Determination of the Transverse Relaxation Time of Nuclear Magnetic Moments

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We propose a new method of determining the transverse relaxation time from the shape of the magnetic resonance signals from atomic nuclei. In applying this method we can simultaneously measure the inhomogeneity of the magnetic field over the volume of the sample.

The experiments indicated the usefulness of this method and agreed with the results of other authors, which were obtained by other methods.

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1 THE shapes of the nuclear magnetic resonance signals depend to a high degree on the relaxation times T_1 and T_2, which are called, respectively, longitudinal and transverse[1]. Furthermore, the shape of the signals depends on the amplitude of the radio frequency magnetic field, and also on the amplitude and frequency of modulation of the longitudinal magnetic field[1-3]. (These latter parameters are at the disposal of the experimenter.)

In the present work, in order to determine the relaxation time T_2, we used the signals generated by a self-excited oscillating system. A description of the use of this apparatus is given in reference 4. It is shown there that when the resonance condition $\omega = |\gamma| H_0$ is realized, where ω is the angular frequency of the radio frequency field, H_0 is the longitudinal component of the vector magnetic field intensity and γ is the gyromagnetic ratio, the amplitude of the oscillation is modulated by the signal

$$v(t) = -\int_{-\infty}^{t} e^{(\xi-t)/T_2} \cos[f(t)-f(\xi)]\,d\xi, \quad (1)$$

and the frequency is modulated by the signal

$$u(t) = \int_{-\infty}^{t} e^{(\xi-t)/T_2} \sin[f(t)-f(\xi)]\,d\xi. \quad (2)$$

In these formulas, T_2 is the relaxation time, $f(t) - f(\xi)$ is a function having the form

$$f(t)-f(\xi) = \int_{\xi}^{t} [|\gamma| H_z - \omega]\,d\eta,$$

H_z is the longitudinal component of the magnetic field.

The amplitude of self-excited oscillations was maintained at a low level. The signals had the form of a damped oscillating function (Fig. 1).

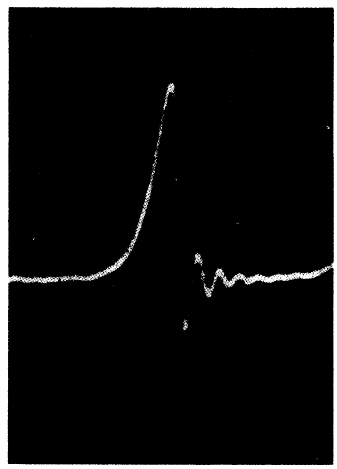

FIG. 1. Oscillogram of the signal $v(t)$ obtained from protons in 0.7 cm^3 of a one molar solution of $CuSO_4$.

2. The method of measuring the relaxation time, used in our work, is based on the fact that the ratio Z of the amplitudes $v(t)$ of the first and second extreme signals depends on T_2. The functions obtained determined the form of the signal, and one can derive the relation

$$T_2 = T_2(Z), \quad (3)$$

as that which determines T_2.

The form of the signal is also influenced by the inhomogeneity of the fixed magnetic field. In the presence of inhomogeneities, the shape of the sig-

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[1] S. D. Gvozdover and A. A. Magazanik, J. Exper. Theoret. Phys. USSR **20**, 705 (1950)

[2] S. D. Gvozdover and N. M. Pomerantsov, Vestn. MGU **6**, 85 (1953)

[3] S. D. Gvozdover and N. M. Pomerantsov, Vestn. MGU **9**, 79 (1953)

[4] N. M. Pomerantsov, Vestn. MGU **2**, 47 (1955)

nal $v(t)$ is of the form[5]

$$v^*(t) = \int_{-\infty}^{\infty} v(\Delta H, t) f(\Delta H)\, d(\Delta H), \tag{4}$$

where ΔH is the deviation of the magnetic field intensity from resonance at a given point of the sample; $f(\Delta H)$ is the distribution function of the inhomogeneities of the field, satisfying the normalization condition

$$\int_{-\infty}^{\infty} f(\Delta H)\, d(\Delta H) = 1. \tag{5}$$

Various distribution functions were applied to the calculation; these are but idealizations of the actual distribution function of the inhomogeneities of the field. The most convenient one for calculations is the Lorentz form of the distribution function

$$f(\Delta H) = \frac{1}{\pi} \frac{\Delta H^*}{(\Delta H^*)^2 + (\Delta H)^2}, \tag{6}$$

where ΔH^* is the mean value of the inhomgeneity. The effect of the inhomogeneous field with the above-mentioned distribution function is a decrease in the relaxation time T_2 as is shown in reference 5.

