

Spin-Lattice Relaxation Times by Progressive Saturation. Application to an AB Spin System

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MANY n.m.r. techniques have been devised for the measurement of spin-lattice relaxation times T_1 . These may be divided into two main classes: those using conventional high-resolution n.m.r. spectrometers, and those based on pulse methods, such as spin-echo experiments. Both these techniques have their disadvantages; the former in that auxiliary equipment such as a fast-response recorder is required, and the latter in that normally only an overall T_1 is obtained for all the transitions of a given nuclear species. We report a new method of measuring T_1 , using a high-resolution spectrometer with no ancillary equipment, and giving individual relaxation times for each transition.

It has been shown¹ that, even for a complex second-order spin system, thermal relaxation between any pair of energy levels i and j (in the absence of degeneracies) occurs according to the equation:—

$$\Delta n_{ij} = \Delta n_{ij}^0 / (1 + 2P_{ij}T_1^{ij}), \quad (1)$$

where Δn and Δn^0 are the equilibrium population differences in the presence and absence (respectively) of the radio-frequency field H_1 , P is the H_1 -induced transition probability, and T_1^{ij} is a relaxation time specific to the transition ij . This time depends in a complex way on all the relaxation probabilities of the spin system, since restoration of the equilibrium population difference between levels i and j can be effected *via* many routes round the energy-level system

in addition to the direct relaxation between i and j . Measurement of the different T_1^{ij} for various transitions in the system thus gives information about relaxation mechanisms.

Our method of measuring values of T_1^{ij} requires only that the absorption envelopes of the individual transitions ij do not show appreciable overlap. The method is based on the expression for the e.m.f., V , giving rise to the measured signal on the spectrometer recorder²:

$$V_{ij} \propto \gamma H_0 n_{ij} P_{ij} / H_1 \quad (2)$$

The transition probability P_{ij} is given by

$$P_{ij} = \gamma^2 H_1^2 g(\nu) Q_{ij} / 4, \quad (3)$$

where $g(\nu)$ is the line-shape function (usually Lorentzian, although its exact form is irrelevant to this discussion), and Q_{ij} is the square of the matrix element of I_+ (the shift operator) between i and j . Since Δn^0 is almost exactly the same for all transitions of a given type of nucleus, equations (1), (2), and (3) show that at constant H_0 and γ ,

$$V_{ij} \propto H_1 g(\nu) Q_{ij} / [1 + \gamma^2 H_1^2 g(\nu) Q_{ij} T_1^{ij} / 2]. \quad (4)$$

Now peak-heights are given by V when $\nu = 0[V(0)]$; with this substitution, equation (4) may be rearranged to give

$$H_1 / V_{ij}(0) = \gamma^2 H_1^2 T_1^{ij} / 2B + 1/B Q_{ij} g(0), \quad (5)$$

where B is a constant containing instrumental factors and is proportional to the number of nuclei/ml. of sample. Thus by measuring peak heights for increasing values of H_1 (going through saturation of the line) and plotting a graph of $H_1 / V_{ij}(0)$ against H_1^2 , a straight line is obtained with slope proportional to T_1 . Absolute values of T_1 may be produced if a calibration of the instrument is carried out with a sample of known T_1 ; thus there is no need to know the absolute value of H_1 —only measurement of a quantity proportional to H_1 is required. Most spectrometers already provide some sort of calibration of their H_1 control, although we found it necessary to recalibrate our control by measuring the voltage produced across the potentiometer of the audiofrequency oscillator which supplies H_1 (by modulation of the 100 MHz centreband) for a Varian Associates HA-100 spectrometer.

We have investigated the relative values of T_1 for the weak outer and stronger inner lines of several AB spectra. The Figure shows the plots obtained for the low-field pair of lines in the proton resonance spectrum of 2,3-dibromothiophen (neat liquid plus a little tetramethylsilane). The ratio $R = T_1(\text{outer}) / T_1(\text{inner})$ is found to be 1.318; similarly the value $R = 1.314$ was found from the high-field pair of lines. This ratio depends on the relaxation mechanism for the system. It can be shown that, if intramolecular (AB) dipole-dipole effects provide the only relaxation mechanism, $R = 1.285$ in this particular case; an identical value for R is obtained if relaxation is by random intermolecular fluctuating magnetic fields which are isotropic, equal, and completely correlated at the two nuclei. The latter case is

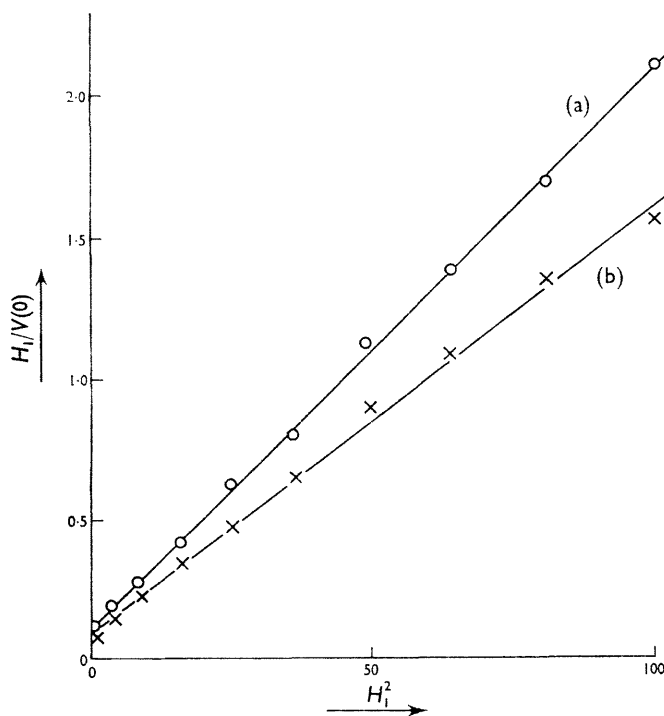


FIGURE. Least-squares lines and experimental points for the plots of $H_1/V(0)$ against H_1^2 for the low-field (a) outer and (b) inner lines of the AB proton spectrum of 2,3-dibromothiophen.

held to be unlikely. The observed result is close to $R = 1.285$ but differs from it by more than the expected error. We suggest that the intramolecular dipole-dipole mechanism is dominant in the case studied, though it is not the only mechanism present. Noggle³ has also studied the relaxation of 2,3-dibromothiophen (but in CS_2 solution) using a saturation-recovery technique; he found if inter- and intra-molecular dipole-dipole interactions form the

only relaxation mechanisms, the results were best fitted if the intramolecular contribution is 55% of the total.

We feel that our novel technique for measuring T_1 is instrumentally simple, accurate and will prove to be applicable to many cases. We believe it to be superior in many cases to the saturation method, which only measures $\sqrt{T_1 T_2}$ directly.⁴

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⁴ A. L. Van Geet and D. N. Hume, *Analyt. Chem.*, 1965, **37**, 979.