significantly faster determination of long T_1 values and which requires no _a priori_ knowledge of their magnitudes measures the return to equilibrium of the spins from a saturated state.[3] A burst of non-selective pulses saturates the system; again at times t_1 later a 90° pulse samples the magnetization for Fourier transformation. A gradient pulse is interposed as before. Method II is advantageous because the system may be resaturated immediately following the collection of the free induction signal.

The equations used to determine T_1 by the two methods are: (I), $\ln(M_0 - M_i) = \ln(2M_0) - (t_i/T_1)$; and (II), $\ln(M_0 - M_i) = \ln M_0 - (t_i/T_1)$, where M_0 is the equilibrium magnetization and M_i is the magnetization at time t_i. T_1 values determined by both methods will have the same accuracy if the errors in M_0, M_i, and t_i are equivalent. the spectral inversion in I effectively doubles the signal-to-noise ratio of the M_i measurements. Four times as many passes are required to achieve equivalent ratios by II. The minimum times required to execute T_1 measurements with equivalent accuracy are as follows.

For I,

$$\text{time(I)} = (t_r + t_d) + \left[n(t_r + t_d) + \sum_{1,n} t_i\right], \tag{1}$$

where t_r is the wait time and t_d the time allocated to digitize the free induction decay. The first term of (1) represents the time required to determine M_0; the second term is the time for collecting the partially relaxed spectra. In a typical experiment consisting of ten data points distributed over equal logarithmic intervals, the sum of the t_i terms equals 2.5 T_1. Substitution of this value into (1) with $t_r = 5\ T_1$ gives,

$$\text{time(I)} = 57.5\ T_1 + 11\ t_d. \tag{2}$$

For II,

$$\text{time(II)} = 4(t_r + t_d) + 4\left[n(t_b + t_d) + \sum_{1,n} t_i\right], \tag{3}$$

where t_b is the duration of the saturating burst. The two terms are analogous to those in (1). Using the same ten-point distribution,

$$\text{time(II)} = 30\ T_1 + 44\ t_d + 40\ t_b. \tag{4}$$

Equations (2) and (4) are plotted in Fig. 1 using $t_d = t_b = 1$ sec. A 1-sec digitizing time yields 1 Hz spectral resolution. Experimentally we find that a 0.5 sec burst of 250° pulses at 10 msec intervals reduces M_0 by 60-80 dB. With these conditions, Fig. 1 shows that II is faster than I when $T_1 = 2.7$ sec. The ratio time(I)/time(II) shown in the upper part of Fig. 1 shows an asymptotic advantage of II by a factor of 1.9. For 0.1 Hz resolution, $t_d = 10$ sec, and II is faster than I when $T_1 = 13.5$ sec.

Since those nuclei that have long T_1 values (e.g. ^{13}C, ^{15}N, ^{31}P) yield weak signals requiring extensive averaging, the nearly two-fold time saving afforded by II is useful. Measurement of the long (11 sec) T_1's of ^{31}P in dilute (0.1 M) biological phosphorus compounds requires 3 hrs by I and 1.5 hrs by II. Agreement between T_1 values obtained by the two methods is within experimental error.

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[1] R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, J. Chem. Phys. <u>48</u>, 3831 (1968).

[2] R. R. Ernst, and W. A. Anderson, Rev. Sci. Instr. <u>37</u>, 93 (1966).

[3] N. Bloembergen, <u>Nuclear Magnetic Relaxation</u> (Benjamin, New York, 1961), p. 72.

[4] White noise could be used as an alternative means of saturation. An analysis of noise saturation is given by R. R. Ernst, J. Mag. Res. **3**, 10 (1970).

Figure Caption

Fig. 1. Bottom: The minimum comparable times required to determine T_1 by Method I (spin-inversion) and Method II (spin saturation) plotted as a function of T_1. The times are calculated using Eqs. (2) and (4) assuming a saturating time t_b of 1 sec and a digitizing time t_d of 1 sec. Top: The relative advantage of Method II over Method I (time(I)/time(II) as a function of T_1 for a 1-sec saturation time and for digitizing times of 1 sec (1 Hz resolution) and 10 sec (0.1 Hz resolution).

