Proc Indian Acad Sci. 33A, 107-111, (1951)
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NUCLEAR RESONANCE IN FLOWING LIQUIDS

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Received December 2, 1950

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. INTRODUCTION

NUCLEAR magnetic resonance is associated with relaxation phenomena (Bloembergen, Pound and Purcell, 1948). The relaxation effects for any given substance are described by means of two relaxation times T_1 and T_2. T_1 is the measure of the rate of attainment of thermal equilibrium of a system of nuclei in a magnetic field. T_2 is the inverse line breadth on a frequency scale and is otherwise called the spin-spin relaxation time. On account of the finite and fairly large (10^{-4} to 3 sec.) magnitudes of T_1 and T_2, several effects such as the saturation of the sample by R.F. field take place. In this paper experiments are described in which the saturated sample is continuously replaced by flow of a liquid, through the R.F. coil of the apparatus. On account of the large value of the relaxation time, even moderate velocities of flow are sufficient to cause several interesting features to be observed which are described below.

2. APPARATUS

In order to show the effects clearly an easily adjustable and sensitive apparatus for detecting nuclear resonance is necessary. It has been found that the self-quenched superregenerator satisfies the requirement of simplicity and sensitiveness. The circuit used functions at radio frequencies ranging from 1 to 20 M.C./s. with a quench frequency of 20 K.C./S. The oscillator coil is wound on a glass former and is capable of being placed with its shield within the $\frac{3}{4}''$ gap of an electromagnet. The magnet pole-pieces are of the truncated pyramid type and have a pole face area 3″ × 3″. The main exciting coils are of thin wire and at a current of 1·5 amperes through them, a field of 6,000 oersteds can be obtained in the $\frac{3}{4}''$ air gap. An extra pair of coils are provided through which a 60 cycle alternating current of magnitude 1 to 3 amperes can be sent by means of a transformer. The audio output of the superregenerator is fed to a Cossor oscillograph whose linear sweep is synchronized with the 60 cycles mains frequency.

Through the R.F. coil passes one limb of a U tube which is connected to the liquid flow system. An arrangement to reverse the flow is also provided. The liquid is kept in a small reservoir at a height of 50 cm. above the R.F. coil and is allowed to flow by gravity.

3. EXPERIMENTAL DETAILS

Experiments will now be described which show the phenomenon of nuclear magnetic resonance relaxation in a very striking manner. The magnetic field is adjusted for obtaining resonance. The flow system should be filled with a liquid or a solution having a fairly large relaxation time of the order of 0·1 to 0·05 sec. in order to exhibit the effects. When the liquid is stationary a signal of about 1 cm. height on the screen of the oscillograph is observed. On flowing the liquid two most striking effects are noticed. Firstly, there is a large temporary rise in signal strength which subsides quickly. Secondly, there is the relatively larger signal obtained when the liquid is flowing steadily. The magnitudes of these effects are conditioned by various factors, *viz.*, the relaxation time T_1 of the liquid, the time it spent in the magnetic field outside the R.F. field, the time it spends in the R.F. coil and the velocity of flow. Initial rises in signal of magnitudes 20 times the no-flow signal value have been observed. Steady flow to no-flow signal ratio are usually about 5 and are dependent on the velocity of flow. The observed results in a particular case are represented in the accompanying graph.

4. DISCUSSION

The experiments mentioned above form a striking demonstration of the facts of nuclear magnetic relaxation. The effects are all quantitatively related to the relaxation time. The finite and long relaxation time leads as mentioned earlier to a saturation of the sample and the saturation is expressed quantitatively by the ratio

$$\frac{n}{n_0} = \frac{1}{1 + \gamma^2 T_1 T_2^* H_1^2},$$

where T_1 is the relaxation time, T_2^* is the inverse line breadths (on the frequency scale) γ the gyromagnetic ratio of the nuclei, H_1 is the effective R.F. magnetic field; and n/n_0, the ratio of the excess number of nuclei in the higher state with and without the R.F. R.F. absorption is proportional to n. In flowing the liquid we have removed the saturated sample and replaced it by unsaturated sample capable of absorbing more R.F. energy resulting in a larger signal, The first effect described above is the initial rise in signal. This could be observed under the following conditions. (1) The liquid should have a long relaxation time of the order of 0·1 sec. or more. (2) It must come to thermal equilibrium in the magnetic field; *i.e.*, it must have spent a time considerably larger than the relaxation time in the magnetic field at or near the resonance value. (3) It must travel with sufficient velocity to displace the contents of the R.F. coil in a time of the order of 1/120 sec. A simple relation between the rise and the relaxation time can be obtained. Assuming that the signal is proportioned to the excess number of nuclei in the lower state, we have

$$\frac{n}{n_0} = \frac{s}{s_0} = \frac{1}{R} = \frac{1}{1 + \gamma^2 T_1 T_2^* H_1^2}$$

R being the ratio of the steady signal s to the initial rise s_0. Then

$$\frac{R - 1}{\gamma^2 T_2^*} = T_1 H_1^2$$

If H_1 could be measured, T_1 can be calculated by performing this experiment. However, the direct determination of H_1 is difficult and only a comparison of T_1 between liquids can be effected.

