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Proton spin-lattice relaxation in acetic acid

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Résumé.

L'évidence expérimentale de l'accroissement non-exponential de la magnétisation des protons dans l'acide acétique liquide à diverses températures est présentée. Ce fait est expliqué par l'existence de deux différents temps de relaxation spin-réseau dans les groupes CH_3 et COOH.

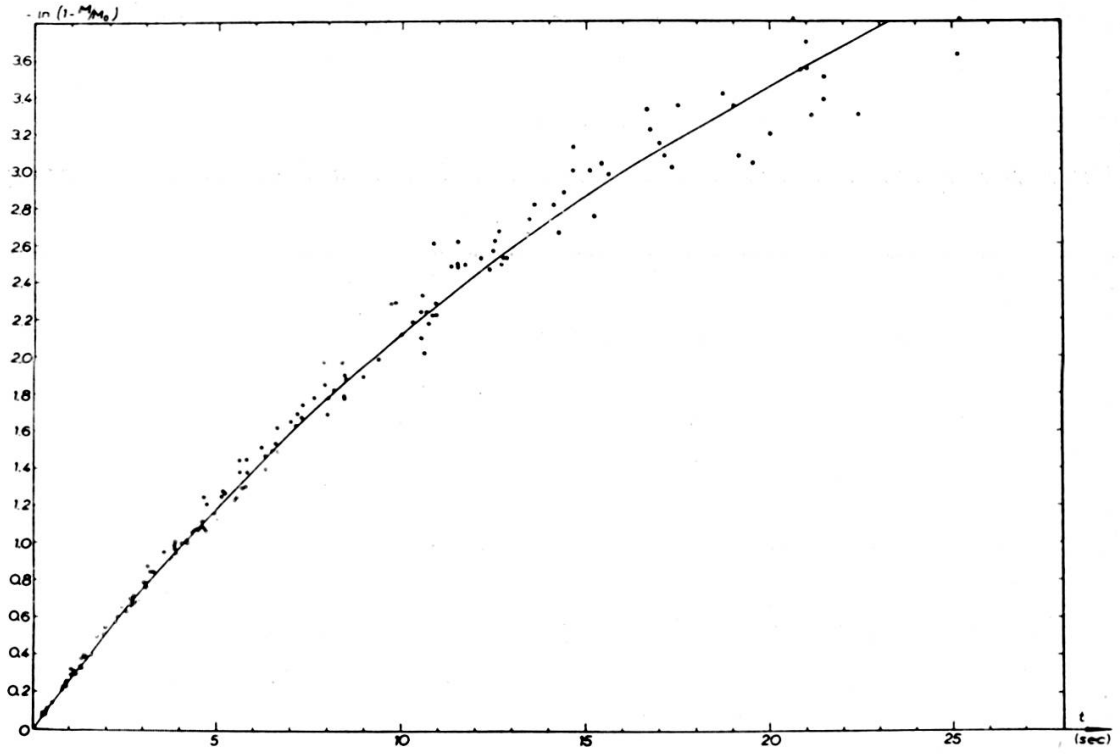
The purpose of this communication is to provide some experimental evidence showing that in liquid acetic acid (CH_3COOH) the protons of the CH_3 group have a different spin-lattice relaxation time, T_1, from the COOH proton.

Similar results have been obtained for methyl alcohol by Powles and Cutler [1] and for liquid toluene by different authors [2, 3, 4]. The simultaneous existence of two T_1 values leads to the non-exponential growth of nuclear magnetization in time.

T_1 measurements for acetic acid have also been reported by Bloembergen et al. [5] and Chiarotti et al. [6], who obtained the single relaxation times of 2.4 sec and 3.8 sec respectively. But the short observation time of the relaxation process involved in the method used made these authors unable to observe the non-exponential behaviour of magnetization. In addition, the sample used by Bloembergen et al. was not oxygen-free.

In the research here reported the sample of CH_3COOH was saturated and then the growth of nuclear magnetization M was observed, using the method of Hennel and Hrynkiewicz [7]. The growth time was varied within sufficiently wide limits to obtain the values of $-\ln(1 - M/M_0)$ between 0 and 3.8. The sample was prepared using C.P. glacial acetic acid. To purify, it was distilled four times. The atmospheric oxygen was removed by boiling at length as described by Hennel et al. [8].

The measurements were carried out at a resonant frequency of 28 Mc/sec at four temperatures, 20, 30, 50 and 80° C. The experimental results obtained for 20° C are shown in figure 1.



Growth of the magnetization M in time in liquid acetic acid at 20° C. The theoretical curve is drawn according to equation (1): $a = 3/4$, $b = 1/4$, $T_1' = 3.12$ sec, $T_1'' = 9.55$ sec.

A theoretical curve of the following form has also been drawn:

$$1 - M/M_0 = a \exp\left(-\frac{t}{T_1'}\right) + b \exp\left(-\frac{t}{T_1''}\right), \qquad (1)$$

where a = 3/4 and $b = 1/4$ according to the abundances of protons in the methyl and carboxyl groups. The relaxation times of these groups, T_1' and T_1'', (3.12 sec. and 9.55 sec.) have been chosen to fit the curve to the experimental points. The values of T_1' and T_1'' shown in table 1 were obtained in the same way. The maximum random error was roughly estimated as 10% for T_1' and 25% for T_1''.

A non-exponential decay of the transversal magnetization for acetic acid is reported by Daszkiewicz [9].

The fact that two different relaxation times, T_1' and T_1'', are present indicates that there is no rapid proton chemical exchange between the carboxyl and methyl groups. This result may be anticipated in view of the strong hydrogen bond (8.2 kcal/mole) in which the COOH proton is involved causing the well-known dimeric structure of acetic acid [10, 11].

TABLE 1.

Experimental values of proton T_1 for the methyl (T_1') and carboxyl (T_1'') groups in acetic acid.

°C	T_1' (sec)	T_1'' (sec)	T_1'/T_1''
20	3.12	9.55	3.06
30	3.58	12.3	3.44
50	4.76	15.1	3.17
80	6.92	19.2	2.77

The translational part of $1/T_1$ was estimated taking the formula of Blicharski et al. [12] as a basis. The viscosity of 1.211 cp at 20° C was taken. The obtained result was $(1/T_1)_{tr} = 0.106$ sec^{-1}, i.e. $(T_1)_{tr} = 9.43$ sec. The agreement with the experimental value $T_1'' = 9.55$ sec means that the spin-lattice relaxation time of the carboxyl group is mainly controlled by the intermolecular interactions.

As shown in table 1, the T_1'/T_1'' ratio is independent of the temperature within the limits of experimental error.

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