DYNAMIC NUCLEAR POLARIZATION IN LIQUIDS AT HIGH MAGNETIC FIELDS

by

K. H. HAUSSER

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The dynamic nuclear polarization (DNP) by relaxation interaction has been
investigated in some detail in the last years. The aim of this paper is twofold :

1) The investigation of DNP is extended both theoretically and experimentally
from two types of spins to systems of three and more types of spins and to
triple resonance.

2) The possibility of applying DNP for signal enhancement in high resolution
NMR is investigated with particular attention to the « high field limit »
of this mechanism. Measurements of the DNP at different temperatures
and related measurements on line width and relaxation lead to the conclusion
that the high field limit in a non viscous solvent as acetone at room temper-
ature is of the order of 10 kilogauss.

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CONTENTS

KEY TO THE FIGURES

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1 — INTRODUCTION

In a system of electronic spins S and nuclear spins I the most important relaxation mechanism of the spins I is in general the interaction with the spins S. In such a system, irradiation with the resonance frequency ω_S of the spins S causes a polarisation of the spins I parallel or antiparallel with respect to the external field Ho. This effect was first predicted by Overhauser [1] for metals, but it was soon realized to be a more general phenomenon of paramagnetic systems [2]. We are here concerned with this type of « dynamic nuclear polarisation » (DNP) which originates from relaxation interactions rather than with another type which results from weakly allowed double quanta transitions in solids.

Several authors [3] have investigated DNP in a two spin system. The importance of removing the paramagnetic molecular oxygen has been emphasized [4, 5]. In a previous paper [6], the interactions in a system of 3 types of spins with pure dipolar interaction have been studied both theoretically and experimentally including triple resonance techniques. This work is generalized here for more types of spins with mixed scalar and dipolar interaction.

Most of the earlier experiments have been done at low magnetic fields (<100 Gauss) because of technical difficulties encountered at higher fields. A method which avoids some of the difficulties encountered in working at microwave and megacycle frequencies simultaneously is briefly discussed in chapter 2.2.

The work at high fields is of particular interest in view of the most important practical application of DNP in liquids, the signal enhancement in high resolution NMR, since for this application the highest possible fields are desirable. However, the efficiency of DNP is not independent of the magnetic field but decreases with increasing field. This « high field limit of DNP » which is, of course, not a sharp limit but a continuous decrease in efficiency has the following origin. The simultaneous flip of an electron and a nucleus occurs only if the energy difference $(\omega_S \pm \omega_I)\hbar$ can be taken by the lattice. This condition requires in a liquid that the correlation frequency ω_c is higher than or at least comparable with the electronic Larmor frequency, $\omega_c \gtrsim \omega_s = \gamma_S H_0$. Since ω_c of most non viscous liquids is of the order of 10^{11}, the corresponding magnetic field H_0 is about 6000 Gauss. For highly viscous solvents the « high field limit », has been shown [7] to occur at much lower fields.

It was our purpose to investigate the « high field limit » and to find out how far it could be pushed to higher fields by reducing the viscosity and increasing the temperature. Most of our experiments have been done for convenience in a magnetic field of 3500 Gauss. Systematic variation of temperature and viscosity allows extrapolation of the results to higher fields and provides valuable information on the properties of the liquid.

In addition, we have used other independent methods in order to obtain a maximum of information on all interactions involved. The line width and the relaxation times of the

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(¹) The importance of removing the paramagnetic molecular oxygen has been emphasized. 4) 5).

electrons have been studied as a function of concentration, solvent and temperature. The nuclear relaxation times T_1 and T_2 of the protons (as a function of the same parameters) have been measured using pulse techniques with the purpose of investigating the line broadening caused by the paramagnetic radicals and its frequency, temperature and viscosity dependence. These related measurements are presented in the third chapter.

2 — Investigation of the DNP in liquids

2.1 — Theory of the interactions in multiple spin systems

In this paragraph we consider the interactions in a three spin system with pure dipolar coupling in somewhat greater detail. Subsequently the extension to four spins and to mixed dipolar and scalar coupling is discussed in a more condensed form since the extension to such systems is straightforward.

