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Dynamic Nuclear Polarization Study of MBBA with Traces of Nitroxide Type Molecules†

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Abstract—The dissolution of paramagnetic impurities in a nematic liquid crystal gives rise to the possibility of dynamic nuclear polarization. The effect obtained is of the hybrid type, characteristic of viscous liquid media. Enhancements are weak and range between -2 and -3.5. Differences between protons belonging respectively to the benzenic rings and to flexible end groups, arise only ten degrees below the nematic–isotropic transition. From the experimental values of enhancements, we derive, for the intermolecular proton–electron interaction, values of the correlation time that range between 1.5 and 3×10^{-10} sec.

1. Introduction

Organic molecules giving rise to mesomorphic phases contain a number of protons sufficiently large for giving complicated proton magnetic resonance spectra. Most of the time, the different lines arising from unequivalent protons (belonging either to alkyl chains or to aromatic rings) are not well or not at all resolved.

Consequently, it is difficult to use these spectra for a study of the molecular motions and fluctuations of orientation.

In order to surmount this difficulty some authors have partially deuterated the molecules and made proton and deuteron magnetic resonance. Another possibility which we chose is the technique of dynamic nuclear polarization (DNP) which allows one to measure

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the correlation time for the motion of nuclei belonging to molecules. In the case of our experiments, the DNP was produced by the dipolar interaction between the nuclear spins of nematic molecules and the electronic spins of dissolved traces of free radicals.

We had in mind that protons in MBBA having different motions might exhibit different types of DNP. In principle one is able to study the nuclear polarization corresponding to each NMR line and to relate it to the motion of the relevant protons.

2. Theory of Dynamic Nuclear Polarization

Let us consider a system of two different kinds of $\frac{1}{2}$ spins. In the presence of a static magnetic field H_0, the Zeeman levels separate from each other. By means of weak periodic magnetic fields having suitable frequencies and directions, one is able to induce transitions between these levels. If there is an interaction between the two kinds of spins, a set of transitions that were formerly forbidden become possible. If we suppose that the nuclear relaxation occurs mainly through the interaction with electronic spins and if we saturate the electronic transitions we can obtain a considerable modification of the nuclear polarization depending on the evolution of the coupling as a function of time.

A complete theory of DNP has been recently published(1) which describes the effects encountered not only in media of moderate viscosity, but also in the two classical limiting cases of solids and liquids containing paramagnetic impurities. This theory takes into account the anisotropy of electronic relaxation which leads to values of electronic relaxation times T_{1e} and T_{2e} that are very different in viscous liquids.

Let us recall the fundamental assumptions of this theory:

1) The proton–electron interaction is of the dipolar type and is modulated by a random rotation of the assembly.

2) The electronic spins relax through an anisotropic g factor modulated by a random rotation of the radical; the interaction with protons does not contribute to that relaxation.

3) The protons relax through their coupling with the electrons.

These assumptions lead to the following Hamiltonian:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_L(t) + \mathscr{H}_d(t) + \mathscr{H}_1(t)$$

where the different terms are:

$\mathscr{H}_0 = \gamma_s H_0 S_z + \gamma_I H_0 I_z$	Zeeman energy
$\mathscr{H}_L(t) = \gamma_s \mathbf{H}_L(t) \cdot \mathrm{S}$	Zeeman energy depending on the orientation
$\mathscr{H}_d(t) = \gamma_I \gamma_s \mathbf{I} \cdot \boldsymbol{\phi}(\mathbf{t}) \cdot \mathbf{S}$	dipole–dipole interaction
$\mathscr{H}_1(t) = \gamma_s \mathbf{H}_{1s} \cdot \mathbf{S}$	energy of the electron in the "pumping" field $\mathbf{H}_{1s}(t)$.

One obtains then a theoretical expression giving the values of the dynamic nuclear polarization. In the cases of Ref. 1 it was necessary to use not a single correlation time but a distribution of correlation times to account for the experimental data, namely the shape of the whole polarization curve.

3. Experimental Arrangement

Our measurements were performed on a double resonance spectrometer which was a combination of a microwave spectrometer and a proton resonance spectrometer. The proton resonance coil was wound around the sample holder made of teflon in such a way that its plane was parallel to the sample tube axis; the whole assemblage was inserted inside a cylindrical microwave cavity the axis of which was parallel to the sample tube axis.

