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Study of the Liquid-State Dynamics by Means of Magnetic Resonance and Dynamic Polarization

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The dynamics of the liquid state of two organic free-radical solutions has been studied by means of EPR, NMR, and DNP (dynamic nuclear polarization). In our spectrometer these effects can be measured simultaneously and over a wide range of temperatures. The aim was to study the gradual transition from the ordinary liquid state to a greatly supercooled liquid state, and in particular the change from the Overhauser-type DNP to the solid-type DNP. The samples were a 0.02-mole/liter solution of tanone in isopropanol and a 0.03-mole/liter solution of tetrachlorosemiquinone in tetraethyleneglycol. The EPR can be explained in terms of random rotational modulation of the anisotropic g factor of the radical, with a correlation time which is an exponential function of reciprocal temperature. At the temperatures of interest, T_{1e} and T_{2e} differ by at least one order of magnitude. The NMR follows from the Torrey model, the protons relaxing through dipole interaction with the electron spin while their molecule is temporarily adsorbed in the solvation layer of a radical. The data can be fitted by a model with a dipole-dipole correlation function based on a rather broad distribution of correlation times, the mean value and temperature dependence being similar as in EPR. The DNP shows a typical gradual transition from the (even) Overhauser effect to the (odd) solid effect as the temperature is lowered. This happens when the correlation time and T_{2e} cross. A theoretical analysis of the DNP on the basis of the liquid structure as revealed by EPR and NMR is given in the following paper.

I. INTRODUCTION

The data reported in this paper were obtained in an experiment designed to study a gradual transition from the inverted Overhauser effect to the solid-state effect. Both these effects describe the result of dynamic polarization in materials containing two distinct systems of spins with a dipolar mutual interaction. The former is typical for a liquid, the latter for a solid.[1]

Besides being an exercise in the measurement of small dynamic polarizations, the experiments yield information about the random motion in the system which is not obtainable from data on spin resonance and relaxation alone. For such an analysis one needs a theory. This is given in the following paper and embodies an extension of earlier work.[2] A preliminary report of the present investigation has been published elsewhere.[3]

II. SELECTION OF MATERIALS

The materials in which we have studied the effect are the radical tanone dissolved in isopropanol with a concentration of 0.02 mole/liter and the radical tetrachlorosemiquinone dissolved in tetraethyleneglycol with a concentration of 0.03 mole/liter. The structure of the radicals is shown in Fig. 1. Each sample contains two systems with spin $\frac{1}{2}$, viz., the electrons of the radical and the protons of the solvent, with widely separated Larmor frequencies. The concentrations are low enough to neglect the energy of dipolar interaction between the electron spins as well as their exchange interaction. The concentrations are however high enough to guarantee that the solvent protons relax primarily (for 90%) through their interaction with the electrons. This is an obvious condition for optimal effects in dynamic polarization.

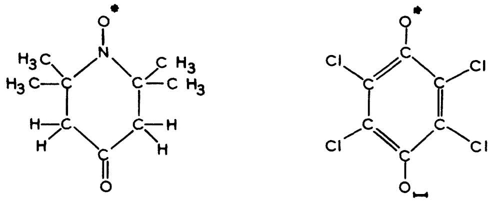

FIG. 1. Molecular structure of tanone and tetrachlorosemiquinone.

Stability and absence of hyperfine structure (hfs) were major considerations in selecting the radicals. Here we had to compromise: While tanone is very stable, it does have a hfs, owing to the nitrogen nucleus, consisting of three equidistant lines with a separation of 15 G; tetrachlorosemiquinone has, as its formula indicates, no hfs, but its short life is rather inconvenient.

The particular solvents were chosen because they do not normally crystallize when cooled to below their melting point. Therefore one can produce the desired gradual transition from the inverted Overhauser effect to the solid-state effect by cooling from well above to well below the melting point. (For pure isopropanol this is − 89 °C, for tetraethyleneglycol 5 °C.) One expects to find this transition when the correlation time of liquid motion, τ, goes from values much shorter to values much longer than the transverse electron relaxation time T_{2e}, although more detailed criteria also involve T_{1e}.

