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Hyperfine Structure and Relaxation of Electron Spin Resonance in liquids¹

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Résumé.

La largeur de raie et par suite la résolution de la structure hyperfine de la résonance paramagnétique électronique dépendent des temps de relaxation. On peut influencer les temps de relaxation par le choix des solvants et de la température. De cette façon, il est possible d'obtenir la meilleure résolution et par conséquence un maximum d'information. Ces considérations théoriques sont illustrées par des exemples expérimentaux concernant des radicaux libres, un biradical et un complexe organométallique.

If a hyperfine structure (HFS) appears in an electron spin resonance spectrum due to the interaction between the unpaired electron and some of the nuclei, a maximum of information can be obtained if the individual HFS lines are of the best possible resolution, i.e. if the line width is as narrow as possible. But the EPR spectrum of a free radical or a metal chelate compound in dilute solution frequently exhibits an unsatisfactory resolution of the HFS or no resolution at all. This will be illustrated by the following figures. Figure 1 gives the electron spin resonance of the radical 1,3-bisdiphenyl-2-phenyl-allyl (BPA) in dilute solution (10^{-3} mol/l), obtained with a Varian EPR-spectrometer. No HFS is observable in heptane nor in benzene nor in carbondisulfide nor in ethanol at room temperature, but in paraffin or in a mixture of ethanol and glycerol (1:1) a HFS appears, being composed of nine lines with an intensity relation 1:8:28:56:70:56:28:8:1, which is the expected pattern for 8 equivalent protons.

The EPR-spectrum of the same radical in ethanol at different temperatures is shown in figure 2.

¹ A detailed paper is submitted for publication in *Z. Naturforsch.*, part A.

In order to understand these experimental results we have to consider the paramagnetic relaxation in liquids because of the close relationship between line width and relaxation times. This consideration follows in analogy with the theory of nuclear relaxation given by Bloembergen, Purcell and Pound [1].

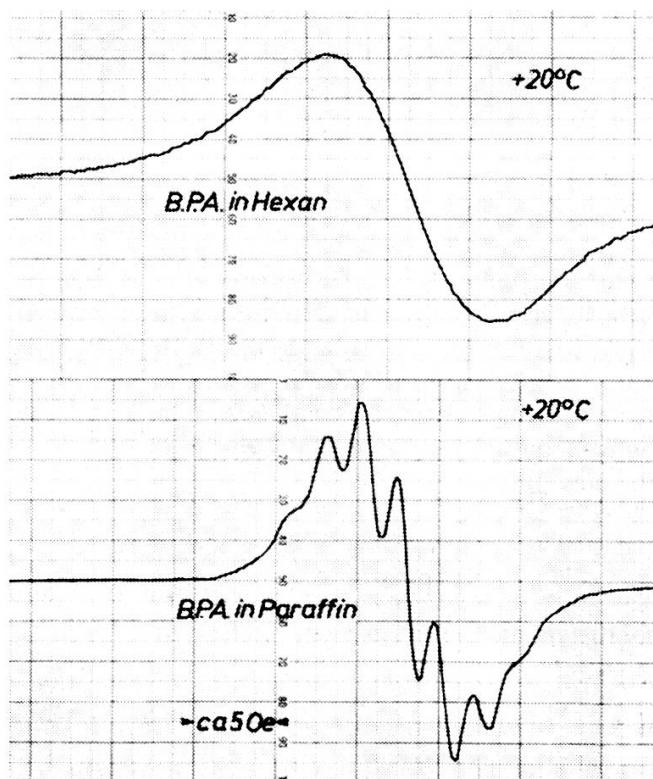


Fig. 1.
BPA in hexane (a) and in paraffin (b).

Paramagnetic relaxation can be divided into two parts. The first part maintains thermal equilibrium between the spin system and its environment generally termed "lattice", even in liquids. It comprises all processes in which energy is transferred between the spin system and the lattice and is described by the spin lattice relaxation time T_1 . The second part describes the loss of phase relations between the preceding magnetic dipoles without involving energy transfer and is measured by the spin-spin relaxation time T'_2 .

