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Audio Frequency Nuclear Resonance Echoes

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Résumé. — Nous avons fait des expériences d'écho de spin dans les champs faibles (0,5 à 2 gauss) sur les protons (2 Kc/s à 8 Kc/s) en utilisant un champ prépolarisant de 200 gauss. La méthode permet de mesurer T_1 et T_2 plus longs qu'une seconde jusqu'à des centaines de secondes au laboratoire, puisqu'elle évite les effets d'hinhomogénéité du champ terrestre et de perte par rayonnement. Les effets dûs à la diffusion sont diminués par l'utilisation d'une série d'impulsions. On propose de mesurer aussi des effets de couplage spin — spin indirect entre des noyaux différents par la modulation des échos, ce qui permettra une étude très poussée des interactions entre deux noyaux et avec leurs voisins. L'avantage principal de cette méthode est qu'elle est très peu onéreuse, on n'a pas besoin d'aimant et toute l'électronique est de basse fréquence.

In the well known free precession experiment [1] a sample containing magnetic nuclei is polarised by a magnetic field of say 200 gauss by passing a direct current through a coil surrounding it. The direct current is then cut and the nuclear magnetisation precesses about the earth's field ($H_0 \simeq 0.5$ gauss) at the Larmor frequency which for protons is about 2 kc/s. The precessing magnetisation induces an alternating voltage in the same coil, or possibly one at right angles [2] at say 2 kc/s which decays for four reasons. (1) Due to the inhomogeneity of the earth's field which may be 100 microgauss cm^{-1} or more in a typical laboratory. For a typical sample of protons this gives a decay time (T_2*) of 0.05 seconds. (2) Due to radiation damping [3] of the precession caused by the currents (i.e. the signal) induced in the receiving coil by the rotating magnetisation. In our case this gives an effective decay time T_R of about 4 seconds (it is not an exponential decay but we shall ignore this complication). (3) Due to the true spin-spin relaxation, T_2, which is a property of the sample. Apart from field measurements [4] one is interested in measuring the time

T_2 and related effects [5]. (1) means that for T_2 longer than a few tenths of a second the experiments have to be done outside or in a special building and in any event for extremely long T_2's, say above 30 seconds, the homogeneity requirements are extremely difficult to satisfy.

We have circumvented the difficulties due to (1) and (2) by an adaptation of the well known spin echo experiment [6]. The free precession

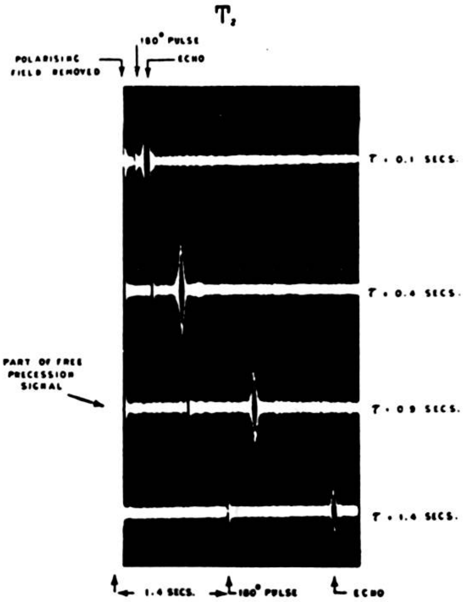

Fig. 1.

experiment is equivalent to a 90° pulse and so we apply a 180° pulse (usually 1 volt on the coil, 2 msec. long at 2 kc/s) a time τ later and observe the echo at $2\,\tau$ of amplitude proportional to $\exp - 2\tau/T_2$ and width approximately T_2* [7]. A series of photographs showing the attenuation of the echo with τ, thus determining T_2 (at $H_0 = 0.5$ gauss) is shown in Fig. 1. This result is obtained despite the inhomogeneity of the earth's field and so removes difficulty (1). It also in large measure removes difficulty (2) since evidently the radiation damping of the nuclear signal depends on the *macroscopic* nuclear magnetisation present and in the echo experiment the nuclear magnetisation has only appreciable value during the initial decay after the polarising field is cut and during the echo itself, as compared with the free precession experiment where it is present throughout. Since our free precession decays and echoes last only some tenths of a second we shall never be adversely affected by radiation damping for even extremely long T_2.