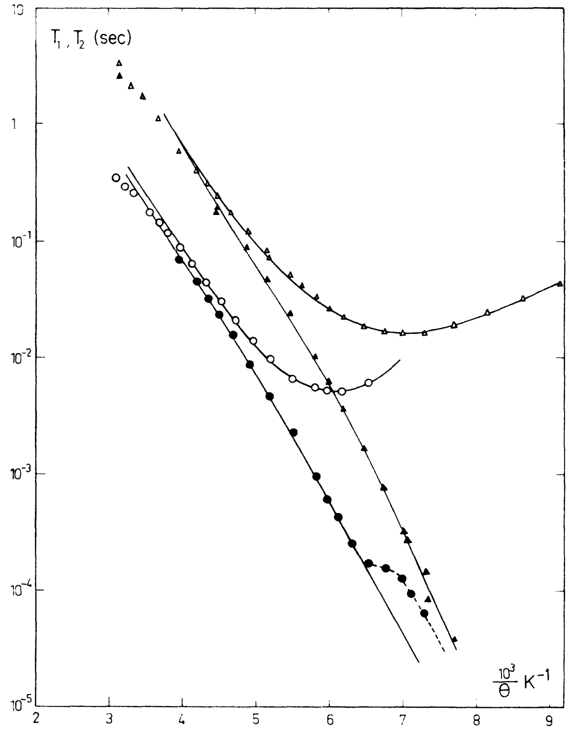

FIG. 2. Proton relaxation times as a function of reciprocal temperature for pure isopropanol (T_1 open triangles, T_2 filled-in triangles), and for a 0.02-mole/liter solution of tanone in isopropanol (T_1 open circles, T_2 filled-in circles). Drawn curves are best fits with theory using a distribution of correlation times.

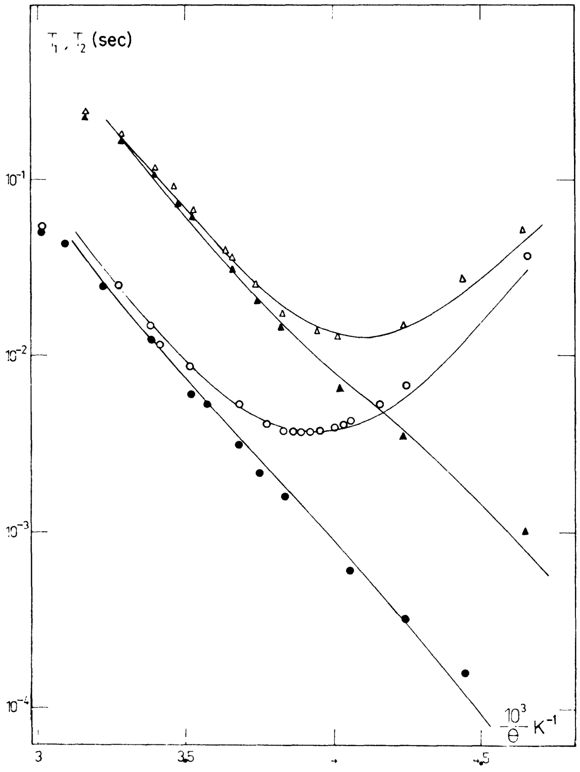

FIG. 3. Proton relaxation times as function of reciprocal temperature for pure tetraethyleneglycol (triangles) and for a 0.03-mole/liter solution of tetrachlorosemiquinone in tetraethyleneglycol (circles). Drawn curves are best fits with theory using a distribution of correlation times.

III. APPARATUS

Almost all measurements were done with one and the same spectrometer. This allows simultaneous observation, on a given sample, of EPR and NMR in a constant magnetic field H_0 of about 3300 G, i.e., for an electron Larmor frequency $\Omega_0 \approx 9380$ MHz, and a nuclear Larmor frequency $\omega \approx 14$ MHz. The uhf was fixed at $\Omega = 9380$ MHz. The measuring cell consists of a cylindrical cavity, tunable by means of a moving piston. A 15-mm-diam hole is drilled all the way through along the axis, through which a cryostat containing the sample can be inserted. The NMR coil is also inside the cryostat, wound on a Teflon mandrel that surrounds the sample. The temperature is regulated