In addition to these two, there is a third relaxation time T_2 which is a measure of the line width $\Delta\nu$, $T_2 = C/\Delta\nu$, where C is a constant of the order

of magnitude 1, its value depending on the individual line shape. Between these three relaxation times the relation exists

$$1/T_2 = 1/2T_1 + 1/T_2'$$

provided the external magnetic field is sufficiently homogeneous.

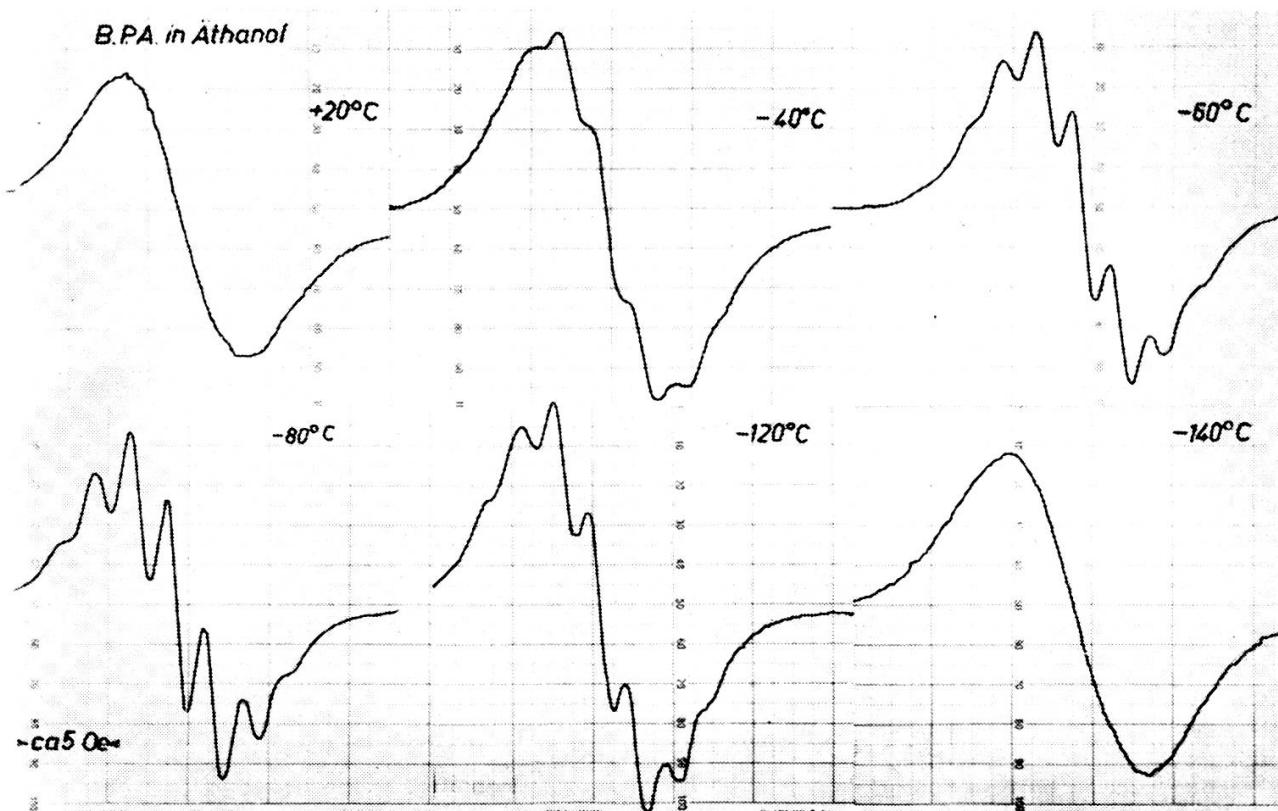


Fig. 2.
BPA in ethanol at $+20^\circ$ (a), -40° (b), -60° (c), -80° (d),
 -120° (e), and -140° (f).