We operated in a 3300 G static field, which corresponds to a proton frequency of 13.8 MHz and electronic frequency of 9870 MHz. The microwave power was 470 mW, giving a pumping field of 0.64 G.

The samples consisted of MBBA containing 10^{-2} mole per liter nitroxide type free radicals placed in pyrex glass sample tubes three millimeters in diameter, evacuated and sealed. The thickness of the tube walls was only $\frac{1}{10}$ mm to provide a good heat contact with the gas flow temperature control system. In spite of this small diameter and small thickness of the walls there was still not negligible microwave power heating.

The correction for obtaining real sample temperature was determined by comparing recordings made with and without microwave irradiation for a value of the magnetic field far enough from the DNP conditions. In a range of 40 °C including the nematic range the heating due to microwave power was found to be 2.5 °C.

We used two free radicals. One was tetramethyl-2-2-6-6-piperidinol-4-oxyle-1, abbreviated as Tanol; the other was derived from this one and was the tetramethyl-2-2-6-6-brosylate-4-oxyle-1, abbreviated as TBO. The last one has an elongated shape and aligns better than Tanol which is quasi-spherical. These radicals are stable and their hyperfine structure, composed of three lines separated from each other by 13 G, is convenient for DNP studies.

4. Experimental Data

Because of numerous interactions, the proton resonance spectrum of MBBA is complicated and not entirely resolved with continuous wave methods. Our spectra were similar to those often described in literature for PAA; they were composed of three lines consisting of two satellites (hereafter designated as $+\delta$ and $-\delta$) symmetrically located on each side of a central pike that we attributed to CH_3 and C_4H_9 groups. The splitting of the satellites was mainly due to dipolar interaction between the two nearest neighbour protons situated on the same benzenic ring.

On Fig. 4 is plotted the satellite splitting versus temperature. The dotted line represents the data obtained with pure MBBA we have previously published.(6) The solid line represents the data obtained with MBBA containing a small concentration 1.2×10^{-2} mole per liter of TBO molecules (i.e. a concentration of 3.2×10^{-3} mole TBO per mole MBBA, or a mass concentration of 4.7×10^{-3}). The change in the splitting values is striking and shows, as reported in literature, how sensitive is the orientational order to the presence of impurities.

We made the two following preliminary measurements to insure we were in good DNP conditions.(7)

First of all, the presence of paramagnetic impurities increases the relaxation by shortening the nuclear relaxation time T_1 this shows that protons relax predominantly by their interaction with electrons. For our samples, in the case of pure MBBA, T_1 was varying very little, in the nematic phase, ranging, from 82 to 89 msec (sense of increasing temperature). In the case of MBBA containing 1.2×10^{-2} mole/liter of TBO, T_1 was ranging from 15 to 28 msec for the same interval.

Secondly, electronic relaxation times T_{1e} and T_{2e} were found to have very different values. For example, for the upper mentioned sample, T_{1e} was ranging between 3.2 and 2.6×10^{-6} sec and T_{2e} between 2.2 and 2.5×10^{-8} sec in the nematic phase (sense of increasing temperature). A discontinuity was found at the nematic–isotropic transition (e.g. the T_{2e} value doubles).

Our DNP experiments were carried out from the isotropic phase to the crystalline phase through the whole nematic phase. The results are typical of an hybrid type effect similar to what is encountered in media of moderate viscosity. Figures 1 and 2 show results obtained on each end of the nematic range in the case of the TBO radical. A represents the amplitude of absorption lines in the presence of microwave power and A_0 the same quantity when microwave power is turned off, so that P is the enhancement. P is reported as a