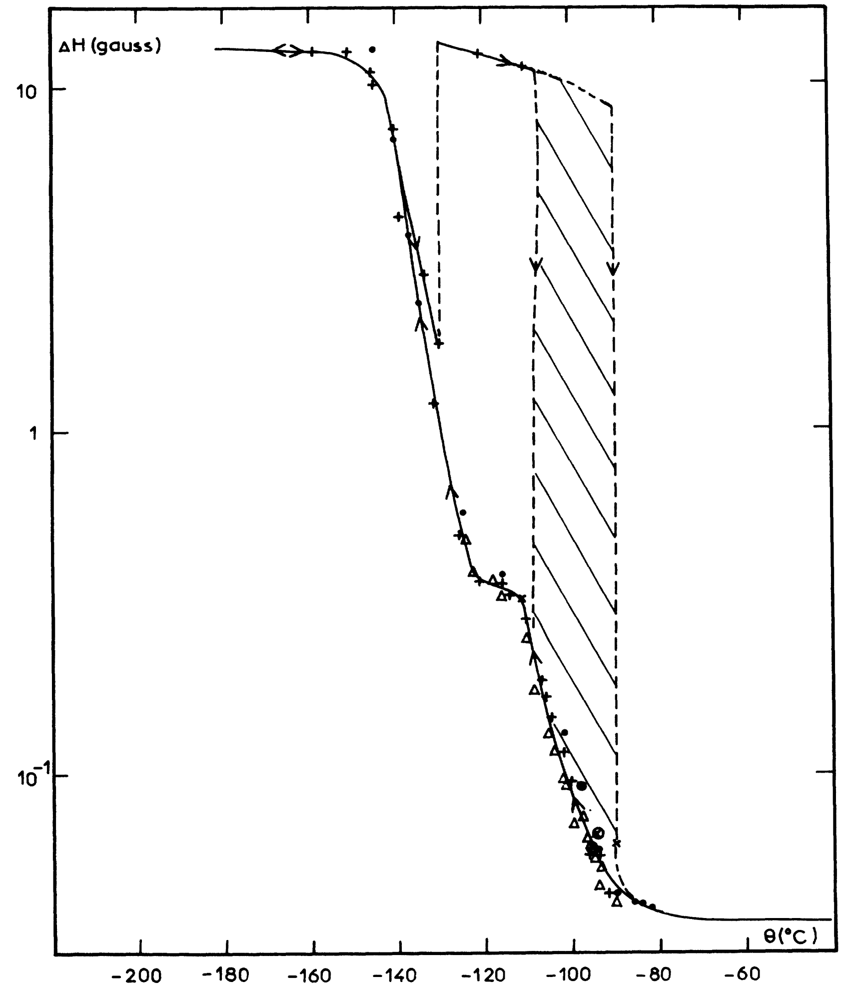

FIG. 4. Hysteresis of the solid-liquid transition of pure isopropanol revealed by measurement of the NMR linewidth.

by a gas flowing through the cryostat at 25 liter/min. The mandrel has been cut away as much as possible to allow the gas to flow by the sample. The gas temperature can be regulated between −180 and +200 °C with an accuracy of 0.5 °C. All other parts of the apparatus are standard.

IV. PRELIMINARY MEASUREMENTS, NMR

A. Experimental Results

The experimental determination of T_1 and T_2 of the proton resonance gives information about the stochastic properties of the samples and thereby reduces the ambiguity of the analysis of the dynamic polarization experiments. We have measured T_1 and T_2 as a function of temperature for the two samples mentioned above and for the pure solvents. The measurements were made with a 15-MHz Brücker pulse spectrometer[4] using the spin-echo technique. The results are given in Figs. 2 and 3, which also show the best fit with a stochastic model discussed below. Care was taken that the samples did not crystallize. In a separate run we detected the hysteresis of T_2 associated with crystallization. An example of this is given in Fig. 4. There, while the sample is cooled slowly, one sees the normal supercooling, as in Fig. 2, but over a wider temperature range there is complete solidification. Upon slow reheating, the sample crystallizes at −130 °C, as indicated by the sudden jump in linewidth from 1.5 to 13 G, which is the value in the solid. At −110 °C a narrow line as for the liquid begins to appear which grows in intensity until, at −90 °C, it accounts for all the protons.

B. Analytical Presentation

The data for the pure solvents can be interpreted as the relaxation of a proton due to the dipole interaction with the other protons in an aggregate that has an isotropic random rotation. The relaxation rates are in that case of the general form[5]

$$\frac{1}{T_1^0}=\tfrac{3}{10}\,\gamma_I^4\hbar^2\,\frac{1}{n}\sum_{i,k=1}^{n}\rho_{ik}^{-6}\left[g_{ik}(\omega)+4g_{ik}(2\omega)\right], \tag{1}$$

$$\frac{1}{T_2^0}=\tfrac{3}{10}\,\gamma_I^4\hbar^2\,\frac{1}{n}\sum_{i,k=1}^{n}\rho_{ik}^{-6}\left[\tfrac{3}{2}g_{ik}(0)+\tfrac{5}{2}g_{ik}(\omega)+g_{ik}(2\omega)\right], \tag{2}$$

where the summations are over all n spins of an aggregate. ρ_{ik} is the distance between spin i and k; $g_{ik}(\omega)$ is the Fourier transform of a rotational correlation function. One sees at once that the Bloembergen model does not apply. This model describes the random rotation as rigid and Markoffian, which leads to