After this formal description let us consider the mechanism by which the relaxation phenomena originate. The Brownian Motion of the molecules containing magnetic dipoles (unpaired electrons or nuclei) causes a magnetic noise whose Fourier Component in the Larmor Frequency ν_L induces transitions between the Zeemann Levels and so determines T_1 . The loss of phase relations results from the local magnetic field H_{loc} due to the neighbouring magnetic dipoles superimposed upon the static field H_0 . Its component in the direction H_0 is of the order of magnitude $\pm \mu (3 \cos^2 \theta - 1) r^{-3}$, where μ is the magnetic moment of the particle causing

H_{loc} , r is the distance between this particle and the point considered, and θ is the angle between r and H_0 . Since the contribution of the higher frequencies of the magnetic noise is averaged out because of the $(3 \cos^2 \theta - 1)$ term, only the "near zero" frequencies contribute to the spin-spin relaxation time T_2' , where "near zero" means a frequency width of the order of $\Delta\nu$.

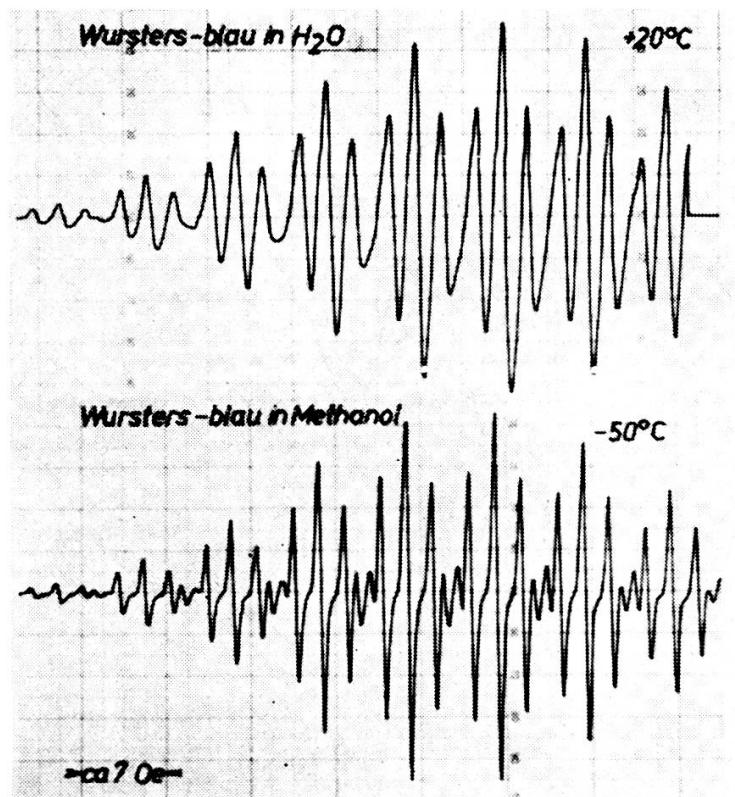


Fig. 3.
Wurster's blue perchlorate in water at room temperature (a)
and in methanol at -50°C (b).

A suitable quantity to measure the intensity of the magnetic noise spectrum as a function of frequency is the correlation time τ which occurs in Debye's theory of dielectric dispersion. τ is of the order of the time a molecule requires to turn through a radian (τ_{rot}) or to move through a distance comparable with its dimensions (τ_{trans}); it is defined by the equations:

$$\tau_{\text{rot}} = \frac{4\pi\eta a^3}{3kT}; \quad \tau_{\text{trans}} = \frac{\pi\eta ar^2}{2kT}$$

(η = viscosity, a = radius of the molecule, r = average distance between the molecules).

It should be noted, however, that these relationships are not more than a very crude approximation. In particular the use of the macroscopic viscosity is not sufficient to give the dependence of τ on the different intermolecular interactions. Therefore, it would appear problematic to attempt a quantitative theory for the relaxation mechanism.