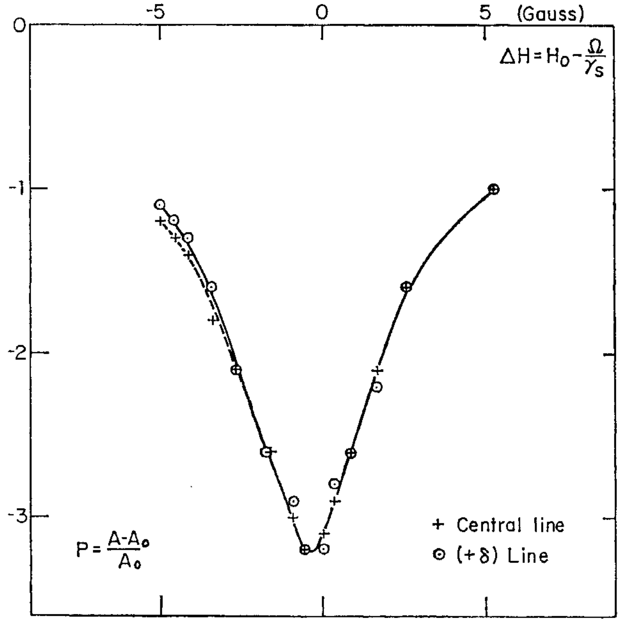

Figure 1. Proton DNP in MBBA containing 1.2×10^{-2} mole/liter TBO at $T - T_c = -3.5\,°C$ (nematic phase).

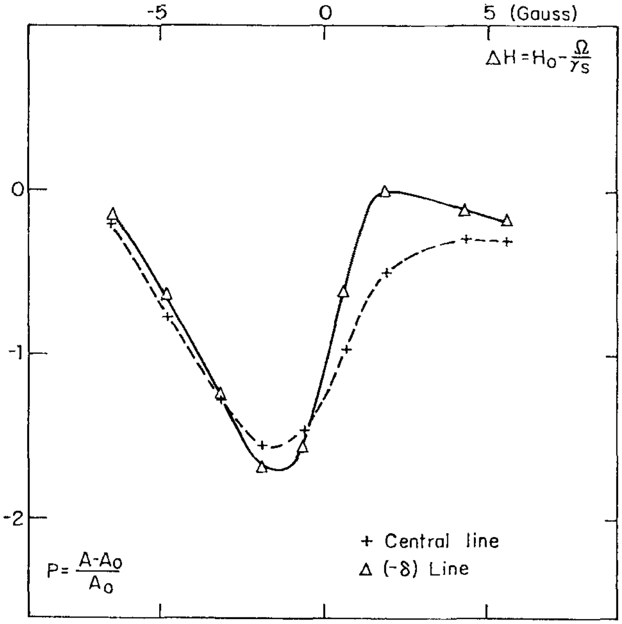

Figure 2. Same sample at $T - T_c = -23\,°\mathrm{C}$ (nematic phase).

function of the field as the field is tuned through the electron-spin resonance field. Ω is the electronic Larmor frequency and γ_s the electronic gyromagnetic ratio.

In all cases, even in the liquid state (Fig. 3), the enhancements are weak; they do not go beyond -3.5. In the vicinity of the nematic–isotropic transition, the three lines show the same DNP effect which is close to inverted Overhauser effect (liquid type effect).

This indicates that the free radicals and the different protons of the MBBA molecules have such a relative motion that DNP does not distinguish between these protons. This implies that the correlation time of the corresponding interaction is the same for these different protons and that the characteristic time of the predominant motion is shorter or equal to this correlation time.

As the temperature is decreased in the nematic phase the polarization curves tend to separate from each other; the curves corresponding to lines $+\delta$ and $-\delta$ becoming systematically narrower than that corresponding to the central line, and this mainly below $T - T_c = 10\,°\mathrm{C}$.

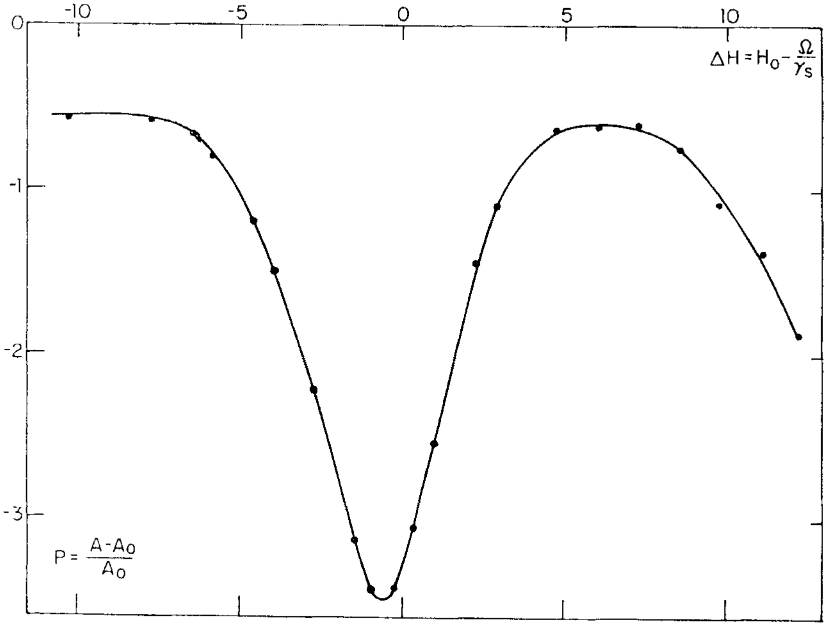

Figure 3. Same sample at $T - T_c = +0.3\,°\text{C}$ (liquid phase).