The polarisation $\langle I_{1,z} \rangle$ of the spin I_1 obtained when irradiating with the Larmor frequency ω_S of the spin S is given by [3]

$$\langle I_{1,z} \rangle = I_0 \left(1 - \xi_S f \frac{\gamma_S}{\gamma_{I_1}} \right) \tag{1}$$

In this equation I_0 is the polarisation in thermal equilibrium, $0 \leqslant s < 1$ is the saturation factor, $-\frac{1}{2} \leqslant \xi \leqslant + 1$ is a constant whose value and sign depends on the type of interaction and $0 < f < 1$ is the « leakage factor » taking into account other relaxation mechanisms of the spin I which do not contribute to the DNP.

Substituting I_2 for I_1, equation (1) describes also the polarisation of the spins I_2 due to their interaction with the S. However, a second term has to be added which takes into account the interaction of the I_2 with the I_1-spins. This interaction can be described by an equation similar to (1) but leading to a positive polarisation since the sign of γ_{I_1} is positive. Consequently, the resulting polarisation $I_{2,z}$ is due to a competitive effect of the interaction with the S and with the I_1 both pushing $I_{2,z}$ in opposite directions. This statement holds in general for any combination of the signs of γ_S, γ_{I_1} and γ_{I_2}, provided the interactions are either all purely dipolar or all purely scalar.

In order to obtain the magnitude of the second term one has to consider that the I_1 are not saturated but highly polarised. Taking this into account by multiplying the second term with the polarisation factor for the I_1 from equation (1) we obtain :

$$\langle I_{2,z} \rangle = I_{2,0} \left(1 + \frac{sf_2}{2} \frac{\gamma_S}{\gamma_{I_2}} - \frac{f_2}{2} \frac{\gamma_{I_1}}{\gamma_{I_2}} \cdot \frac{sf_1}{2} \frac{\gamma_S}{\gamma_{I_1}} \right) = I_{2,0} \left(1 + \frac{sf_2}{4} \frac{\gamma_S}{\gamma_{I_2}} (2 - f_1) \right) \tag{2}$$

Equation (2) does not contain γ_{I_1} ; within the approximation of (2) the magnitude of the magnetic moment of the spins I_1 is irrelevant for the polarisation of the spins I_2. However, equation (2) leaves out of account the relative degree of coupling between the I_2-spins and the S- and I_1-spins respectively. Suitable weight factors which measure this coupling are the partial transition probabilities $\sigma = 1/T_1^{I_2 S}$ and $\rho = 1/T_1^{I_2 I_1}$. Introducing these into (2) we obtain :

$$\langle I_{2,z} \rangle = I_{2,0} \left(1 + \frac{sf_2}{2} \frac{\sigma}{\sigma + \rho} \frac{\gamma_S}{\gamma_{I_2}} - \frac{sf_2}{4} \frac{f_1 \rho}{\sigma \times \rho} \frac{\gamma_S}{\gamma_{I_2}} \right) = I_{2,0} \left(1 + \frac{sf_2}{4} \frac{2\sigma - f_1 \rho}{\sigma + \rho} \frac{\gamma_S}{\gamma_{I_2}} \right) \tag{3}$$

The polarisation calculated from equation (3) is, in contrast to equation (2), not independent of the I_1-spins since ρ increases with increasing magnetic moment μ_{I_1}.

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Since the leakage usually is negligible in samples with high concentrations of electronic spins S, the leakage factors f_1 and f_2 can be set equal to one and equation (2) and (3) become :

$$\langle I_{2,z} \rangle = I_{2,0} \left(1 + \frac{s}{4} \frac{\gamma_s}{\gamma_{12}} \right) \tag{2a}$$

$$\langle I_{2,z} \rangle = I_{2,0} \left(1 + \frac{s}{4} \frac{2\sigma - \rho}{\sigma + \rho} \frac{\gamma_s}{\gamma_{12}} \right) \tag{3a}$$

In some cases, it may be assumed for simplicity that this condition is fullfilled. However, one should keep in mind that at very high fields the ability of the electron-nuclear interaction to induce nuclear polarisation decreases. This can be expressed in terms of an increasing leakage, and consequently one has to use the complete equation (3).

