Experimental Results on the Dynamic Polarisation in a Solid by Variation of Temperature

J. Haupt

Magnetic Resonance Laboratory, Physics Division, Ispra, Italy

(Z. Naturforsch. **28a**, 98—104 [1973]; received 4 December 1972)

A description of the apparatus for a new dynamic polarization effect by variation of temperature, and the experimental results obtained, are presented. As described earlier a temperature jump produces a very large enhancement of the dipolar signal (about 10.000) in solid γ-picolene due to the dipolar couplings between the protons of the CH_3-group and the modes of the CH_3-rotator with the crystal phonons. A simple phenomenological model for the interpretation of the experimental data is introduced. Within the experimental errors agreement between model and data is obtained.

From the shape of the measured polarization curves a dipolar polarization time T_p and the dipolar relaxation time T_d is determined. From the maxima of the polarization at different temperature jumps a curve dependent only on the temperature is constructed, which together with T_p and T_d characterizes completely the dynamic polarization behaviour.

A comparison of the Zeeman- and dipolar relaxation with earlier measurements on similar molecules containing CH_3-groups shows that the CH_3-rotation in solid γ-picolene is almost unhindered and that the "relaxation efficiency" is very low. These last conditions are important for a large enhancement of the dipolar polarization.

Introduction

The principle of a new effect of dynamic polarization in a solid obtained after a temperature jump has been already described in an earlier paper [1]. A temperature jump of a few degrees in the temperature region of 20 °K produces in γ-picolene an enhancement of the dipolar signal of the order 10.000. The effect has been explained by the coupling of the combined nuclear spin system of the methyl group and the methyl-rotator with the phonons of the crystal. The emission (or absorption) of phonons between the states of the combined rotator-spin-system causes a partial transfer of the order of the rotator-spin-system to the dipolar system.

The effect is therefore observed in the non equilibrium thermodynamic state after a temperature jump and disappears when thermal equilibrium is reached. The sign of the change of dipolar energy is reversed with the direction of the temperature jump.

In this paper detailed experimental results and a description of the apparatus is given. A simple phenomenological model is introduced and the experimental results are interpreted in terms of this model. A theoretical derivation of such a model from quantum mechanics will be given later, since a simplified quantum mechanical description of the polarization principle is published in Ref. [1].

Experimental

a) Cryogenic device

For the realization of the temperature jumps needed in the region between 5° and 50 °K a flow cryostat [2] was used. The liquid helium is pumped via a thin suction pipe of 0.5 mm diameter from a commercial helium container to the heat exchanger of the sample chamber (Fig. 1). Then the gas passes the cryostat and a regulation valve and arrives via the pump in the gasometer. With a regulation system the temperature can be kept constant better than 0.1 °K.

If a jump to a higher temperature is to be executed, the desired temperature value is selected on the regulator, and the heater under the sample is simultaneously switched on. After the selected temperature is reached the heater is switched off and the remaining deviation is regulated to zero with a calibrated needle valve as rapid as possible. A jump to lower temperature is executed in the same way, but with the difference, that the heater is replaced by opening a valve

---

[1] J. Haupt, Phys. Letters **38A**, 6, 389 [1972].

[2] J. Haupt, Z. angew. Phys. **23**, 377 [1967].

which bypasses the needle valve. With the present device a jump to lower temperature takes a little longer than the higher temperature jump and depends also on the amplitude of the temperature jump. Typical times are between 10 and 20 sec.

Since these times are small compared to the characteristic times of the sample (see Fig. 8), one may consider the temperature jump, for the sake of simplicity, as a perfect step function. Eventually one can correct small errors by slightly delaying the time of the step.

b) Device for the measurement of the polarization curves and the relaxation time

The measurement of the free decays is made with an incoherent 15 Mc/s pulse spectrometer. In order to effect the magnetization only negligible, r. f. pulses of only a few degrees length are given. Such a pulse can measure a dipolar signal just as well as a Zeeman-signal, if the measured signal is larger than the other type, which is shifted 90° in phase. Figure 2a is a photo of the free induction decay at different times after a temperature jump. It shows the typical shape of a dipolar signal. In thermal equilibrium the usual Zeeman signal (Fig. 2b) is obtained. In order to obtain a more precise and rapid measurement, both amplitude and time difference are automatically stored in a minicomputer (IBM S/7) (see Figure 3). The stored values can be displayed on an xy-recorder in the form of small crosses (Figure 4), or printed by the operator station.