However the inhomogeneity of the main field introduces another effect (4) which is due to self diffusion of the nuclei in the inhomogeneous field producing a random dephasing and hence an attenuation which although it is not exponential may be characterised by the decay time [6, 8, 9] $T_D = (12/D\gamma^2G^2)^{1/3}$, where D is the self diffusion constant and G is the field gradient, assumed to be linear. In our experiment diffusion atte-

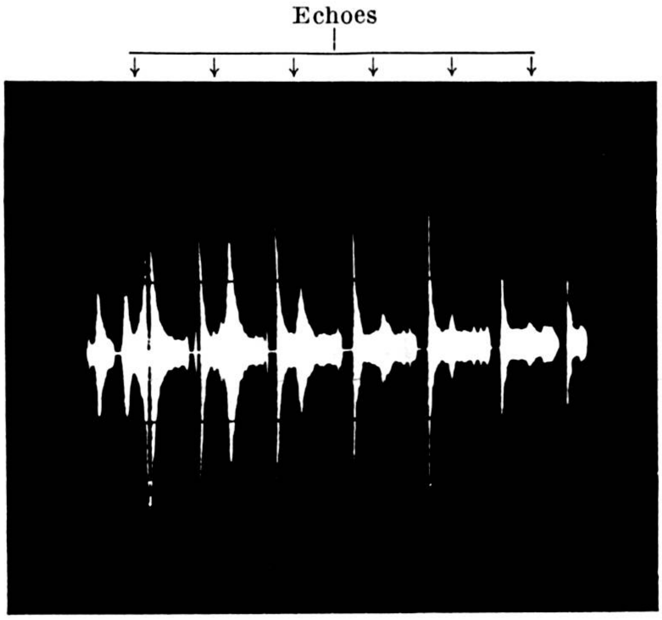

Fig. 2.

nuation is expected and found corresponding to $T_D \simeq 4$ sec. in water (which has a typical value of D). We have reduced this attenuation by the method employed at higher frequencies, namely, the application of a series of 180° pulses at τ, 3τ, 5τ, etc. which produces echoes at 2τ, 4τ, 6τ etc. where the echo amplitude is still proportional to $\exp - i2\tau/T_2$ but T_D is increased by the factor $n^{2/3}$, where n is the factor by which the number of echoes in a given time has been increased. A typical photograph is shown in Figure 2 which is a single exposure. This method also has the advantage of giving T_2 much more quickly and accurately since only one polarisation is required.

The spin-lattice relaxation time, T_1, can be measured by polarising for a range of times T comparable with T_1 and producing an echo at a fixed time (τ fixed $< T_2$) whose amplitude is proportional to $(1 - \exp - T/T_1)$. A series of echoes for the determination of T_1 is shown in Figure 3. The T_1 value refers of course to the polarising field of about 200 gauss.

We are able to get a signal to noise ratio for protons in water of about 10 with a 100 ml sample. A large proportion of the noise is pickup but we have found great difficulty in shielding from this low frequency noise by simple methods without adversely affecting both the field homogeneity (which means increasing the bandwidth of the amplifiers to pass the sharper echo and so passing more noise) and the electrical properties of the coil