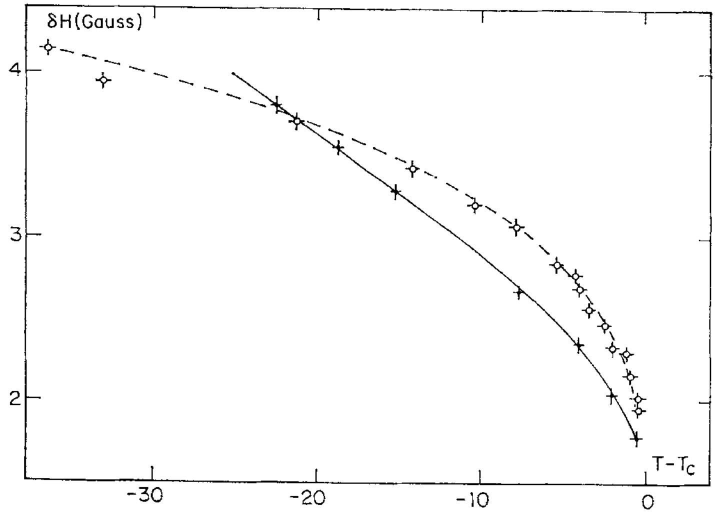

Figure 4. Satellite splitting versus temperature. Dotted Line: Pure MBBA; Solid Line: MBBA containing 1.2×10^{-2} mole/liter TBO; Crosses represent typical errors.

In the vicinity of the nematic–crystal transition, the three lines exhibit DNP effect closer to the solid-state effect. The effects are slightly different for the different types of protons. Those belonging to the benzenic rings and having the same motion as the molecule, exhibit a solid type effect more strongly than those belonging to the flexible ends of the molecule. This leads to different values of the correlation time for the different kinds of protons. However, the weakness of the difference tells that even for such a temperature the relative motion is approximately the same for the two kinds of protons.

The results obtained in the case of Tanol show effects much closer to the liquid effect. Typical data are presented on Fig. 5 for two different temperatures. We can see that the polarization curves are narrower and have a smaller amplitude at their maximum, the position of which is closer to $\Delta H = 0$. This indicates that this radical orients very little in the nematic phase and we shall not discuss any more this case which is similar to that described in Ref. 1.

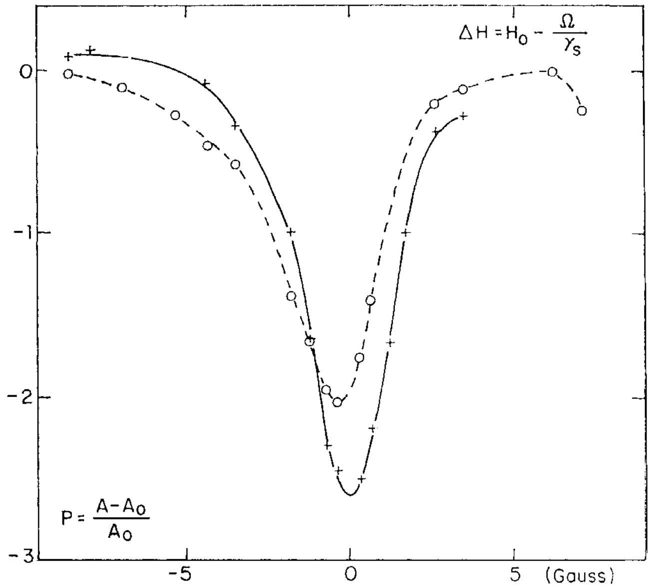

Figure 5. Proton DNP in MBBA containing 10^{-2} mole/liter tanol. Solid Line: At $T - T_c = -0.5\,°\mathrm{C}$ (central line); Dotted Line: At $T - T_c = -7.5\,°\mathrm{C}$ (central line).