Next we consider a three spin system with scalar coupling between the I_1 and the S and dipolar coupling between the I_2 and both the S and the I_1

With scalar interaction one has to distinguish two types of relaxation of the nuclei [3]. In any case the interaction between the S and the I must be time-dependent and the time dependence must contain the Fourier-component of the nuclear Larmor frequency ω_I. In the first type of relaxation the time dependence originates from the motion of the S and I relative to each other which varies the coupling constant. The value of ξ for this first type of relaxation is $\xi = +1$, an example is the interaction between conduction electrons and nuclei in metals. In the second type of relaxation the coupling is constant and the time dependence originates from the flipping of the electronic spins. In this case which prevails in our systems the value of $\xi = + 1/2$.

If the relaxation interaction between the I_1 and the S is of the first type, one obtains :

$$\langle I_{2,z} \rangle = I_{2,0} \left(1 + \frac{s}{2} f_2 \frac{\sigma + f_1\rho}{\sigma + \rho} \frac{\gamma_s}{\gamma_{12}} \right) \tag{4}$$

In the case $f_1 = 1$, the weight factors σ and ρ cancel, the DNP becomes the same as in a two spin system.

If, on the other hand, the relaxation is of the second type, we find :

$$\langle I_{2,z} \rangle = I_{2,0} \left(1 + \frac{s}{4} f_2 \frac{2\sigma + f_1\rho}{\sigma + \rho} \frac{\gamma_s}{\gamma_{12}} \right) \tag{5}$$

It is perhaps illustrative to plot the obtained DNP as a function of $\frac{\sigma}{\sigma + \rho}$ for the three cases discussed so far, figure 1. In the derivation of the equations (3), (4) and (5) and figure 1 it was tacitly assumed that the DNP of the I_1-spin is determined by their interaction with the S and independent of the I_2. This condition is certainly fullfilled to a very good approximation in a system of electrons, protons and C^{13}-nuclei in natural abundance, but in other systems with comparable numbers and magnetic moments of the I_1 and I_2 the equations require modification.

These equations are readily extended to four types of spins S, I_1, I_2, and I_3. One obtains with dipolar coupling between all 4 types of spins

$$\langle I_{3,z} \rangle = I_{3,0} \left(1 + \frac{s}{4} f_3 \frac{2\sigma' - f_1\rho_1' - \alpha f_2\rho_2'}{\sigma' + \rho_1' + \rho_2'} \frac{\gamma_s}{\gamma_{13}} \right) \tag{6}$$

$$\alpha = \frac{2\sigma - \rho}{2(\sigma + \rho)}$$

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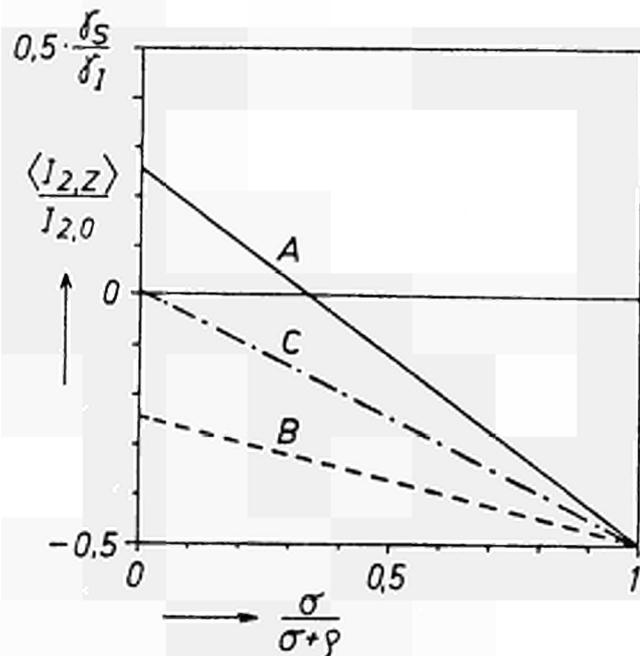
Fig. 1 — DNP of the I_2 in a three spin system as a function of the partial transition probabilities σ and ρ. A : Dipolar interaction between all three types of spins; B : Scalar interaction between the S and the I_1, dipolar between the I_2 and both the S and the I_1; C : Triple resonance, simultaneous saturation of the S and the I_1.