Secondly, there is a rise in signal when the liquid is flowing steadily with a uniform velocity. Here the conditions of observation are the following: (1) The relaxation time must be of the order of 0·1 to ·01 sec. (2) The liquid must travel for sufficient time in the magnetic field before entry into the R.F. coil for attaining thermal equilibrium. (3) It must travel with sufficient velocity to displace at least a part of the contents of the R.F. coil in a time of the order of 1/60 sec. For these moderate velocities it is possible to calculate the steady state rise. It will suffice to give the results of the calculation. If l is the length of the R.F. coil, v the velocity of flow, T_1 the relaxation time, s_0 the signal when the liquid is at rest and s the signal when the liquid is flowing, then

$$\frac{s - s_0}{s_0} = \frac{W T_1^2}{1 + W T_1} \times \frac{v}{l}.$$

where

$W = \frac{1}{2}\gamma^2 H_1^2 T_2^*$ and if WT_1 is large

$$\frac{s - s_0}{s_0} = T_1 \frac{v}{l} \text{ approximately.}$$

This also affords a method of estimating the relaxation time T_1. Fig. 1 shows an experimental curve for N/1,000 $FeCl_3$ solution and T_1 given by the slope of the curve is 0·06 sec.

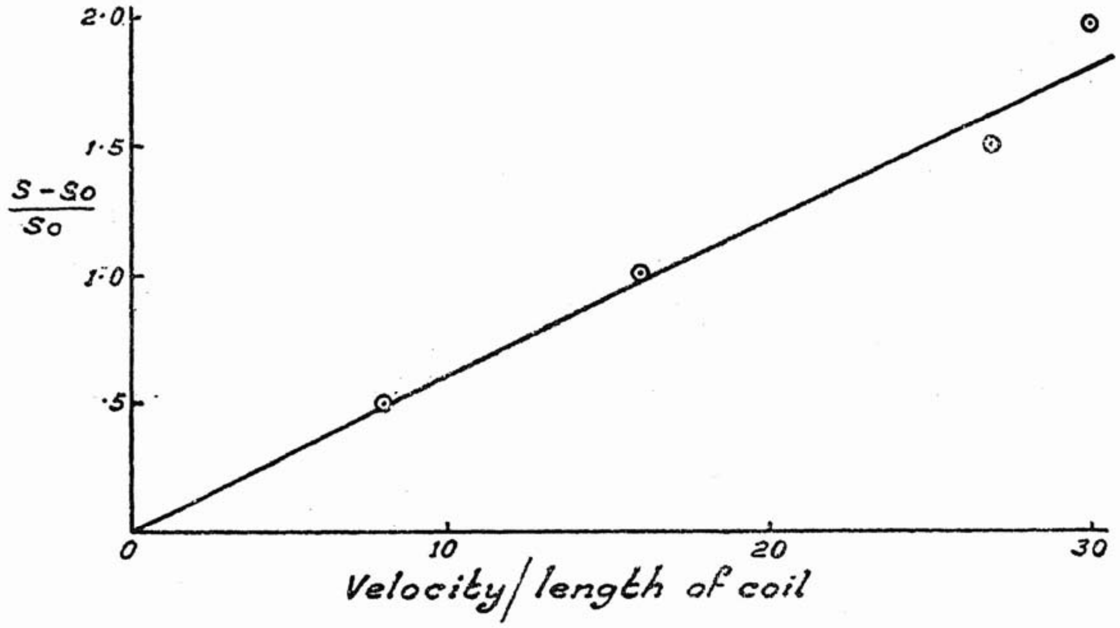

FIG. 1

There is another possibility of steady state rise under conditions described in case 1 above. If the liquid is allowed to flow steadily, then the time it spends outside the R.F. field but still in the magnetic field is small and the liquid will not come to proper thermal equilibrium. Therefore the signal on steady flow will not be as large as the initial rise. Here the rise is determined by the time the fluid travels in the magnetic field before entry into the R.F. field.

These experiments afford a clear demonstration of relaxation time and saturation in nuclear magnetic resonance and offer a unique method of answering questions regarding the behaviour of nuclei within and without the R.F. field. One of the questions is whether the time taken to come to thermal equilibrium in a magnetic field is the same as the time taken to come to thermal equilibrium in the presence of an R.F. field also. Experiments have been performed which answer the question in the affirmative.

Another question is whether the free precession of the nuclei after they have left the R.F. field could be detected. Experiments have been performed by placing a pick up loop on the return limb of the U tube through which the liquid flows and connecting the loop to a highly sensitive communications receiver. If the liquid is flowed and the nuclei are precessing coherently, the output of the receiver must change. With $FeCl_3$ solutions used and the velocities obtained, no definite change could be observed. This, however, is not surprising in view of the fact that the phase memory time T_2 is small and the magnetic field inhomogeneity contributes to make it still smaller. If as is suspected, fluids exist with T_2 of the order of 0·1 sec. or more the above mentioned experiment will yield positive results.

I thank Professor R. S. Krishnan for his kind interest and encouragement.

SUMMARY

Nuclear magnetic resonance in flowing liquids has been investigated experimentally. The experiments afford a striking demonstration of the effects of finite relaxation time and afford a method of measuring relaxation times directly.

REFERENCE

1. Bloembergen, Pound and Purcell .. *Phys. Rev.*, 1948, **73**, 679.