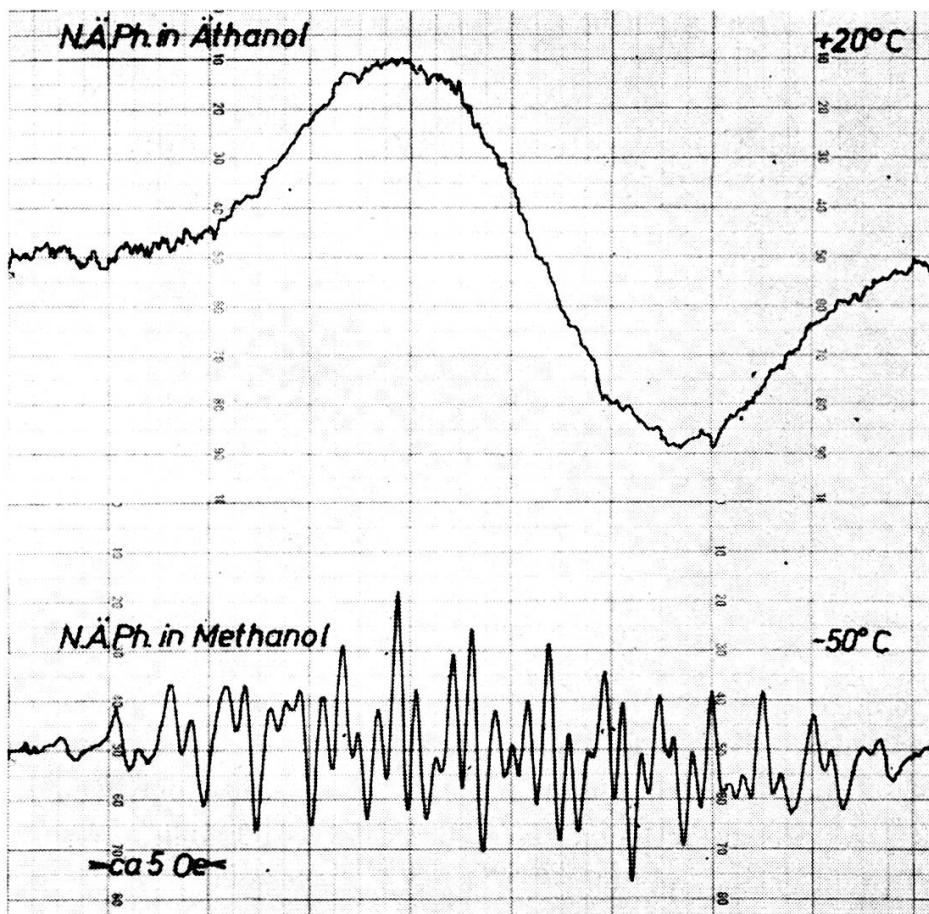


Fig. 4.
N-ethyl-phenacyl in methanol at room temperature (a)
and at -50°C (b).

However, the considerations given here lead to a qualitative understanding of the experimental results. The line width and therewith the resolution apparently depends very much on the viscosity. In figure 2a e.g., at room temperature (low viscosity), the correlation time is very short, $2\pi\nu_L \tau \ll 1$. Consequently T_1 is very short and determines T_2 and hence the line width which becomes so large that no HFS appears. With decreasing temperature τ becomes longer, the intensity of the Fourier component

ν_L decreases, T_1 and T_2 increase, the HFS can be resolved. At very low temperatures (high viscosity), the correlation time is very long, $2\pi\nu_L\tau \gg 1$, T_1 becomes negligible with respect to T_2' . The line width is determined by the spin-spin relaxation time T_2 , which owing to the high intensity of the "near zero" frequencies becomes so short, that the HFS is completely smeared out. At an intermediate temperature (in figure 2 at -80°C), $\Delta\nu \approx 1/T_2$ has a minimum and optimum resolution is obtained.

