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Spin-spin nuclear magnetic relaxation in liquid hydrogen chloride acetic acid and methyl formate

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Hydrogen Chloride HCl.

The direct nuclear dipole-dipole interaction leads in liquids of low viscosity to equal values of spin-lattice T_1 and spin-spin T_2 relaxation times. Nevertheless some experimental results of $T_2 < T_1$ were reported [1]. In some cases this discrepancy is caused by indirect electron-coupled interaction between nuclei in the same molecule [2, 3, 4]. This report presents experimental evidence that $T_2 < T_1$ for protons in liquid HCl.

Taking the obtained T_1 and T_2 values as a base and assuming that also in this case the nonequality of T_1 and T_2 is caused by indirect electron-coupled interaction, the interaction constant J , the correlation time for this interaction τ_{ex} and the pure dipolar part T_{1dip} of spin-lattice relaxation time is calculated.

A glass sealed sample of anhydrous and carefully degassed liquid HCl were used. The results at 22° C are, $T_1 = (18.0 \pm 0.5)$ sec., $T_2 = (0.5 \pm 0.01)$ sec. at 14 Mc/sec. The same sample was used by Blicharski who obtained $T_1 = (21.0 \pm 1.0)$ sec. at 28 Mc/sec. [5].

For computation of J , τ_{ex} and T_{1dip} the formulas obtained by Blicharski et al. [6, 7] were used. This formulas have in case $\omega_I \tau_c \ll 1$, $\omega_s \tau_c \ll 1$ following form:

$$\frac{1}{T_1} = \frac{1}{T_{1dip}} + \frac{2}{3} J^2 S(S+1) [\tau_{ex}/1 + (\omega_I - \omega_s)^2 \tau_{ex}^2] \quad (1)$$

$$\frac{1}{T_2} = \frac{1}{T_{1dip}} + \frac{1}{3} J^2 S(S+1) [\tau_{ex} + \tau_{ex}/1 + (\omega_I - \omega_s)^2 \tau_{ex}^2]$$

These expressions are similar as those of Solomon and Bloembergen [4] but concern spins larger than 1/2. If the relaxation times $T_1 = T_{1b}$, $T_2 = T_{2b}$ at the frequency ω_b and $T_1 = T_{1a}$ at $\omega_a = 2\omega_b$ are known the Eq. (1) can be solved. We have:

$$\frac{\frac{1}{T_{2b}} - \frac{1}{T_{1b}}}{\frac{1}{T_{1b}} - \frac{1}{T_{1a}}} = 2 + \frac{8}{3} \left[\frac{\omega_b}{\gamma_I} (\gamma_I - \gamma_s) \right]^2 \tau_{\text{ex}}^2 + \frac{1}{3} \left[\frac{\omega_b}{\gamma_I} (\gamma_I - \gamma_s) \right]^{-2} \tau_{\text{ex}}^{-2} \quad (2)$$

where γ_I , γ_s is the giromagnetic ratio of proton and chlorine nucleus respectively. From this equation s_{ex} may be obtained. Than Eq. (1) give J and $T_{1\text{dip}}$.

In this way, assuming $\gamma_s = 417$ c/sec. Oe which is the value for ^{35}Cl following results are obtained: $\tau_{\text{ex}} = 0.12 \mu$ sec., $J/2\pi = 286$ c/sec. and $T_{1\text{dip}} = 21.6$ sec.

The assumption of $\gamma_s = 347$ c/sec. Oe (^{37}Cl) leads to results different by few percent and they are laying within the limits of experimental error.

The obtained values of J and τ_{ex} is of the same order of magnitude as found by Solomon and Bloembergen [4] for HF.

Acetic Acid CH_3COOH and Methyl Formate HCOOCH_3 .

It is known that in few liquid compounds two spin-lattice relaxation times for different protons in the same molecule were observed [8, 9]. It is still impossible to give a general rule in which cases this effect may exist. In order to solve this problem it seems to be reasonable to examine the relaxation processes in isomeric compounds. In the research here reported two isomeric compounds are investigated by observing the spin-spin relaxation. In the case of methyl formate single relaxation time $T_2 = (19.3 \pm 0.9)$ sec. at 22°C and 14 Mc/sec. is only found. A semi-logarithmical plot of echo decay investigated up to 20 sec. gives a straight line.

Quite different results are obtained for acetic acid. In this case the semi-logarithmic plot of echo decay is not a straight line. The existence of two relaxation times was found graphically $T_{2a} = 3.6$ sec., $T_{2b} = 12$ sec.

For a decay which is composed from two exponentials:

$$m(t) = a \exp\left(-\frac{t}{T_{2a}}\right) + b \exp\left(-\frac{t}{T_{2b}}\right) \quad (3)$$

where $a + b = 1$, following relations for $m(t)$, $n = m(2t)$, $p = m(3t)$, $s = m(4t)$ are valid

$$\frac{\gamma\delta}{p - m(t)n} = 1 \quad (4)$$

$$\sqrt{\frac{a}{b}} = \frac{2m(t)\gamma - \delta}{2\gamma^2} + \sqrt{\left[\frac{2m(t)\gamma - \delta}{2\gamma^2}\right]^2 + 1} \quad (5)$$

$$T_{2b} = -2t/\ln \left[n + \sqrt{\frac{a}{b}} \delta \right] \quad (6)$$

where $\gamma = \sqrt{n - m^2(t)}$, $\delta = \sqrt{s - n^2}$. It was found that the experimental curve obeys exactly Eq (3). By means of Eq (5) and (6) the following values are found: $a = 0.744$, $b = 0.256$, $T_{2a} = (3.48 \pm 0.2)$ sec., $T_{2b} = (12.6 \pm 1.0)$ sec.

The agreement of a and b with the known abundances of protons enables to decide that T_{2a} corresponds to the methyl group and T_{2b} to the carboxyl group. Also two spin-lattice relaxation times are reported by Hryniewicz et al. [10].

All measurements at 14 Mc/sec. were made by spin echo technique. T_1 was measured by the zero method of three pulses (π , $\pi/2$, π). T_2 was measured by the Carr-Purcell method [11], with the phase modulation of the first pulse [12]. The measurements of T_2 were made at different numbers of pulses per sec. in order to eliminate the influence of self-diffusion.

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