$$g_{ik}(\omega)=\tau/(1+\omega^2\tau^2) \tag{3}$$

for all i and k, where τ is the correlation time. This makes the ratio T_1^0/T_2^0 at the temperature where T_1^0 has a minimum equal to 1.6, whereas we find 48 for isopropanol and 2.3 for tetraethyleneglycol. A good fit is obtained by using in Eqs. (1) and (2) the relations

$$\frac{1}{n}\sum_{i,k}\rho_{ik}^{-6}\,g_{ik}(\omega)=n\langle\rho\rangle^{-6}\,\bar{g}(\omega)\,, \tag{4a}$$

$$\bar{g}(\omega)=\int_0^\infty\left[G(\tau)\,\tau/(1+\omega^2\tau^2)\right]d\tau\,, \tag{4b}$$

$$G(\tau)=\frac{1}{\tau\sigma(2\pi)^{1/2}}\exp\left[-\tfrac{1}{2}(\ln\tau-\ln\tau^*)^2/\sigma^2\right]. \tag{5}$$

Equation (5) is a Gaussian distribution for $\ln\tau$ with mean value $\ln\tau^*$, variance σ. $\langle\rho\rangle$ is some average of ρ_{ik}, and $\bar{g}(\omega)$ can be interpreted as the average correlation function over a distribution of Markoffian processes[6] with probability law (5). By using $\ln\tau^*$, σ, and $n\langle\rho\rangle^{-6}$ as adjustable parameters, we obtain the drawn curves for the pure solvents in Figs. 2 and 3. The best values of $\ln\tau^*$ and σ are shown in Table I. They are, within the accuracy of our determination, linear functions of the reciprocal temperature $1/\theta$.

TABLE I. Parameters $\ln\tau^*$ and σ in the Gaussian of Eq. (5) as a function of temperature.

Samples	$\ln\tau^*$	σ
Pure isopropanol	$-36.75+2.50\times10^3\,\theta^{-1}$	$1.83+120\,\theta^{-1}$
Isopropanol + tanone ($c=0.02$ mole/liter)	$-33.45+2.50\times10^3\,\theta^{-1}$	$1.37+49.5\,\theta^{-1}$
Tetraethyleneglycol	$-38.8+4.85\times10^3\,\theta^{-1}$	0.92
Tetraethyleneglycol + tetrachlorosemiquinone ($c=0.03$ mole/liter)	$-37.50+4.85\times10^3\,\theta^{-1}$	0.92

The results for the radical solutions show a strong enhancement of the proton relaxation which must be due to the electron-proton spin dipole interaction at distances much smaller than the average. Torrey[7] has explained an effect of this type by assuming that nearly all protons of the solvent are intermittently closely attached to a radical during a time τ_s satisfying $\tau\ll\tau_s\ll T_1$, where T_1 is the observed proton relaxation time and τ is the rotational correlation time of an aggregate containing a radical and the proton. Under these conditions the protons undergo a normal electron-proton relaxation during these periods τ_s, but are replaced sufficiently often by protons in other solvent molecules to homogenize the system. Neglecting the signal from protons permanently attached to the radical, the observed rate is of the form

$$\frac{1}{T'}=\frac{N'}{N}\,\frac{1}{T}+\left(1-\frac{N'}{N}\right)\frac{1}{T^0}\,, \tag{6}$$

where N'/N is the fraction of solvent molecules thus temporarily attached to the radicals at a given time. T^0 is the relaxation time due to proton-proton interaction in free molecules and is given by Eq. (1) or (2). T is the proton relaxation time due to dipole interaction with the electron spin to which it is thus attached. It is given by[5]

$$\frac{1}{T_1}=\tfrac{3}{10}\,\gamma_I^2\gamma_S^2\hbar^2\,\frac{1}{n'}\sum_{i=1}^{n'}r_i^{-6}\left[g_i(\omega)+\tfrac{1}{3}g_i(\Omega_0-\omega)+2g_i(\Omega_0+\omega)\right], \tag{7}$$

$$\frac{1}{T_2}=\frac{1}{2}\,\frac{1}{T_1}+\tfrac{3}{10}\,\gamma_I^2\gamma_S^2\hbar^2\,\frac{1}{n'}\sum_{i=1}^{n'}r_i^{-6}\left[\tfrac{2}{3}g_i(0)+g_i(\Omega_0)\right]. \tag{8}$$

As applied to the present model, the summation is over all protons temporarily attached to a radical; r_i is the distance from the electron spin.