Figure 3 shows a block diagram of the apparatus. The signal obtained after a pulse is amplified and rectified and can be seen on a scope. With the gate device the region between 7 and 15 μs after the r. f. pulse is gated out of the signal and integrated. The voltage obtained which decays with a time constant of about 0.1 sec, is converted on external synchronization with the computer internal AD-converter. The gating device proved to be necessary, since the AD-converter was not sufficiently rapid.

To measure the longitudinal relaxation time T_1 the magnetization was saturated before each measurement, and the growth of the magnetization was registered with short pulses. With weak signals the registration

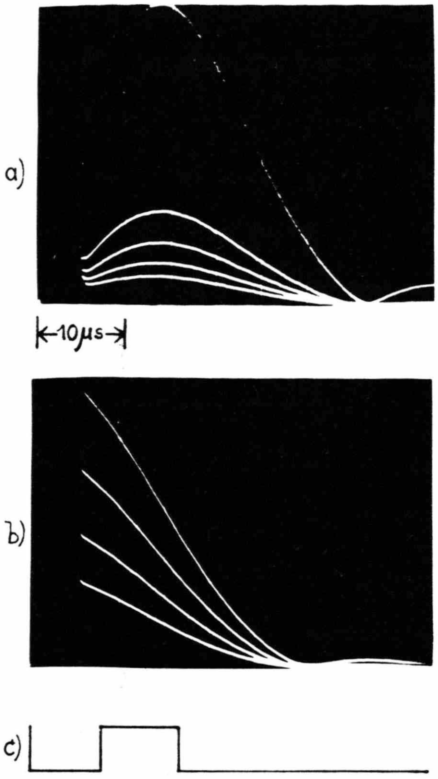

Fig. 2. a) free induction decays at different times after a temperature jump; b) the same with higher amplification in thermal equilibrium, the parmeter is the time after a saturation of the signal; c) timing of the gate device.

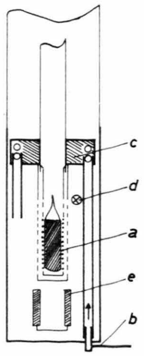

Fig. 1. Inner part of the flow cryostat: a) sample with r. f. coil; b) suction pipe to liquid helium container; c) heat exchanger; d) temperature sensitive element; e) heating resistances.

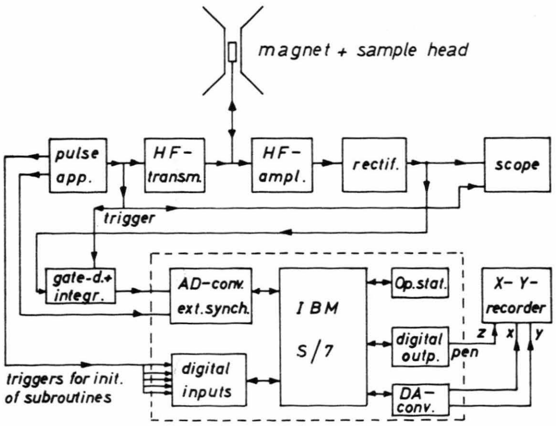

Fig. 3. Block-diagram of the pulse spectrometer.

was made by a 90° pulse and the different points were obtained by repetition of the saturation with variation of the time difference to the 90° pulse.

The dynamically enhanced induction decay (Fig. 2a) has the typical form of a dipolar signal [3]. For a further confirmation the phase of the signal was also determined with a coherent pulse-spectrometer with phase sensitive detection. For a jump to higher temperature the dipolar signal appears 90° in advance of the Zeeman signal, and for a jump to lower temperature 90° behind the Zeeman signal. This is a further confirmation that the enhanced signal is of the dipolar type.

For the measurement of the polarization curves, the coherent spectrometer was not used, because the signal amplitude is too sensitive to small changes in the magnetic field or to phase changes, and also the adjustment is more difficult. Since the enhanced dipolar signals are usually larger than the Zeeman signals no problems arise with the incoherent spectrometer.

Two typical polarization curves are given in Figure 4. Curve a) corresponds to a jump from 11.2 °K to 25.8 °K and curve b) to the reverse jump. The amplitudes and shape of the two curves differ strongly from one another.

