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Effect of O₂ on Line width and Relaxation in ESR

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Résumé.

La résolution de la structure hyperfine de la résonance paramagnétique électronique dépend de la concentration de l'oxygène moléculaire dans la solution. L'influence de l'oxygène sur la largeur de raie est démontrée avec l'exemple de radical (SO₂)₃NO⁻. Le spectre du radical 2, 4, 6-triphenyl-phénol, pas résolu en condition normale, montre plus que cent composants hyperfins après avoir ôté l'oxygène. En cas de Wursters Bleu il est possible de résoudre tous les 325 composants hyperfins qu'on s'attendait théoriquement.

High resolution ESR is less developed than high resolution NMR. This may be due to the fact that high resolution NMR is mainly a technical problem, particularly a question of the homogeneity of the magnetic field, while the line width of ESR is primarily determined by the sample itself, i.e. by the relaxation phenomena involved. Consequently, obtaining high resolution ESR requires a knowledge of the relaxation mechanisms in order to be able to minimize the line width.

The narrowest lines can be expected for dilute solutions of free radicals containing first row elements only, since in those the line broadening due to the spin-lattice relaxation mechanism involving spin-orbit coupling is negligible. For that reason we have studied the factors influencing the line width of free radicals in solution. It turned out, that by far the most important factor in determining the line width of dilute solutions is the dissolved molecular oxygen. This is not surprising if one considers that the concentration of the dissolved oxygen in most organic solvents in contact with air is in the order of $1-2 \times 10^{-3}$ mol/l.

I would like to illustrate the effect of the oxygen with the example of a solution of 2,4,6-triphenyl-phénol in benzene. Fig. 1 *a* gives the spectrum of a solution prepared in the usual way, while Fig. 1 *b* shows the same spectrum after the oxygen has been removed. The spectrum shows about 100 HFS components distributed over a range of about 12 G; the splitting between the components is .12 G, the line-width is .07 G.

We have so far not been able to analyze the spectrum, probably because of the still insufficient resolution.

In order to observe the effect with a single line we have investigated the ESR-spectrum of the disulfonate ion $(\text{SO}_3)_2\text{NO}^{--}$ in water under exclusion of oxygen, in contact with air and saturated with oxygen. We found a line width of .15 G, .29 G and 0.90 G resp.; it is linearly dependent on the concentration of the unpaired spins within the error of the experiment.

Other free radicals investigated which exhibit well resolved HFS with line width below .1 Gauss include 1,3-bisdiphenylene-2-phenyl-allyl (BPA), N-ethyl-phenacyl and Wurster's blue perchlorate.

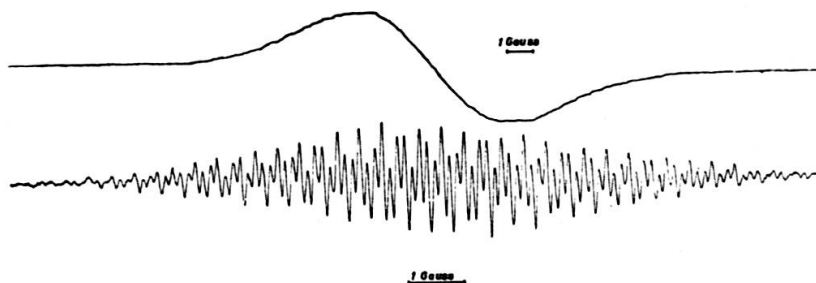


Fig. 1.

2, 4, 6-Triphenyl-phenoxy in benzene, concentration 5×10^{-4} mol/l.
a: saturated with air. *b*: after the exclusion of oxygen.

The general feature that the ESR is easier saturated after the exclusion of the oxygen has been studied with the example of BPA; it turned out that the spin-lattice relaxation time T_1 is one order of magnitude longer without oxygen compared with an air-saturated solution, but our results are too preliminary to give quantitative data on T_1 .

Two markedly different spectra of N-ethyl-phenacyl in benzene and ethanol seem to indicate an effect of the solvent on the distribution of the wave-function of the unpaired electron, but quantitative results on this solvent effect would require a still much better resolution.

