A COMPARISON OF THE THERMAL EQUILIBRIUM SPIN POLARIZATION
OF PROTONS IN CH₄, HD AND OTHER COMPOUNDS

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SUMMARY

The values of the thermal equilibrium spin polarization of protons, at 1.06°K and 25 kG magnetic field, were compared for various frozen organic liquids and solidified gases. The results from methanol, ethanol, toluene, CD₃H, and CClF₂H showed no deviation from Boltzmann distribution between the Zeeman levels of free proton spins. In CH₄ this polarization was twice as high as in the previous samples. This is an indication that the methane molecule is in its para-state with total spin $I = 2$ in the solid. The proton polarization in HD was 1.5 times higher than expected for free proton spins.

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1. INTRODUCTION

The question of the molecular ground state in solids at very low temperature has been raised in connection with polarized proton targets; as the value of the thermal equilibrium polarization (TEP) is generally used to calibrate the nuclear magnetic resonance detection system, it enters as a multiplicative factor in the final results of experiments using such targets. If some spin states are forbidden in the ground state of the molecules, this can influence the TEP in such a way that it does not correspond to the Boltzmann distribution of independent spins between their Zeeman levels. This is best visualized by the example of hydrogen: its ground state is a non-magnetic para-state, and the TEP depends on how far the conversion is advanced and vanishes when it is completed.

In order to obtain information on the molecular ground state in molecular solids, we have compared the RF susceptibility of some frozen organic liquids and solidified gases at low temperature and high magnetic field.

2. EXPERIMENTAL TECHNIQUE

All measurements were made using a continuous helium-flow cryostat¹⁾ stabilized at 1.06°K in a 25 kG magnetic field. The proton susceptibility was measured with a single sweep frequency modulated Q-meter²⁾ detecting the absorptive part of the paramagnetic resonance signal. Three different sample holders were used: two of them were made of copper with a detection coil inside, the third one was a glass bulb on the end of a copper tube with a detection coil around it. All of them were filled through a stainless steel tube connected to a reservoir outside the cryostat. As we did not have a safe technique for filling the sample holder completely with condensed gases, the samples were warmed slightly above their melting point after each measurement and then cooled again. After repeating this procedure a few times, the proton resonance signal approached a constant value within 5%.

3. THE SAMPLES

Frozen methanol, ethanol, and toluene are substances in which the protons have been polarized to more than 25% by dynamic methods^{3,4)}. CH₄ and HD are interesting candidates for the brute-force polarization method^{5,6)}.

CClF₂H and CD₃H as well as HD have a single hydrogen atom per molecule, and the TEP is therefore not expected to be influenced by molecular statistics. The CH₄ gas contained less than 1% air (0.1% O₂), HD contained about 5% H₂ and 1% air. CD₃H and CClF₂H were of commercial quality and were not controlled for impurities.

4. RESULTS

The samples were left at 1.06°K with the magnetic field on until the equilibrium signal was obtained. In the case of CH₄, a complicated conversion occurs that seems to be completed after 100 hours⁷⁾. In most of the measurements with CH₄ this conversion was followed for 24 hours, and the signal was then corrected for the missing 3% of its final value. No conversion was observed in the HD and CD₃H samples. Systematic errors in the results are expected to depend mainly on the filling factor of the sample holder. It is not known if the density of the liquid or that of the solid at the freezing point has to be used in each case. This introduces an uncertainty of about 5% in the final result.

In the following table, we have indicated the proton density in the liquid state at the freezing point and the measured TEP, as discussed below. The errors are the sum of statistical and possible systematic errors. The results from CH₄ samples are used as reference values for each sample holder.

5. DISCUSSION

As it is well known, the measured resonance signal is proportional to the mean proton magnetization of the sample. Therefore as we keep the experimental conditions unchanged, the relative TEP in different samples is equal to their signal ratio divided by the proton density ratio.