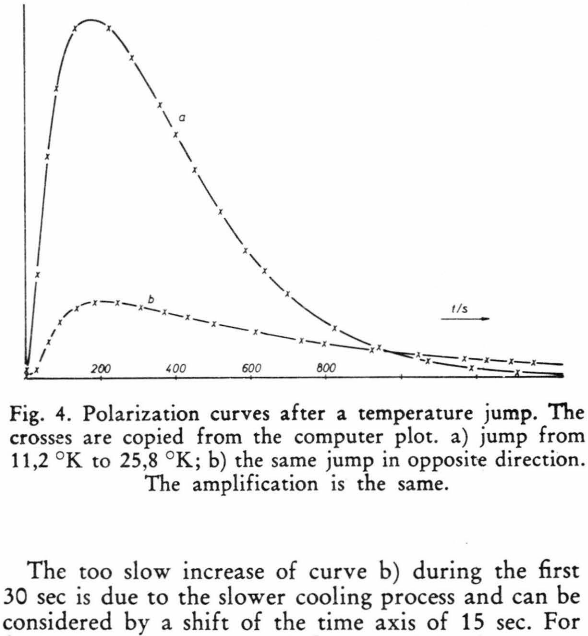

Fig. 4. Polarization curves after a temperature jump. The crosses are copied from the computer plot. a) jump from 11,2 °K to 25,8 °K; b) the same jump in opposite direction. The amplification is the same.

The too slow increase of curve b) during the first 30 sec is due to the slower cooling process and can be considered by a shift of the time axis of 15 sec. For future measurements the influence of the heat conductivity by variation of the sample geometry and the helium gas pressure inside the sample will be studied.

For the actual measurements the γ-picolene (bought at Fluka AG, type purum) was vacuum disstilled, degassed and sealed in a glass tube. The sealed sample was maintained for some days in helium gas. The freezing process and different temperature procedures[4] had in contrast to earlier measurements on other systems no considerable influence on γ-picolene. With different samples of γ-picolene small differences in the dynamic polarization behaviour were obtained. For the actual measurements a several week old sample was used.

Introduction of a simple model

The change of dipolar degree of order in connection with transitions between states of the rotator system after a temperature jump is due to the coupling [1] between both systems. Since the energy differences within the dipolar system are very small compared to those of the rotation, the polarization rate will be almost independent of the polarization degree, except if the absolute polarization is high. In the simplest case it is given by an exponential:

$$\mathrm{d}p/\mathrm{d}t = \pm K \cdot e^{-t/T_\mathrm{p}} \qquad (1)$$

K depends on the temperature jump and the system. T_P we define as polarization time. With a given sample it depends only on the temperature. P is the dipolar polarization, which is proportional to the dipolar degree of order [3]. The + or − sign depends on the direction of the temperature jump.

Due to the relaxation the polarization created by (1) is permanently depolarized. The depolarization rate will be given in the simplest case by

$$\mathrm{d}p/\mathrm{d}t = -(p-p_0)/T_\mathrm{d} \, . \qquad (2)$$

T_d is to be identified with the dipolar relaxation time and P_0 is the thermal equilibrium value of the dipolar polarization. Because of the high enhancement factors considered in this paper, it can be ignored in the following. Taking both processes into consideration we obtain the differential equation:

$$\mathrm{d}p/\mathrm{d}t = -p/T_\mathrm{d} \pm K \cdot \exp\{-t/T_\mathrm{p}\} \, . \qquad (3)$$

The solutions of this diff. eq. are:

$$\text{for } T_\mathrm{p} > T_\mathrm{d} \, , \quad p(t) = \pm K \, (T_\mathrm{p} T_\mathrm{d} / T_\mathrm{p} - T_\mathrm{d}) \cdot (e^{-t/T_\mathrm{p}} - e^{-t/T_\mathrm{d}}) \, , \qquad (4a)$$

$$\text{for } T_\mathrm{p} = T_\mathrm{d} \, , \quad p(t) = \pm K \, t \, e^{-t/T_\mathrm{p}} \, . \qquad (4b)$$

[3] J. Jeener, Adv. Magnetic Resonance **3**, 205 [1968].

[4] K. Grude, J. Haupt and W. Mueller-Warmuth, Naturforsch. **21a**, 1231 [1966].

The case $T_p < T_d$ will not be discussed, since it is unreasonable from the physical point of view. Polarization processes are relaxation processes in thermal equilibrium.

Equations (4a) or (4b) with a proper T_p and T_d correspond to the measured curves. One has to subtract only the Zeeman signal under consideration of the phase.