For the majority of liquids at room temperature we have the equality[5,6]

$$T_1 = T_2. \tag{7}$$

Hence the relaxation time T_2 is found experimentally by the presence of inhomogeneities in the fixed magnetic field, and in this case can be written in the form[5]

$$\frac{1}{T_2} = \frac{1}{T_1} + |\gamma| \Delta H^*. \tag{8}$$

3. The construction of the functional relation (3) for experimentally determining T_2 from the ratio Z of the amplitudes $v(t)$ of the first and second extreme signals is carried out in the following manner. We use the function derived in reference 1 [Formulas (33), (33a)],

$$Z = \frac{v(t_1)}{v(t_2)} = \int_{-\infty}^{r_1} e^{\alpha(\xi - r_1)} \times \cos(r_1^2 - \xi^2)\, d\xi \Big/ \int_{-\infty}^{r_2} e^{\alpha(\xi - r_2)} \cos(r_2^2 - \xi^2)\, d\xi, \tag{9}$$

where

$$r = \sqrt{\frac{a}{2}}\, t, \quad \alpha = \frac{1}{T_2}\sqrt{\frac{2}{a}}, \quad a = |\gamma| \frac{dH_z}{di}, \tag{10}$$

t_1 and t_2, and correspondingly, r_1 and r_2 are the moments of time at which the function $v(t)$ is an extremum.

The integral in Eq. (9) can be reduced to tabulated functions in the following manner. We combine Eqs. (1) and (2) and obtain, with the substitution of Eq. (10),

$$w(r) = -v + iu = \sqrt{\frac{2}{a}}\, e^{-\alpha r + ir^2} \int_{-\infty}^{r} e^{\alpha\xi - i\xi^2}\, d\xi. \tag{11}$$

After substituting

$$\xi = -i\left(\frac{\alpha}{2} - \eta\right) \tag{12}$$

the expression for $w(r)$ takes the form

$$w(r) = i\sqrt{\frac{2}{a}} \exp\left\{-\alpha r + i \times \left(r^2 - \frac{\alpha^2}{4}\right)\right\} \int_{(\alpha/2)+i\infty}^{(\alpha/2)-ir} e^{i\eta^2}\, d\eta. \tag{13}$$

We use the residue theorem and carry out the shift in the path of integration (Fig. 2), so that

$$\lim_{R\to\infty} \int_{(\alpha/2)+iR}^{(\alpha/2)-ir} e^{i\eta^2}\, d\eta = \int_0^{(\alpha/2)-ir} e^{i\eta^2} d\eta - \int_0^{\infty} e^{i\eta^2}\, d\eta. \tag{14}$$

In the latter integral the right hand side of Eq. (14) is equal to $\sqrt{\pi/2}\,(1+i)/2$.

We change the variable

$$\eta = (i-1)\, t/\sqrt{2} \tag{15}$$

and assume

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[5] B. A. Jacobson and R. K. Wangsness, Phys. Rev. 73, 942 (1948)

[6] V. N. Faddeeva and N. M. Terente'v, *Tables of Values of the Probability Integral for Complex Argument*, GITTL, 1954

$$z' = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{2} + r\right) + i\frac{1}{\sqrt{2}}\left(\frac{\alpha}{2} - r\right) = x + iy, \quad (16)$$

and reduce the expression for $w(r)$ to the form

$$w(r) = i\sqrt{\frac{2}{a}}\exp\left\{-\alpha r + i\left(r^2 - \frac{\alpha^2}{4}\right)\right\} \times \left\{\frac{i-1}{\sqrt{2}}\int_0^{z'} e^{t^2}\,dt - \frac{\sqrt{\pi}}{2}\frac{1+i}{\sqrt{2}}\right\}. \quad (17)$$

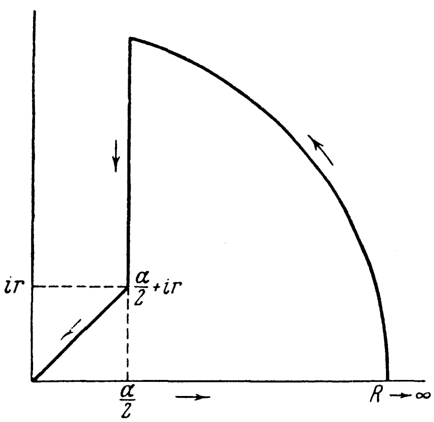

FIG. 2. Shift of path of integration for the integral of Eq. (13).