and with scalar coupling between the I_1 and the S and dipolar between all other types of spins for the relaxation of the I_1 of the first and second type respectively :

$$\langle I_{3,z} \rangle = I_{3,0} \left(1 + \frac{s}{4} f_3 \frac{2\sigma' + 2f_1\rho'_1 - \alpha'' f_2 \rho'_2}{\sigma' + \rho'_1 + \rho'_2} \frac{\gamma_s}{\gamma_{I3}} \right) \tag{7}$$

$$\langle I_{3,z} \rangle = I_{3,0} \left(1 + \frac{s}{4} f_3 \frac{2\sigma' + f_1\rho'_1 - \alpha' f_2 \rho'_2}{\sigma' + \rho'_1 + \rho'_2} \frac{\gamma_s}{\gamma_{I3}} \right) \tag{8}$$

$$\alpha' = \frac{2\sigma + f_1\rho}{2(\sigma + \rho)} \quad ; \quad \alpha'' = \frac{\sigma + f_1\rho}{\sigma + \rho}$$

σ', ρ'_1 and ρ'_2 are again the partial transition probabilities of the I_3 due to their interactions with the S, I_1 and I_2 resp. and σ and ρ are the corresponding quantities for the I_2-spins.

Finally, we consider the DNP of the I_2 in a three spin system in which the S and the I_1 are saturated simultaneously. For this « triple resonance » we obtain instead of equation (3) assuming full saturation of the I_1 :

$$\langle I_{2,z} \rangle = I_{2,0} \left(1 + \frac{sf_2}{2} \frac{\sigma}{\sigma + \rho} \frac{\gamma_s}{\gamma_{I2}} + \frac{f_2}{2} \frac{\rho}{\sigma + \rho} \frac{\gamma_{I1}}{\gamma_{I2}} \right) \tag{9}$$

This equation holds for all types of interactions of the I_1 provided the coupling of the I_2 is dipolar.

If the S are electrons, the I_1 protons and the I_2 C^{13}-nuclei, f_2 can be set equal to one in very good approximation and s can always been made approximately one by using high

microwave power. It is interesting to note that in this case the ratio σ/ρ can be determined from the triple resonance experiment and than f_1 can be determined unambigously from equation (3).

2.2 — Experimental technique

The helix has been used for many years as a microwave delay line in the construction of travelling wave tubes [8]. Its application to ESR and double resonance measurements has been first suggested by Robinson [9], a somewhat more detailed description has recently been given by Webb [10].

Our experimental arrangement using the helix technique for DNP has been described previously [4]. Its main advantage is that one obtains at a given power level H_1-fields comparable to the ones obtained in a high Q cavity without the difficulties arising from the introduction of the receiver coil of the NMR into the cavity.

For most of the results given here we have used our first setup [4] in which the helix serves in agreement with Robinson's proposal simultaneously as the receiver coil for the NMR. However, this most simple and seemingly logical arrangement has one important drawback : The ideal dimensions of the helix from the point of view of a high microwave field and from the point of view of a good L/C-ratio of the nuclear resonance detection are not identical and are difficult to reconcile. This discrepancy increases with increasing magnetic field and frequency ; it becomes particularly important for nuclei with a smaller magnetogyric ratio, i.e. C^{13}. We have therefore developed a somewhat different method in which the helix is immersed in the solution after the manner of an immersion heater. The NMR-receiver coil is arranged to be coaxial with the helix but outside the sample tube. Thus its dimensions are independent of the helix and can be chosen for optimal detection of the NMR, figure 2.
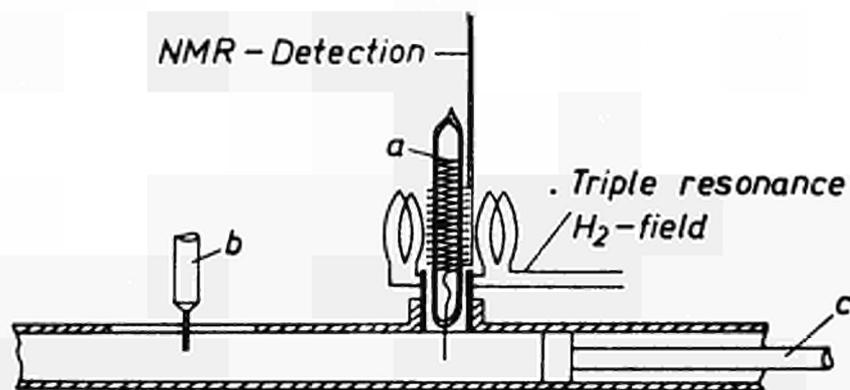
Fig. 2 — Sample arrangement for DNP and triple resonance using helix technique

The helix technique also considerably facilitates the performance of a triple resonance experiment, i. e., the measurement of the DNP of one type of nuclei when saturating simultaneously the electrons and the other type of nuclei. One has simply to add another coil perpendicular to the H_0-field and to the receiver coil. This cross coil arrangement similar to the one used by Bloch is also shown in figure 2.