Shape of the polarization curves

For the discussion of the measured points the curves obtained from formula (4a) and (4b) are calculated as a function of t/T_p with T_p/T_d as parameter. In order to determine from the symmetry of the experimental results the ratio T_p/T_d, the amplitude and the time scale of the calculated curves have been multiplied with a factor chosen so that the maximum occurs at 1; 1 (see Figure 5). The amplitude is then plotted in logarithmic scale and the time in linear scale. The same is done for the measured curves on transparent paper. By putting both over one another T_p/T_d can be determined. The accuracy is of course not high since due to reasons mentioned above the position of the maximum might have in some cases an error of 10 %. The values T_p/T_d are given in Fig. 6. It should be mentioned that the experimental points below 15 °K have been obtained with a more accurate method described below. It uses the different height of the polarization maxima measured for temperature jumps in opposite direction.

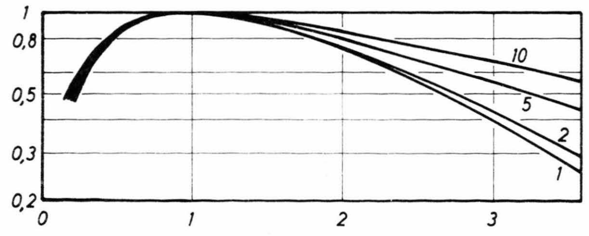

Fig. 5. Normalized polarization curves deduced from formula (4 a) and (4 b). Parameter is the ratio T_p/T_d.

In a more simplified way one obtains T_p/T_d as follows: one has to determine first the times t_1 and t_2 for half the polarization amplitude of the maximum. The quotient $(t_{max}-t_1)/(t_2-t_{max}) = A/B$ is a direct measure for T_p/T_d. Fig. 7 gives A/B in dependence of T_p/T_d as obtained by fomula (4). The values A/B derived from the experimental curves vary systematically a little with the direction of the temperature jump for the reason given above, but the results of Fig. 6 are confirmed.

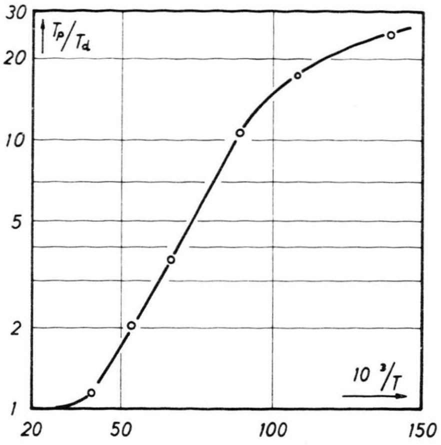

Fig. 6. T_p/T_d as a function of the reciprocal temperature.

With the results obtained above and the positions of the maximum the polarization time is also determined. The position of the maximum from Eq. (4) is:

$$t_{max} = T_p \cdot (T_d/T_p - T_d) \cdot \ln(T_p/T_d) \text{ for } T_p > T_d \quad (5a)$$

and

$$t_{max} = T_p \text{ for } T_p = T_d \, . \quad (5b)$$

The polarization time is

$$T_p = t_{max} \cdot (T_p/T_d - 1)/\ln(T_p/T_d) \, . \quad (6)$$

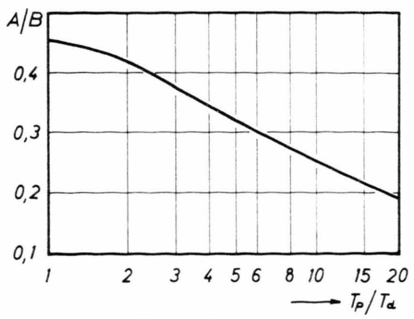

Fig. 7. See text.

---

[5] R. VAN STEENWINKEL, Naturforsch. 24a, 1526 [1969].

Since T_p/T_d is already known, we get now also T_p and T_d.

In Fig. 8 T_p and T_d is given as a function of the temperature. In principle, T_d can also be measured directly [5]. Due to the necessary adjustements this becomes rather difficult and tiring for the long relaxation times and it can be left until later. The longitudinal Zeeman relaxation time T_1 can be measured more easily. The experimental results are also given in Figure 8.

Polarization maxima as a function of the temperature jump

The amplitudes of the measured maxima at different temperature jumps are given in Figure 9. They are indicated by vertical arrows with a length proportional to the amplitude. The calibration length in the upper right corner corresponds to a 50-fold enhancement of the dipolar signal as compared with the Zeeman signal at the inverse temperature of $10^3/T = 39$. The dipolar enhancement factor is in addition about 1000 times larger. The arrows in direction of the abscissa characterize the initial and final temperature of the jump.