The integral in Eq. (17) can be expressed by means of the tabulated functions of a complex variable[6]:

$$W(z') = U(x, y) + iV(x, y) = e^{-z'^2}\left(1 + \frac{2i}{\sqrt{\pi}}\int_0^{z'} e^{t^2}\,dt\right). \quad (18)$$

We finally have

$$w(r) = -v + iu = \sqrt{\frac{\pi}{a}}\left\{-\frac{1}{2}(V+U) + e^{-\alpha r}\left[\cos\left(r^2 - \frac{\alpha^2}{4}\right) + \sin\left(r^2 - \frac{\alpha^2}{4}\right)\right] + i\left[\frac{1}{2}(U - V) + e^{-\alpha r}\sin\left(r^2 - \frac{\alpha^2}{4}\right) - e^{-\alpha r}\cos\left(r^2 - \frac{\alpha^2}{4}\right)\right]\right\}. \quad (19)$$

4. The formula given above permits calculation of Eq. (9), but for this it is necessary to know the moments of time t_1 and t_2 at which the function $v(t)$ takes on its extreme values. The values of t_1 and t_2 are found as solutions of the transcendental equation for the extremes of the function $v(r)$

$$r = \frac{\sqrt{\frac{2}{\pi}} - \frac{\alpha}{2}\left\{U + V - 2e^{-\alpha r}\left[\sin\left(r^2 - \frac{\alpha^2}{4}\right) + \cos\left(r^2 - \frac{\alpha^2}{4}\right)\right]\right\}}{U - V + 2e^{-\alpha r}\left[\sin\left(r^2 - \frac{\alpha^2}{4}\right) - \cos\left(r^2 - \frac{\alpha^2}{4}\right)\right]}, \quad (20)$$

which can be derived by differentiating Eq. (1). The solution of this equation is obtained by the method of successive approximation. The values of t_1 and t_2 (obtained approximately) are made more precise by substituting these values into Eq. (20)

The functional dependence of

$$\alpha = \sqrt{\frac{2}{a}}\frac{1}{T_2}$$

on Z obtained by the method described above is presented in Table I and is shown graphically in Fig. 3.

5. This method was used in some experiments. According to existing theory[7], for the presence in solution of paramagnetic ions, the relaxation time is inversely proportional to the concentration of the latter

$$1/T_1 = CN, \quad (21)$$

where N is the number of ions per unit volume, and C is the proportionality coefficient. From Eqs. (8) and (21) we deduce

[7] N. Bloembergen, *Nuclear Magnetic Relaxation*, Leiden, 1948

TABLE I. Dependence of the parameter $\alpha = \frac{1}{T_2}\left(\frac{1}{2}|\gamma|\frac{dH_z}{dt}\right)^{-1/2}$ on the ratio Z of the first and second extrema of the absorption signal.

α	0.000	0.283	0.707	0.990	1.412
Z	0.907	1.280	2.227	3.712	15.300

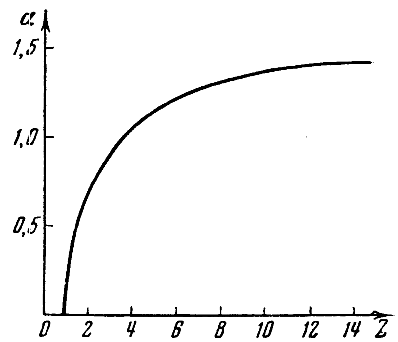

FIG. 3. Functional relation of the parameter $\alpha = \frac{1}{T_2}\left(\frac{1}{2}|\gamma|\frac{dH_z}{dt}\right)^{-1/2}$ to the ratio Z of the amplitudes of the first and second extreme signals.

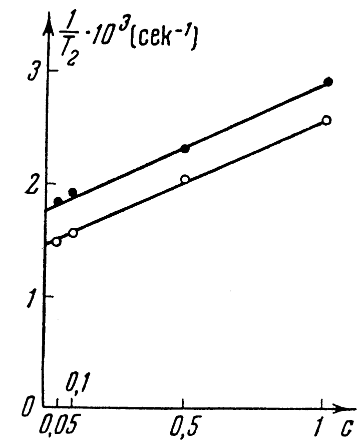

FIG. 4. Dependence of the measured experimental relaxation time T_2 on the concentration c of paramagnetic ions in a solution of $CuSO_4$ [see Eq. (22)] for two values of the inhomogeneous magnetic field; c is measured in moles.

$$1/T_2 = CN + |\gamma|\Delta H^*, \qquad (22)$$

i.e., a linear equation.

In Fig. 4 is presented the experimentally determined dependence of $1/T_2$ on the concentration of ions in a solution of $CuSo_4$ for different values of the inhomogeneous magnetic field. The graph confirms the relation (21) and enables one to determine the average inhomogeneity of the magnetic field over the volume of the specimen (from the value of the intercept with the axis of ordinates). We find good agreement with the experiments of other authors[7].

Furthermore, with the method described above, we measured the relaxation time of the nucleus F^{19} in the compound $BF_3 \cdot 2H_2O$. We obtained the value $T_2 = 0.9 \times 10^{-3}$ sec.

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