In calculating the amount of DNP one has also to consider transport phenomena in the liquid caused by diffusion or convection. If the saturating H_1-field is not homogeneous

over the whole volume the transport of polarized nuclei increases the average DNP; more information on this effect as well as details of the actual experimental technique will be given elsewhere [11].

Several radicals have been used but most of the measurements have been made with the 1,3-Bisdiphenylen-2-p-chlorphenyl-allyl (BCPA). BCPA is chemically stable and dissolves easily in high concentration ($c \approx 10^{-2}$ mol/l) in many polar and unpolar solvents. The unresolved HFS results in an inhomogeneously broadened ESR-absorption line with a width of about 5 Gauss at medium concentrations which is reduced at the highest concentrations by exchange interactions to less than one Gauss. The dependence of the line width on concentration, temperature and viscosity is discussed in chapter 3, 3.1 because of its relation to the microwave power required for complete saturation.

2.3 — Experimental results

1. Protons. The experimental results are presented in terms of the signal enhancement V :

$$V = \frac{\langle I_z \rangle - I_0}{I_0} \tag{10}$$

The signal enhancement V of a solution of 5×10^{-2} mol/l BCPA in toluene is plotted in figure 3 as a function of temperature. The increase in V in the temperature range from 15° to 80° C is found to be approximately a factor of two.

2. C^{13}. The C^{13}-resonance could not be measured with our sensitivity without signal enhancement because of the low natural abundance; the enhancement factors have therefore been determined by comparison with the proton resonance at the same frequency. With a solution of 2×10^{-2} mol/l BCPA in benzene an enhancement factor V = 300 was obtained. The dependence on the temperature is not significantly different from the result obtained with the protons in the same solution I, figure 3.

3. Triple resonance. The absolute value of the enhancement factor V is determined by the competetive interaction with the electrons and the protons, equation (3). Theoretically, one would expect from equation (9) an additional enhancement of the C^{13}-nuclei (I_2) if the protons (I_1) are also saturated. This additional enhancement has actually been found experimentally with the same solution of 2×10^{-2} mol/l BCPA in benzene mentioned above. Using triple resonance we find V = 600 as compared with V = 300 with ordinary DNP. The measured enhancement of the signal is really 1200, the additional factor of two being caused by the coalescence of two lines into one.

3 — RELATED MEASUREMENTS OF LINE WIDTH AND RELAXATION

3.1 — Electronic spins S

The saturation parameter s for an homogeneously broadened line is proportional to the square of the radio-frequency field H_1, while for an inhomogeneously broadened line it has been shown [12] to be linearly proportional to H_1. The ESR-absorption lines of our radical solutions are inhomogeneously broadened at low concentrations and temperatures, their total width is determined by the unresolved hyperfine structure. The effect of « exchange narrowing » in reducing the total line width is proportional to the exchange frequency f_{ex}, which in turn

in a liquid [13] is proportional to the concentration c and the temperature T and inversely proportional to the viscosity