As could be seen already in Fig. 4 the maximum has a different height after a jump from the temperature T_i to T_f than in the inverse case. The reason lies in the fact that the ratio T_p/T_d varies with the temperature and so does the amplitude of the maximum.

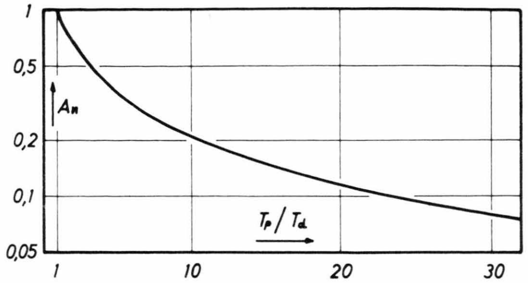

Fig. 10. Normalization factor A_n as a function of T_p/T_d.

In Fig. 10 a "normalization factor" A_n in dependence of T_p/T_d as obtained from formula (4) is given. It is set equal to 1 for the most favourable case $T_p/T_d = 1$. By multiplying the amplitudes in Fig. 9 with $1/A_n$, the absolute value of the polarization maxima becomes within the experimental errors independent of the direction of the temperature jump. With these "normalized amplitudes" it is possible to construct by integration a function depending only on the temperature (see Fig. 11), which gives the normalized am-

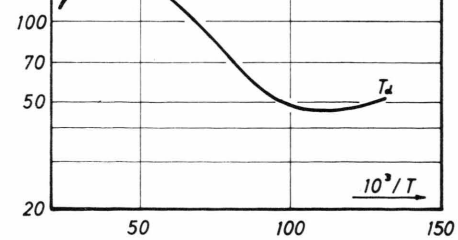

Fig. 8. The longitudinal Zeeman relaxation time T_1, the dipolar polarization time T_p and the dipolar relaxation time T_d as function of the inverse temperature.

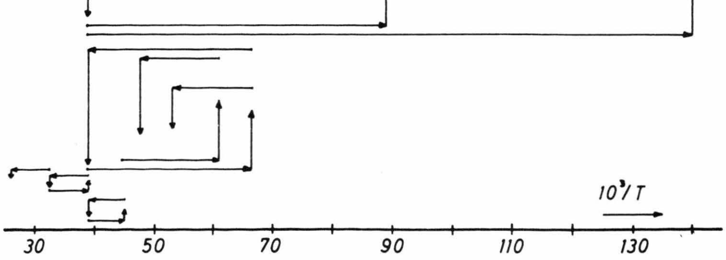

Fig. 9. The amplitude of the polarization maximum as function of the temperature jump. More details are given in the text. The amplitude of the Zeeman polarization at $10^3/T = 39$ is measured as described in the experimental part.

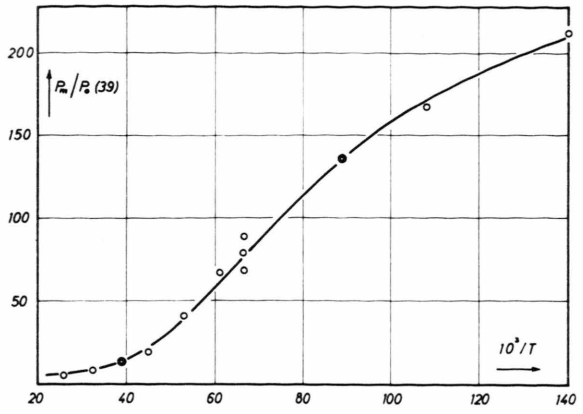

Fig. 11. The normalized amplitude of the polarization maximum is obtained by the ordinate differences for a given jump. The ordinate scale is determined only within an additional constant.

plitudes for a certain temperature jump by the difference of the ordinate values. The measured maxima are obtained by multiplication with A_n, which can be derived from Fig. 10 and Figure 6.

If one assumes that the normalized amplitudes for opposite temperature jumps are equal, one can deduce information about the ratio T_p/T_d from the normalization factors needed to fit the experimental data of opposite jumps. Since this method turned out to be more precise for temperatures below 15 °K, it has been used for the improvement of the ratio T_p/T_d in Fig. 6 in the temperature region under consideration.