It is well known[8] that Eqs. (7) and (8) are not generally applicable, but should be modified in order to account for the effect of the relaxation of the S spin caused by its coupling to the "lattice." If g_i is characterized by a correlation time τ, a reasonable approximation is obtained by replacing $1/\tau$ inside the functions $g_i(0)$ and $g_i(\omega)$ of Eqs. (7) and (8) by $1/\tau+1/T_{1e}$ and inside $g_i(\Omega_0+\omega)$ by $1/\tau+1/T_{2e}$, where $1/T_{1e}$ and $1/T_{2e}$ are the electronic relaxation rates produced by the spin-lattice coupling. We will return to this problem at the end of the following paper.

For the experiments under discussion this modification is of no importance. The terms without Ω_0 are hardly changed because, as will be shown, $\tau\ll T_{1e}$ for all temperatures of interest. On the other hand, terms with Ω_0 are negligibly small compared with the former, because $\tau\Omega_0\gg1$ in our experiments. However, the modification of these terms, which is essentially connected with the transition from the Overhauser effect to the solid effect ($\tau\approx T_{2e}$), will be important with smaller external fields.

The drawn curves for the radical solution in Figs. 2 and 3 were obtained from Eqs. (6), (7), and (8) by writing $(1/n')\sum g_i r_i^{-6} = \langle r\rangle^{-6}\bar{g}$, where $\bar{g}$ is given in Eqs. (4) and (5), but with values of $\ln\tau^*$ and σ differing from those of the pure solvents. They are given in Table I. Deviations from the Bloembergen model are again noticeable: The "theoretical" T_1/T_2 ratio at the minimum T_1 equals $\frac{11}{6}$ while the experimental result is 10.5 for the tanone and 3.1 for the tetrachlorosemiquinone solution.

C. Interpretation

We have thus been able to parametrize the T_1, T_2 data of the four samples. The scale factors, viz., $n\langle\rho\rangle^{-6}$ for the solvents and $(N'/N)\langle r\rangle^{-6}$ for the solutions, take reasonable values. $\ln\tau^*$ varies linearly with $1/\theta$ with slopes that do not change upon dissolving the radicals. This strong exponential variation of τ^* with reciprocal temperature is not unexpected, of course. The values of σ for isopropanol and for the radical solution with tanone differ by a fair amount and have a mild linear variation with $1/\theta$. For the samples based on tetraethyleneglycol, σ is small and nearly constant. At this stage one can only speculate about the physical meaning of σ and its temperature dependence. Non-Markoffian motion, different size of aggregates, inequivalent spin pairs, and nonrigid motion of aggregates could all contribute to deviations from Bloembergen's model.

The only large discrepancy in Fig. 2, viz., the bump in the T_2 curve of the radical solution and its approaching the free solvent values at low temperatures, obtains a natural explanation in Torrey's model. It signifies that at this point $\tau_s \approx T_1$ so that at lower temperatures the molecules become permanently attached to the radical and thereby are eliminated as a source of relaxation. The existence of only one bump suggests that only one layer of molecules, the so-called solvation layer, attaches itself to the radicals.

V. PRELIMINARY MEASUREMENTS, EPR

A. Spectra

The paramagnetic resonance spectra of pure tanone and solutions of tanone in isopropanol and other solvents as a function of temperature are available from the literature.[9] The shape of the three hyperfine components has obtained a quantitative interpretation which can be summarized as follows: The g factor and the hyperfine interaction are anisotropic, the principal axis being parallel to the symmetry axis of the radical. This anisotropy gives rise to line broadening (T_{2e}) via a random rotation of the radical and its solvation layer.[10] This rotation can be considered to be Markoffian. We have measured the EPR spectrum of our sample of tanone solution and verified the above properties. The correlation time of random motion is approximately equal to τ^* of Sec. IV for all temperatures. The width σ does not enter in the description, which suggests that it is not a property