The central part of the spectrum of Wurster's blue in oxygen-free ethanol is given in fig. 2¹. The outer wings disappear in the noise; this is not surprising if one considers the intensity ratio of 16632: 1 between the most intense central line and the weakest outer line of the spectrum. Apart from that the fully resolved spectrum shows all the 325 HFS-components to be expected theoretically. Every observed line can be accounted for in terms of three coupling constants, namely 6.8 Gauss for the 12 methyl-

protons, 1.9 Gauss for the 4 ring-protons and .28 Gauss for the two nitrogen-atoms.

A more detailed examination of the spectrum reveals one more result I think worth mentioning. The central group of lines exhibits the symmetric pattern of 5 components expected from the coupling with the two nitrogens, but the farther out to the wings the more the symmetry disappears gradually until one observes 4 rather than 5 components of which the

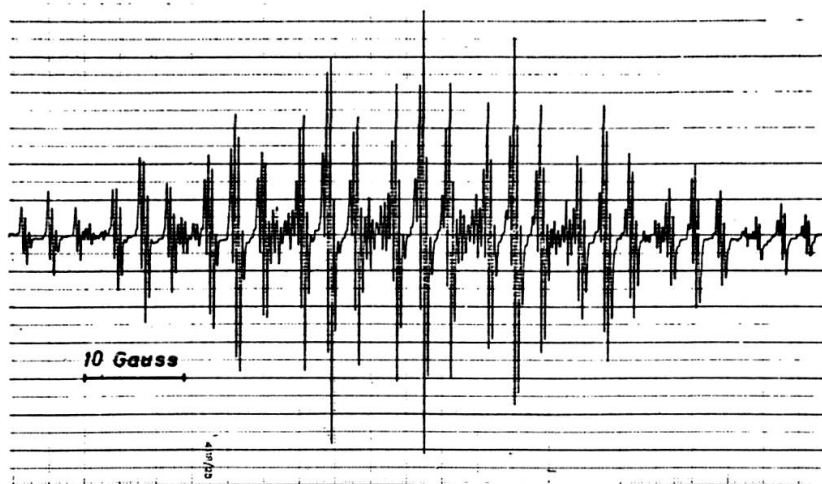


Fig. 2.

Wurster's blue perchlorate in ethanol, concentration 5×10^{-4} mol/l, without oxygen.

2 middle ones have almost equal intensity in contrast to the expected pattern. This is probably due to second order effects for which it is difficult to give a quantitative theoretical explanation.

From the experimental results presented here I think we may draw the following conclusions:

1) The line width and therewith the resolution of the HFS of dilute air-saturated solutions is determined by the dissolved molecular oxygen. Consequently, high resolution ESR requires a carefull exclusion of the oxygen of the solvent. For this reason, the narrowest HFS-lines have been obtained in the past with radicals which are chemically sensitive to oxygen.

2) A solution of a free-radical of a concentration of about 10^{-3} mol/l leads after the exclusion of oxygen to a line width of about .1 Gauss. A still

considerably narrower line width can probably be obtained by further dilution and by other means about which one may learn more by studying the relaxation mechanism in detail. At present, the by far most important problem is a technical one, namely higher sensitivity, because all requirements for higher resolution such as more dilute solutions and lower microwave power to avoid saturation broadening lead to a decreased signal to noise ratio. For this reason a spectrometer using low frequency modulation is certainly unsatisfactory but the possibility of increasing the sensitivity by using high frequency modulation is limited by the modulation broadening effect. Therefore, a superheterodyne spectrometer carefully designed for the highest possible sensitivity seems to me desirable for high resolution ESR-work; without going into details I would like to remind you of Feher's paper on "Sensitivity considerations in ESR-spectroscopy" ¹.

3) Molecular oxygen affects not only T_2 , but also the spin-lattice relaxation time T_1 . This is theoretically plausible, since the spin-lattice-relaxation of the radical seems to involve the unpaired spins of the oxygen. In rigid solvents where other relaxation mechanisms are absent exclusion of oxygen should lead to very long spin-lattice-relaxation times; this prediction is in the process of being tested.

4) Better resolution increases the possibility of analyzing ESR-spectra. In analyzing an observed highly resolved ESR-spectrum one should start from the center, since the intensity relations and even the number of lines may be considerably obscured by second order effects at the wings.

A more detailed paper will appear in *Z. f. Naturf.*

1. HAUSER, K. H., *Naturwiss.*, **47**, 251 (1960).
 2. FEHER, G., *Bell Syst. Tech.*, **36**, 449 (1957).
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