$$f_{ex} \propto \frac{c \times T}{\eta} \tag{11}$$
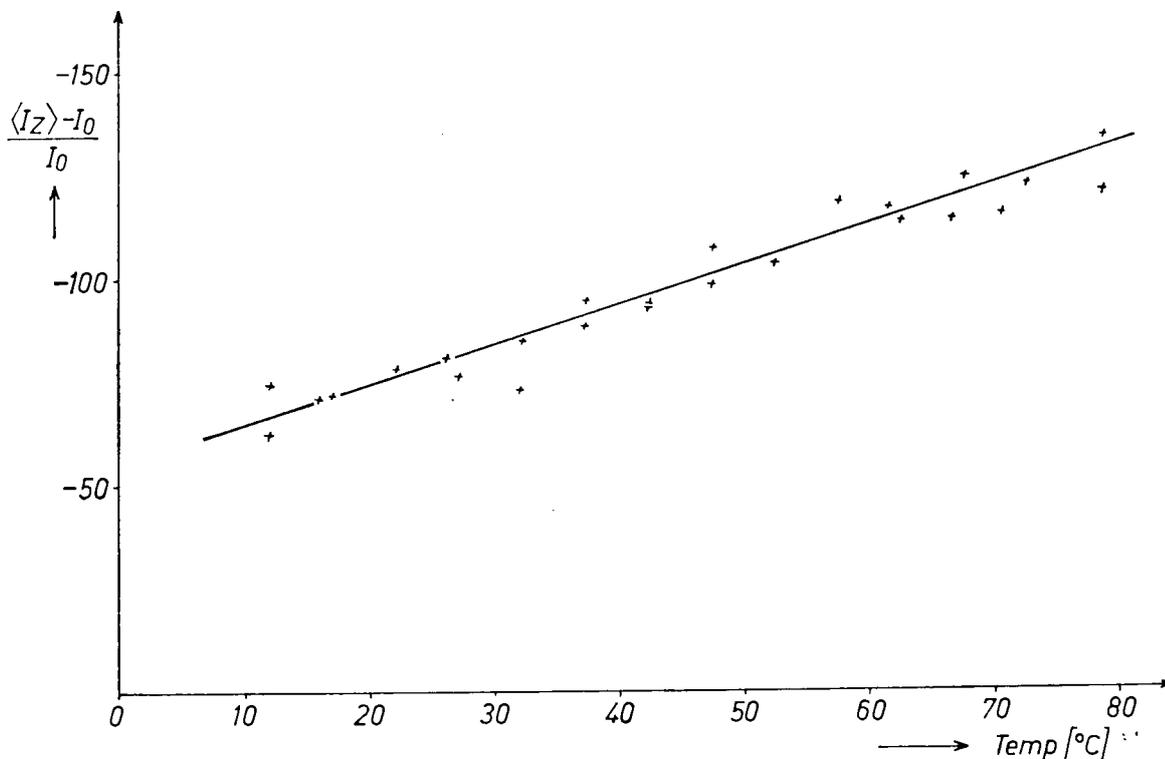
Fig. 3 — Signal enhancement V of a solution of 5×10^{-2} mol/l BCPA in toluene as a function of the temperature.

We have investigated the line width as a function of these 3 parameters [13]. The line width of BCPA in benzene at room temperature as a function of the concentration decreases from 4,5 Gauss at 10^{-3} mol/l to 0,7 Gauss at 5×10^{-2} mol/l.

In order to obtain more information on the ratio of T_1/T_2 both relaxation times have been measured using pulse techniques at X-band frequencies [1]. For a concentration of 5×10^{-2} mol/l of BCPA in benzene T_2 was found to be 5×10^{-8} and $T_1 = 6 \times 10^{-6}$, a ratio of $T_1/T_2 \approx 120$.

A very different result is obtained if the temperature dependence of the linewidth of the radicals is studied in the presence of oxygen. At a medium concentration of 10^{-2} para-magnetic species of which 20 % are BCPA-radicals and 80 % are O_2-molecules the line width increases from 7 Gauss at room temperature to 22 Gauss at 80° C. This effect which is explained in terms of exchange interactions between electronic spins in different energy levels [14] is partly responsible for the very large oxygen effect on the obtainable DNP in liquids [4].

3.2 — Protons

We have measured the relaxation times T_1 and T_2 of the protons of the solvent as a function of temperature fot three solutions of BCPA in benzene, toluene and acetone. The

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(1) We are very indebted to Dr. D. Kaplan for having performed these measurements.

measurements have been made [15] in a magnetic field of about 11.000 Gauss corresponding to a proton resonance frequency of 48 Mc using a Bruker spin echo spectrometer.

The results are as follows :

1. The relaxation times found in a saturated solution of BCPA in acetone are between 2 and 3 seconds corresponding to the comparatively low solubility of the BCPA in acetone.

2. The shortest relaxation time T_2 observed in the more concentrated solutions is toluene, $c = 10^{-1}$ mol/l, was 0,2 sec corresponding to a line width $\Delta\nu = \dfrac{1}{\pi T_2} \approx 2$ Hz.

The relaxation times of a solution of BCPA in acetone, $c \approx 10^{-2}$ mol/l, has also been measured as a function of the magnetic field ([1]).