Remarks and discussion

The absolute polarization obtainable according to Fig. 11 is a few percent. This is still a low value, but since the studies in this field are only just beginning, it cannot be excluded that other materials with a higher absolute polarization will be found.

The polarization mechanism is not necessary restricted to the previously mentioned coupling between the spin system and the states of the CH_3-rotator; other mechanism are in principle possible.

On the other hand it must be emphasized that dynamic polarization in combination with CH_3-group rotation depends upon some limiting conditions. The most important ones are given in the following paragraphs.

In comparing the longitudinal Zeeman relaxation time T_1 given in Fig. 8 with earlier measurements on other similar systems [6–9] a very low relaxation efficiency factor [10] can be stated. Whilst the relaxation time minima of materials with small hindering barrier investigated earlier (at 15 Mc/s) have been shorter than 1 sec, the relaxation times of γ-picolene are, over the entire investigated temperature range, longer than 200 sec. It is not possible to deduce an apparent activation energy from the T_1-dependence, since T_1 is within the experimental errors independent of the temperature. For these two reasons, the calculation of the transition probabilities of the combined system should be treated in the limiting case of a zero-hindering potential. Also in this case preliminary calculations confirm the principle of the effect described in Ref. 1.

The calculations are based on the second order perturbation as described in Ref. 10, but taking into consideration the change of the selection rules in the case of a very low barrier.

The smaller the barrier becomes the more significant is the probability of transitions with a simultaneous change in magnetic and rotational quantum number as compared to nonmagnetic transitions. The coupling of certain magnetic selection rules to the emission or absorption of a phonon as described in Ref. 1 remains unchanged.

In all these calculations the intermolecular interaction of the protons of the CH_3-group with the neighbouring protons is ignored. It seems, that they produce an attenuation of the polarization effect. The case of γ-picolene seems to be in this connection a very favourable constellation.

In the phenomenological model described above the dipolar relaxation time T_d given in Fig. 8 plays an essential role. As is known from earlier measurements [5], the dipolar relaxation time, below the temperature of the maximum Zeeman relaxation, becomes considerably shorter than the Zeeman relaxation time.

---

[6] J. Haupt and W. Mueller-Warmuth, Naturforsch. **24a**, 1066 [1969].

[7] J. Haupt and W. Mueller-Warmuth, Naturforsch. **23a**, 208 [1968]

[8] G. P. Jones, R. G. Eades, K. W. Terry, and J. P. Llewellyn, J. Phys. C. **1**, 15 [1968].

[9] P. S. Allen and A. Cowking, J. Chem. Phys. **49**, 789 [1968].

[10] J. Haupt, Naturforsch. **26a**, 1578 [1971].

This behaviour is only valid if the motion can be described classically, but not if the relaxation is determined by quantum effects. Some additional interpretations following from Ref. 10 give a very small "dipolar relaxation efficiency factor" in the temperature region of the maximum of the dipolar relaxation, in the case of a small hindering barrier. For a very small barrier T_d should become equal to T_1 within a factor of the order 1. Some unpublished experimental results of T_d in m-xylene and other materials confirm this behaviour.

The relaxation times T_1 and T_d in γ-picolene in the investigated temperature region differ from one another less than a factor 5. Because of the long relaxation times it cannot be excluded that especially below 20 °K paramagnetic impurities play a role. Therefore a more detailed interpretation of T_1 and T_d cannot be given. Further measurements for the solution of this problem are planned with modified samples.

Application to polarized targets

Apart from the restricted choice of material three difficulties for the application of this method in the field of polarized targets exist.

i) the dipolar system is polarized. ii) the polarization is not stationary. iii) the absolute degree of polarization is still rather low. Point (i) can be solved by transfer of the dipolar degree of order to Zeeman degree. This is possible with the irradiation of proper r. f. pulses[3]. For the solution of point (ii) one could polarize two or more samples successively. The most highly polarized sample will be used as target for some minutes. Another possibility might be to transfer the dipolar polarization to Zeeman polarization and to cool the sample down to a temperature, at which T_1, and therefore the decay of the polarization are very long. Point (iii) will create more troubles. But since these are the first measurements on this effect a further development is possible. It can also not be excluded that repeated and correct temperature procedures with polarization transfer at the right time will allow accumulation of the Zeeman polarization. In the near future, however, a more detailed understanding of this new effect must be obtained.

Acknowledgements

The author wishes to thank Dr. R. van Steenwinkel for helpful discussions.