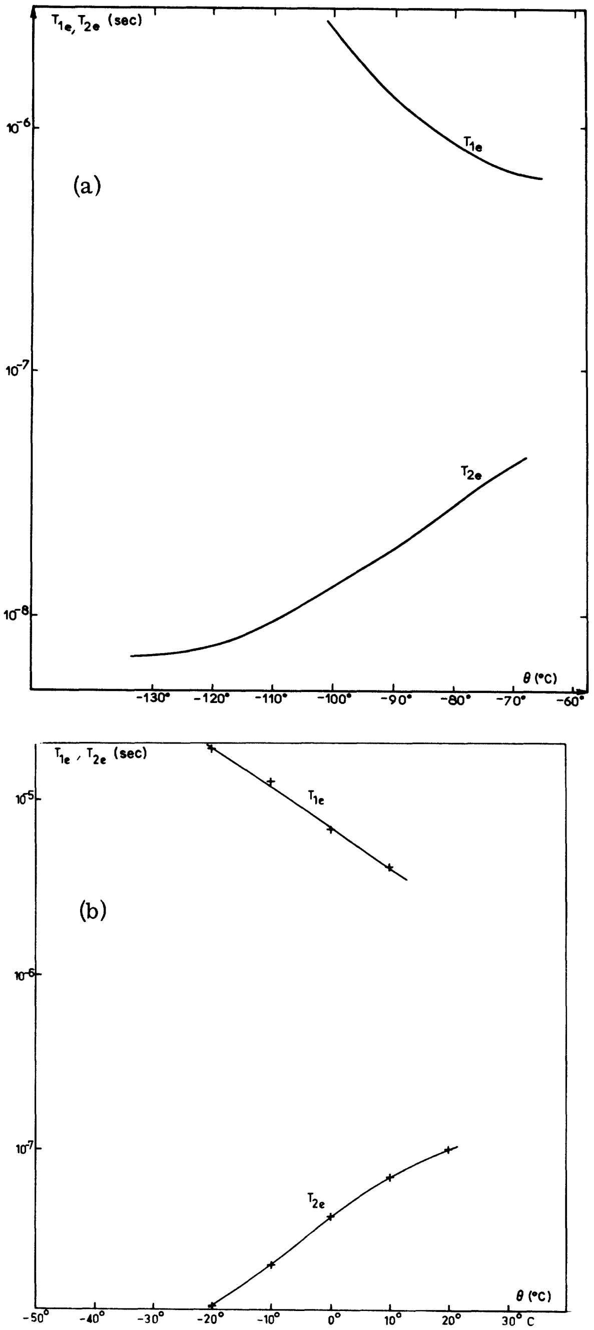

FIG. 5. (a) Electron-spin relaxation times of tanone in isopropanol as a function of temperature. (b) Electron-spin relaxation times of tetrachlorosemiquinone in tetraethyleneglycol as a function of temperature.

of the rotational process of the radical ion.

We have also measured the EPR spectrum of our sample of tetrachlorosemiquinone in tetraethyleneglycol as a function of temperature. There is no hfs. The g factor is again anisotropic and the line form can be explained as above, with the difference that the correlation time equals $2.7\tau^*$ of Sec. IV for all temperatures. A tentative explanation for this fact is that the solvation layer of the semiquinone is rather loosely formed. We have no direct evidence for its existence.

B. Saturation

Observation of the saturation of the EPR signal reveals that the lines are homogeneous, i.e., that the Bloch equations apply. This allows a determination of T_{2e} from the linewidth, with which the saturation curve gives T_{1e}. Figure 5(a) and 5(b) show the results. One sees that the ratio T_{1e}/T_{2e} ranges from 10 to 1000 for the temperature at which we made the measurements. This was to be expected because one has $\tau^*\Omega_0 \gg 1$, i.e., the temperature remains well below the values for extreme narrowing. The relaxation times are much shorter than the times that can be expected from the electron-proton interaction known from Sec. IV or that can be estimated from the dipole interaction between the electron spins. The relaxation process mentioned above due to the spin-orbit-lattice interaction of the individual radical ions is therefore dominant, just as for line broadening. This is important for the dynamic polarization experiments, to be discussed next, and their interpretation.

VI. DYNAMIC POLARIZATION

A. Experimental Procedure

An amplitude $H_1 = 0.75$ G of the uhf field of frequency Ω was used to produce dynamic polarization of the protons. We measured this polarization, i.e., the NMR signal amplitude, at several temperatures as a function of the separation $\Delta\omega = \Omega_0 - \Omega$ of the applied frequency from the resonant frequency. Precautions were needed to keep the samples at the desired temperature because both the radical solutions are polar, and dielectric heating due to the saturating field could give rise to unacceptable changes of the temperature. With the tanone sample, which is stable, this was done under steady-state conditions by lowering the gas temperature just so much that the dielectric heat was dissipated. To this end the sample temperature was monitored by the NMR signal at large values of $\Delta\omega$, for which the dynamic polarization is zero. This method could not be used for tetrachlorosemiquinone because its finite lifetime limits the useful time of an experiment to about 15 min. We managed to measure the dynamic polarization for ten different values of $\Delta\omega$ at a fixed temperature in that time by adopting the following procedure: A sample tube was made with small (2 mm) diameter and very thin (0.1 mm) walls. This reduced the temperature drift to an acceptable level. A multichannel integration was used to extract the signal from the