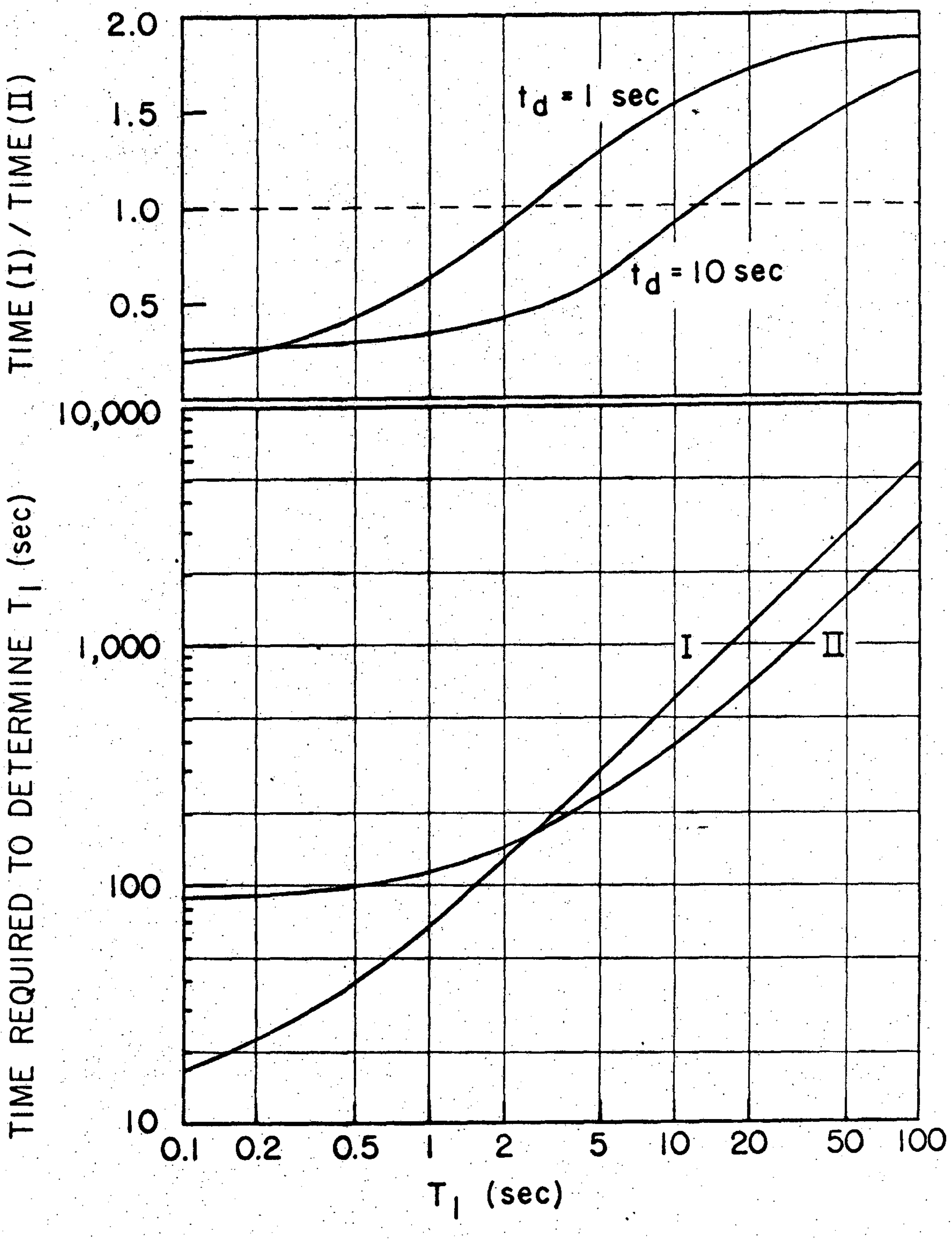

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Fig. 1

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LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720