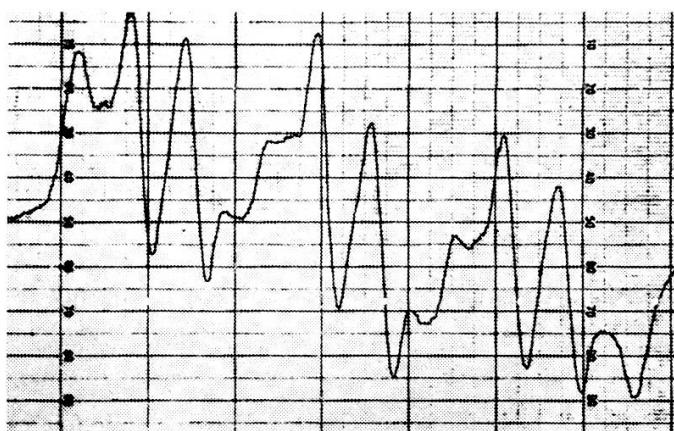


Fig. 5.
Porphyrindene in dimethyl-sulfoxide at -50°C .

The influence of solvent and temperature may be illustrated by a few more examples. Following Weissman [2], Wurster's blue perchlorate in aqueous solution shows 13 triplets but theoretically one would expect 13 quintetts. Using methanol at -50°C , it was possible to resolve quintetts. The intensity relation 1:4:6:4:1 corresponds to 4 equivalent protons.

The electron spin resonance of N-ethyl-phenacyl, whose unusual magnetic and spectroscopic behaviour has been described earlier [3] is shown in figure 4.

At low temperature one observes over 40 HFS lines. The great number of lines is due to the low symmetry of the molecule. It has so far not been possible to give a detailed explanation of the origin of these lines.

The biradical porphyrindine gives, in dilute solution, according to HUTCHISON et al. [4] one broad absorption line with two shoulders. Using dimethyl-sulfoxide, a hyperfine structure could be obtained of at least 3×4 components as illustrated in figure 5. Finally the EPR spectrum of a metal chelate compound, the dibenzene chromium kation is given in

figure 6. Figure 6a shows the spectrum obtained by Calvin et al. [5] using ethanol at room temperature. Figure 6b illustrates the almost complete resolution one observes in the same solvent at -80°C .

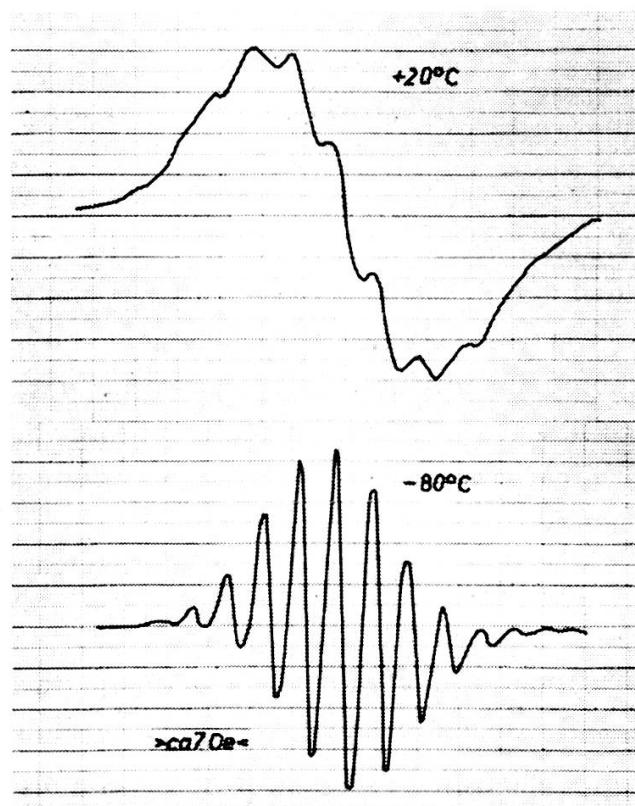


Fig. 6.

Dibenzene-chromium-kation in ethanol: (a) room temperature,
(b) -80°C .

The results given here can be summarized as follows: by choosing suitable solvents and temperatures it is possible to minimize the line width and hence to obtain the best resolution of the individual HFS components.

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