In figure 4 the spin-lattice relaxation time T_1 is plotted as a function of the Larmor frequency of the protons. One finds a region of dispersion at fields of about 10.000 Gauss indicating that the dominating relaxation mechanism at low fields, the flip-flop process which produces DNP, becomes less efficient in this region. At a higher temperature this region of dispersion should be shifted to higher fields, but it was impossible to obtain an experimental verification of this expectation in time for this conferences.

4 — DISCUSSION

The experiments on the line width and the relaxation times of the ESR show that a careful removal of the paramagnetic oxygen is vital for good efficiency of the DNP. In
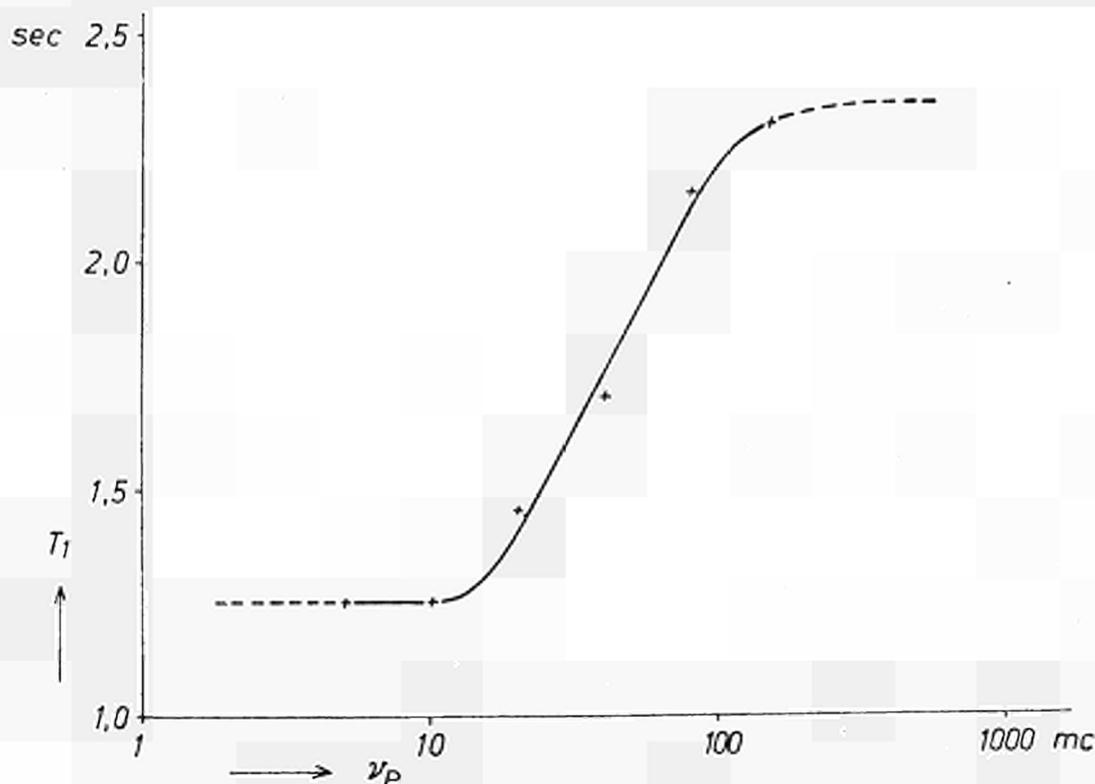
Fig. 4 — Spin lattice relaxation time T_1 of the protons of a solution of 10^{-2} mol/l BCPA in acetone as a function of the Larmor-frequency ν_P.

([1]) We are very indepted to Mr. F. Noack for having performed these measurements.

oxygenfree solutions high temperature and low viscosity are favorable conditions for saturation with a minimum microwave power. In favorable cases, the required H_1-field is of the order of 1 Gauss, but 5-10 Gauss required for saturation of the inhomogeneously broadened line of a more dilute radical solution can be obtained in principle with microwave powers of the order of 100 Watt.

From the point of view of the line width of the nuclear resonance high temperature and low viscosity are also desirable. At the highest concentrations of the radicals ($c \approx 10^{-1}$ mol/l) the line width $\Delta\nu = \dfrac{1}{\pi T_2}$ is of the order of 2 Hz, but such concentrations are not necessary for obtaining high signal enhancements. At concentrations of about 10^{-2} mol/l the loss in resolving power is negligible even for high resolution proton resonance.