In order to interpret the results, we derive formulas for the TEP of the protons in the solid if their spins are coupled to a common spin vector within the molecule. From the definition of spin polarization

$$P = \sum_m m N_m / (I \sum_m N_m) ,$$

where m is the magnetic quantum number of the spin I and N_m the population of the m th state, we obtain in the first approximation the TEP for any spin I :

$$P = (I + 1)\gamma\hbar H / (3kT) .$$

γ is the gyromagnetic ratio, H the applied magnetic field and T the temperature. If there are different spin species in the sample (for example, in methane one would expect para-, ortho-, and meta- species with total spin $I = 0, 1$, and 2) the mean TEP of the protons is

$$P = \sum_i (I_i + 1)(2I_i/n)b_i\gamma\hbar H / (3kT) . \quad (1)$$

The factor $2I_i/n$ accounts for the coupling of the n protons in the molecule to the spin species I_i ; b_i is the relative population of this species.

Let us first compare the results from CClF_2H and CD_3H with the frozen organic liquid samples. The first two are expected to exhibit the free proton spin susceptibility. Within the accuracy of the measurements, these organic samples had the same TEP as CClF_2H and CD_3H . This indicates that their TEP is not affected by molecular statistics, and that the high polarization values found in dynamic polarization experiments⁴⁾ with alcohols and toluene are true.

The proton spin polarization of CH_4 was found to be twice as high as in the five previous samples. This is expected if the ground state of CH_4 molecules in the solid has a total nuclear spin $I = 2$, as it has in the free CH_4 molecules⁸⁾. This state has twice the polarization of independent proton spins, as it is easily seen by using formula (1).

There are indeed several experimental indications that the CH_4 molecule is freely reorientating in the solid at low temperature, deduced from infra-red⁹⁾ and Raman spectra¹⁰⁾, neutron scattering¹¹⁾, and nuclear magnetic resonance¹²⁾. A conversion to this state is also indicated by the slow increase of the signal after cooling, and by the complicated variation of the spin relaxation time during this period⁷⁾.

The measured susceptibility of HD was found to be 1.5 times larger than expected for free proton spins. This anomaly might originate in some

intermolecular spin ordering. $(H_2)_2$, $(HD)_2$, and $(D_2)_2$ complexes are known; a sharp NMR signal loss has been observed in para- D_2 below the λ -point of the heat capacity¹³⁾. In HD no deviation from Curie law was found at temperatures between 1 and 0.2°K¹⁴⁾, but measurements at higher temperature were not done.

6. CONCLUSION

The thermal equilibrium polarization of proton spins near 1°K in CD_3H , $CClF_2H$, CH_3OH , C_2H_5OH , and C_7H_8 is that of independent spins $I = \frac{1}{2}$. For protons in CH_4 , this polarization is twice as large as for these compounds; it can be explained by considering that the molecules are in their lowest rotational state, with a total proton spin $I = 2$. For protons in HD, the polarization was found to be 1.5 times larger than for the normal samples (independent spins); the explanation of this fact, which may involve molecular clusters, remains to be established.

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Proton density and the measured thermal equilibrium polarization in the various compounds at 25 kG and 1.06°K.

Sample	Proton density g/cm ³	Proton polarization (%) sample holder No.		
		1	2	3
CH ₄	0.1258	0.5	0.5	0.5
CH ₃ OH	0.1177	0.29 ± 0.04		
C ₂ H ₅ OH	0.1180	0.27 ± 0.04	0.28 ± 0.03	
C ₇ H ₈	0.0846		0.23 ± 0.03	
CClF ₂ H	0.01908		0.24 ± 0.04	
CD ₃ H	0.0317			0.22 ± 0.03
HD	0.041		0.40 ± 0.05	0.37 ± 0.04

Note added in proof: in a recent paper, Wong et al. quote a value of $\langle I(I + 1) \rangle = 3.75 \pm 0.18$ for methane measured at 4.2°K; it is to be compared with the corresponding value of 5.88 ± 0.3 from our measurements at 1.06°K.

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