5. Determination of the Correlation Time of the Proton–Electron Interaction

In order to simplify the calculations, we use as an approximation a model developed(4,5) for the cases where $T_{1e} = T_{2e} = Te$. This model does not give the correct values of the observed polarization all along the curve. However it has been demonstrated that in the case of a transition between solid and liquid effects characterized by values of the displacement of the maximum of polarization ranging between 0 and 1 Gauss this model gives around this maximum, values that agree with experience.

The value of polarization derived in this model is

$$P = -\frac{\gamma_s^2 H_{1s}^2}{\dfrac{1}{T_e^2} + \gamma_s^2 (H_{1s}^2 + \Delta H^2)} \; \frac{\dfrac{2}{\Lambda^2+\Omega^2} - \dfrac{3}{5}\dfrac{4\gamma_s \Delta H \omega}{\Lambda^4}}{\dfrac{7}{5}\dfrac{2}{\Lambda^2+\Omega^2} + \dfrac{3}{5}\dfrac{2}{\Lambda^2}} \left|\frac{\gamma_s}{\gamma_I}\right| \tag{1}$$

P represents the relative enhancement $(A - A_0)/A_0$ of the nuclear magnetization due to the DNP effect.

γ_s and γ_I are the gyromagnetic ratios.

H_{1s} is the microwave magnetic field, $\Delta H = H_0 - \Omega/\gamma_s$.

ω is the nuclear pulsation and τ_c is the correlation time which characterizes the dipole–dipole interaction (tensor $\phi(t)$) and consequently the intermolecular movement.

$$\Lambda = \frac{1}{T_e} + \frac{1}{\tau_c}$$

The point of the polarization curve corresponding to $\Delta H = 0$ represents a polarization P

$$P = -\frac{\gamma_s^2 H_{1s}^2}{\dfrac{1}{T_e^2} + \gamma_s^2 H_{1s}^2} \cdot \frac{5\Lambda^2}{10\Lambda^2 + 3\Omega^2} \cdot \left|\frac{\gamma_s}{\gamma_I}\right| \tag{2}$$

At this point using the experimental values of P, we can deduce Λ and then τ_c

$$\Lambda^2 = \frac{3}{5} \cdot \frac{\Omega^2}{\left|\dfrac{1}{P} \cdot \dfrac{\gamma_s}{\gamma_I}\right| \cdot \dfrac{\gamma_s^2 H_1^2}{1/T_e^2 + \gamma_s^2 H_{1s}^2} - 2} \tag{3}$$

If we saturate completely one of the three electronic transitions on one hand, we have $\gamma_s^2 H_{1s}^2 \gg 1/T_e^2$, and on the other hand the experimental polarization is $\frac{1}{3}$ of that given by the relation (1).

The relation (3) now becomes:

$$\Lambda^2 = \frac{3}{5} \cdot \frac{\Omega^2}{\left| \frac{1}{3P} \cdot \frac{\gamma_s}{\gamma_I} \right| - 2}$$

In the two cases presented of Figs. 1 and 2 this gives respectively for $T - T_c = -3.5\,^\circ\mathrm{C}$ a value $\tau_c = 1.78 \times 10^{-10}$ sec and for $T - T_c = -23\,^\circ\mathrm{C}$ $\tau_c = 2.95 \times 10^{-10}$ sec for protons belonging to flexible ends (central line) and $\tau_c = 3.15 \times 10^{-10}$ sec for protons belonging to benzenic rings ($-\delta$ line).

6. Conclusion

Our results seem to indicate that the main mechanism which governs the polarization of both types of protons is a very fast, non-collective motion of the nematic molecules and free radical molecules.

Using the approximation we referred to we calculated for this relative motion a characteristic time ranging between 2 and 3×10^{-10} sec in the nematic phase of MBBA.

The free radicals which we used do not orient very well in the MBBA. This is evidenced not only by the form of the EPR spectrum but also by the fact that our results do not give any evidence of some kind of collective motion of the free radical molecules which otherwise should have given a stronger "solid effect" type of contribution to the DNP.

Our results show that the DNP method we used does not seem to enable one to distinguish between the two types of protons motion. In that case, the liability and efficiency of the method are seriously limited by the weakness of the enhancements that does not allow to remove entirely all the ambiguities.

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