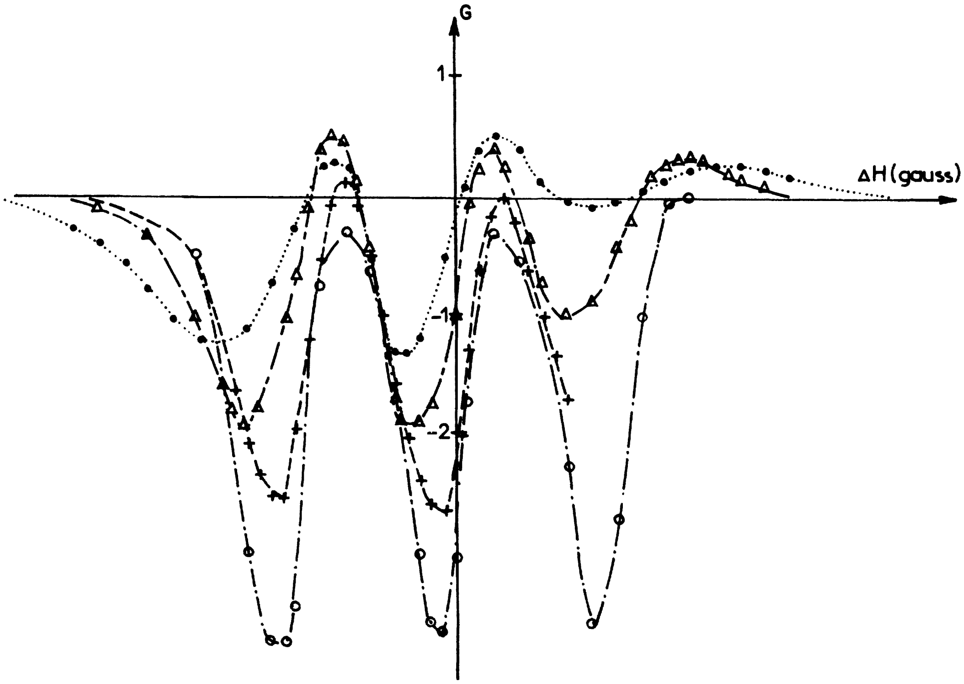

FIG. 6. Dynamic polarization of protons for the solution of tanone in isopropanol as a function of the difference between the applied frequency and the electronic Larmor frequency in units of the proton polarization at thermal equilibrium, $G = A/A_0 - 1$, where A is the enhanced signal amplitude and A_0 is the unenhanced signal amplitude. Open circles at −70 °C, plus signs at −75 °C, triangles at −85 °C, and dots at −98 °C. Curves are inserted to guide the eye.

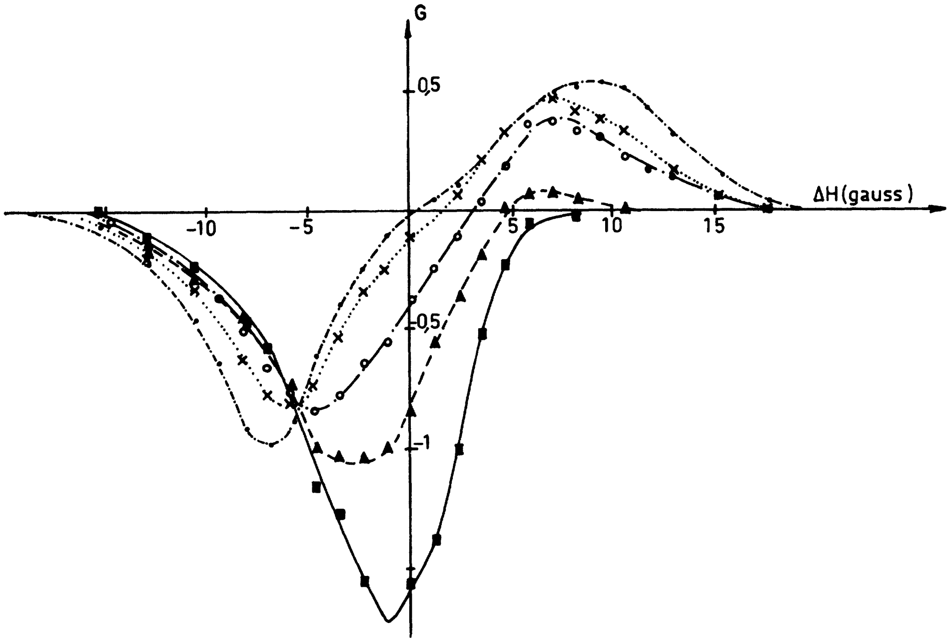

FIG. 7. Dynamic polarization of protons for the solution of tetrachlorosemiquinone in tetraethyleneglycol as a function of the difference between the applied frequency and the electronic Larmor frequency in units of the proton polarization at thermal equilibrium, $G = A/A_0 - 1$. Squares at +20 °C, triangles at +10 °C, open circles at 0 °C, crosses at −10 °C, and dots at −20 °C. Curves are inserted to guide the eye.

noise. This was achieved in about 20 sec. Another 20 sec was required to reset the NMR spectrometer to a new $\Delta\omega$ value.

