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Autor: Hennel, J.W. / Waluga, T.
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Measurements of the Temperature Dependence of the Proton Spin-Lattice Relaxation Time in Liquid Hydrogen Sulphide

by J. W. HENNEL and T. WALUGA

Institute of Nuclear Physics, Polish Academy of Sciences,
Cracow 23, Poland

Résumé.

Le temps de relaxation spin reseau T_1 , des protons dans le H_2S liquide a été mesuré dans le domaine de la température de -18 à $+55^\circ$ C. Les résultats obtenus montrent que T_1 décroît avec l'accroissement de la température. La possibilité d'expliquer ce fait par l'action du champ magnétique provenant de la rotation a été discutée.

Recently Gutowsky et al. [3] presented some results of the spin-lattice relaxation time T_1 measurements showing that the fluorine T_1 in liquid CHF_2Cl and CHF_3 decreases with temperature in the range from about -100° C to at least room temperature. The authors explain this effect as due to spin-rotational interaction. The resulting contribution to the $1/T_1$ was described as proportional to the square of nuclear magnetic shielding constant and as dependent on "quenching" by intermolecular interactions which becomes less important at higher temperature.

The purpose of this report is to present an example of decrease of T_1 in the case of protons. As shown on figure 1 the proton T_1 in liquid hydrogen sulphide decreases by about 30 per cent in a temperature range from -10 to $+55^\circ$ C.

The sample used was prepared from very pure oxygen-free hydrogen and very pure, degassed sulphur in a similar way as that described by Klemenc and Bankowski [7]. The obtained hydrogen sulphide was twice fractionally distilled in vacuum at -60° C and carefully degassed. The measurements were made by the method of Hennel and Hryniewicz [4] at 28 Mc/sec. under the pressure of the saturated vapour.

It should also be noticed that there are numerous liquids in which the increase of T_1 with temperature is much smaller than that predicted by

theory. E.g. T_1 in methyl chloride remains constant within a range from $+10^\circ\text{C}$ to at least $+70^\circ\text{C}$ [1]. The decrease with temperature of the function $T_1\eta/T$ (η is the viscosity, T is the absolute temperature) in the following liquids, CHCl_3 , CHBr_3 , H_2O , H_2SO_4 , CH_2Cl_2 , NH_3 , CH_3Cl , $\text{C}_2\text{H}_5\text{OH}$ shown in our earlier papers [1, 5] and by Guillotto et al. [2] can

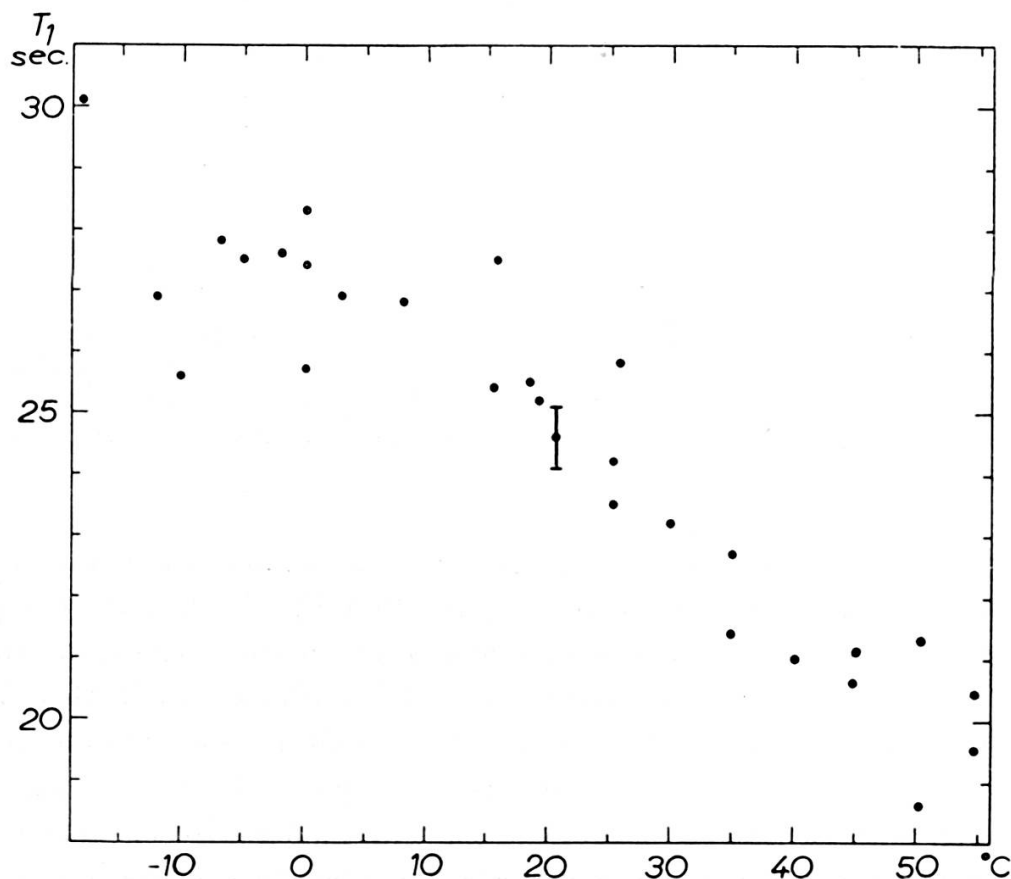


Fig. 1.

Results of measurements of the proton T_1 in liquid hydrogen sulphide.

also be regarded as an "insufficient" increase of T_1 . (The function $T_1\eta/T$ should be independent of the temperature if spin-rotational interaction is not taken into account.) Also in the case of H_2S the decrease of viscosity with temperature is known [6]. The objection may be raised that the relation between T_1 and viscosity is only a rough approximation; nevertheless the fact that all investigated liquids showed a decrease of $T_1\eta/T$ is remarkable. It is also interesting that the smallest decrease of this function was found in water in the temperature range from 0°C to 100°C where the strong hydrogen bonding is known.

It is possible that the decrease of T_1 in H_2S is also caused by spin-rotational interaction. Although the magnetic shielding constant is small for protons [3] on the other hand the intermolecular interactions in H_2S , in the temperature region concerned, are weak and therefore the "quenching" may be small. It is interesting to investigate the temperature dependence of T_1 in other liquids not much below the critical temperature. Work along these lines is in progress.

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