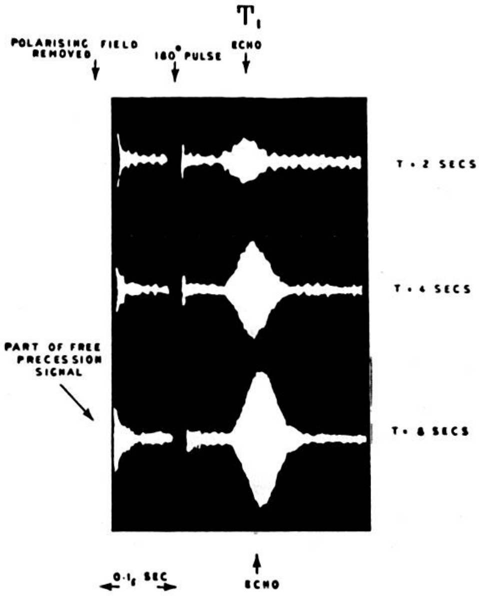

Fig. 3.

system. In the course of experiments carried out in larger fields, up to 2 gauss (8 kc/s for protons) produced by an auxiliary field coil system giving a highly homogeneous field [10] we have found the local noise to vary quite sharply within the range 2 kc/s to 8 kc/s. It is of course essential to avoid harmonics of 50 c/s. By judicious choice of frequency in this range, i.e. using the highest possible since the signal is proportional to the field (we recall that the polarising field and hence the polarisation is constant and so there is less than the usual improvement in signal with frequency) and searching for minimum noise we have been able to improve the signal to noise ratio, by a factor of two or more.

The length of the 180° pulse is 2 msec. which is only 4 cycles at 2 kc/s. It would be quite possible, although apparently of no scientific interest except perhaps where more than one nuclear species is to be irradiated (see below) to in fact apply a short d.c. pulse to produce the 180° rotation of magnetisation i.e. $H_1 > H_0$! We have so far been prevented from doing this experiment by ringing of the coil but it appears quite feasible.

We are currently using this method for measuring rather long T_2's of organic liquids which are not conveniently accessible by other methods.

We have found in the case of liquids of low viscosity that self diffusion effects are not readily removed even by the Carr-Purcell method [8] at radio frequencies where T_2 is greater than a few seconds [11]. However the parameters are more favourable for the audio frequency echo method and we think will allow a considerable extension upwards of the range of measurement of T_2 in many liquids.

Self diffusion constants may also be measured by deliberately introducing a known field inhomogeneity by means of auxiliary coils. We note however that it is difficult to obtain accurate values of D since it enters T_D as $D^{1/3}$.

We are hoping to investigate cases in which T_2 and T_1 differ in pure liquids as has been reported for water [12]. However our preliminary measurements on water suggest that those measurements [12] were seriously affected by dissolved oxygen. The effect of atmospheric oxygen is very serious for T_2 longer than about 3 seconds and we have found that almost all mobile organic liquids have $T_2 \simeq 3 \pm 1$ seconds before being degassed.

We are also proposing to investigate indirect spin-spin coupling (J) between inequivalent nuclei by the echo amplitude modulation method [13]. Although the chemical shift (∂) between nuclei of the same species will usually be much smaller than J at fields as low as 0.5 gauss, ∂ is still amply large for different nuclei such as say F^{19} and H^1 so that echo modulation should be found provided both the F^{19} and H^1 signals are observed and the pulses excite both sets of nuclei. This can be achieved at 2 kc/s where the F^{19} and H^1 resonant frequencies are only some 150 c/s apart but it would be very difficult at radio frequencies.

We can also readily polarise, pulse and observe one, the other or both of two species of nuclei and also polarise one and observe the other etc. so that a very detailed study of the interactions between the two sets of not too dissimilar nuclei and their surroundings can be made.

The greatest advantage of the audio-frequency pulse method is that the apparatus is very simple and cheap since in particular no magnet is required. We have shown also that the considerable change in parameters as between operating at a few thousand gauss and at one half gauss are in some cases advantageous. On the other hand, of course, the range covered is more restricted than in the conventional spin echo method particularly in that only materials with rather long relaxation times can be measured and rather large samples are required.

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