B. Results

Our data for the tanone sample at four temperatures in the transition region are shown in Fig. 6. For $\theta > -60$ °C, we found a curve of the type already approached by that for −70 °C, having the even character under change of sign of $\Delta\omega$ characteristic for a liquid. For $\theta < -120$ °C, we found the odd symmetry typical for a solid and already approached at −98 °C. The data for tetrachlorosemiquinone at five temperatures are given in Fig. 7. For temperatures above 30 °C, the sample behaves as a liquid, below −30 °C as a solid. The absence of hfs makes the transition stand out more clearly.

VII. CONCLUSIONS

General considerations had made us expect results of the type observed. An important condition for the existence of dynamic polarization is that the spins to be polarized relax due to interaction with the spins to be pumped, but that the latter have a different souce of relaxation. The NMR shows convincingly that the former condition is met: enhancement of relaxation in the dilute radical solutions as compared to the solvent detailed verification of Torrey's model, and plausible parametrization of the data. The EPR shows that the second condition is met, simply because the electronic relaxation rates are much too large to come from the electron-proton interaction.

Besides, the preliminary measurements have given a fairly complete picture of the spin-spin interactions and their random variations: homogeneous electron lines; random Markoffian modulation of the tensor components of the Zeeman and hyperfine interaction through rotation of the radical; rotational modulation of the electron-proton dipole interaction for protons in molecules temporarily attached to the radical, with nearly the same "average" correlation time (although we have no precise picture of what corresponds to the apparent distribution of correlation times). The situation is simplified by the fact that the electron dipole-dipole interaction is negligible, as this allows one to consider each electron and its immediate surroundings separately.

With these details available, a numerical prediction of the dynamic polarization should be possible. Unfortunately two circumstances prevent the immediate application of a theory which we developed earlier[2] for this purpose: The first is that the modulation of the electron-proton interaction seems to be non-Markoffian. This can be incorporated by taking appropriate averages in the theoretical equations. The second is that the electronic longitudinal and transverse relaxation rates instead of being equal, as assumed in Ref. 2, differ by orders of magnitude. This introduces some complications in the algebra.

In the following paper we will show how these difficulties can be overcome and an acceptable account of the data be given without introducing any further empirical parameters.

[*] This paper is based on a thesis submitted to the Faculté des Sciences de Paris, 1969 (unpublished).

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Stochastic Theory of Dynamic Spin Polarization in Viscous Liquids with Anisotropic Electron-Spin Relaxation

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A previously developed theory of dynamic nuclear polarization (DNP) in liquids is extended and applied to viscous liquids with anisotropic electron-spin relaxation ($T_{1e} \gg T_{2e}$). It is based on a Schrödinger equation for two spins, S and I, in which the influence of the "lattice" motion is incorporated by a randomly time-dependent field acting on the spin S and a random time dependence of the dipole interaction between S and I. The quantum-mechanical equations of motion in an applied rotating field near S-spin resonance are solved and the DNP of the I spin is expressed in terms of the stochastic parameters which characterize the liquid motion. Using values of these parameters as obtained from EPR and NMR experiments on two dilute organic radical solutions, one finds excellent agreement with our DNP measurements on these systems as reported in the preceding paper. It is characteristic of these solutions that the NMR requires a distribution of relaxation times. The analysis of DNP measurements confirms this; it gives a somewhat different distribution and permits a more specific correlation between it and the structure of the liquid. The range of applicability of the theory is discussed, and in an appendix a completely general set of equations for the two-spin relaxation in our model is derived. Using these, the only restrictions on the application of our theory would be that the S-S as well as the I-I interactions must be small and that the amplitude of the rotating field must be substantially smaller than the constant external field.

I. INTRODUCTION

In the preceding paper[1] we have presented data on the dynamic polarization of protons in two solutions of organic radicals at temperatures covering a wide range of viscosities. We will now show how this quantity can be calculated on the basis of known dynamical and stochastical properties of these systems. The theory to be used is an extension of one developed previously for this type of problem.[2]

The relevant properties of the two samples, viz., a 0.02-mole/liter solution of tanone in isopropanol and a 0.03-mole/liter solution of tetrachlorosemiquinone in tetraethyleneglycol, are described in Paper I and can be summarized as follows: (i) The electron spin of each radical ion has a dipolar interaction with the spins of protons in the molecules of its solvation layer. (ii) This interaction, modu-