For other nuclei with smaller magnetic moments and correspondingly longer relaxation times no broadening at all is to be expected. The reduction of the long relaxation times of such nuclei persists us to use a higher radio frequency H_2-field and thereby to increase the sensitivity of the detection of the NMR.

While the line broadening due to the unpaired electrons is not a serious limitation to the application of DNP to high resolution NMR, the « high field limit » is more critical.

The measurements of the field dependence of the spin lattice relaxation time of the protons (fig. 5) show that even with a non viscous solvent such as acetone the proton-electron flip-flop-interaction which is an important relaxation mechanism of the protons at low fields begins to decrease at about 3 kilogauss at room temperature and becomes negligible at about 30 kilogauss. This region of dispersion can be shifted to higher fields by increasing the temperature, but from the variable temperature results obtained at 11 kilogauss as well as from the variable field measurements it looks as if the high field limit of the flip-flop-process responsible for the DNP would be at fields of this order.

Similar results are obtained from the temperature and viscosity dependence of the DNP. The signal enhancement V with sufficient microwave power for complete saturation is essentially inversely proportional to the viscosity of the solution. The decrease in V with increasing field and viscosity can be expressed in terms of the leakage factor f, which becomes a function of the ratio of the correlation frequency ω_c to the electronic Larmor frequency ω_S, $f(\omega_c, \omega_S)$. In low fields, $\omega_c/\omega_S \gg 1$, the electron nuclear flip-flop-process is an important relaxation mechanism for the nuclei, the leakage is negligible, $f \approx 1$. In the region of $\omega_c/\omega_S \approx 1$ the efficiency of the flip-flop-process decreases and consequently the relative importance of the other processes increase, At very high fields $\omega_c/\omega_S \ll 1$, the probability of nuclear relaxation by the flip-flop-process vanishes, the leakage factor f becomes zero. We define a « critical field H_c » for which $f(\omega_c, \omega_S) = 0.5$. Since this critical field is a function of the correlation time ω_c, it depends on the viscosity and the temperature of the solvent.

We propose to use for $f(\omega_c, \omega_S)$ tentatively the function

$$f(\omega_c, \omega_S) = \frac{1}{1 + (\omega_S/\omega_c)^m}$$

Using this expression and the definition of the critical field given above, we obtain for H_c the condition $\omega_S = \omega_c$. Since the line width and therewith the power required for complete saturation as well as the transport phenomena mentioned in II_c depend also on η a detailed analysis of the dependence of H_c on the viscosity is difficult and will be discussed elsewhere [11]. However from the experimental results presented here we get an estimate of the order of magnitude of H_c. In acetone at room temperature H_c is of the order of 10.000 Gauss, while for benzene we find a value of H_c of about 5000 Gauss.

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What does this mean for the application of DNP to high resolution NMR ? For protons the highest possible fields are important because of the small chemical shifts. Fields of 20 or more kilogauss used today in commercial equipment are above our definition of critical fields and it seems not to be possible to obtain an appreciable signal enhancement. Furthermore, a certain loss of resolution by a factor of 2 or 3 due to the paramagnetic radicals may occur. However, for the many cases where the information obtainable in a field of about 10.000 Gauss or less with a line width of the order of 1 Hz is sufficient an increase in sensitivity by a factor of 100 or more will certainly increase considerably the range of application.

Nuclei with $I > 1/2$ will be in general much less suitable for dynamic polarisation because the quadrupole interaction is the dominating relaxation mechanism with these nuclei ; it leads to low values of the leakage parameter f and consequently low efficiencies of DNP.

However, for other nuclei with spin $I = 1/2$ such as C^{13}, N^{15}, F^{19}, and P^{31} the chemical shifts are larger and fields of the order of 10.000 Gauss are sufficient in most cases. The application of DNP seems to be particularly usefull for C^{13}-resonance. No loss in resolving power is to be expected and signal enhancements as high as three powers of 10 will partially compensate for the low natural abundance 1,1 % of C^{13} and for the reduced sensitivity due to the comparatively small magnetic moment. An extension of C^{13}-resonance as a widely applicable method could provide valuable information in addition to the proton resonance.

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