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HYPERFINE INTERACTION IN THE DIPHENYLPICRYLHYDRAZYL MOLECULE

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The structure of the proton resonance line due to the magnetic interaction between the unpaired electron and the protons in the diphenylpicrylhydrazyl (DPPH) free radical was measured in fields from 500 to 5000 oe, mainly at helium temperatures. When H/T is large enough, the resonance line splits into four components. One component is unshifted, one is shifted toward the low-frequency side, and the other two are shifted to the high frequency side. The twelve protons in DPPH can be assigned to the three shifted components in a manner that is consistent with the relative intensities of the lines. The existence of an unshifted line is unexpected and its origin remains unexplained.

INTRODUCTION

RECENTLY there has been a large amount of work, both experimental and theoretical, devoted to the study of the interaction between nuclei and unpaired electrons in free radicals (cf., for example, reference 1). Precise information on the unpaired electron probability distribution within the molecules has been obtained; in particular, a negative spin density has been found at certain nuclear positions. Most of these experimental studies have used electron paramagnetic resonance; there has been only a small amount of work devoted to studying the same phenomenon with nuclear resonance techniques. Yet it is just nuclear resonance that can apparently give more precise information about this interaction.

The free radical diphenylpicrylhydrazyl (DPPH), the structure of which is indicated schematically in Fig. 1, is typical of the materials studied in electron paramagnetic spectroscopy. A large amount of work has been devoted to the study of DPPH. It is known that every DPPH molecule has one unpaired electron; its paramagnetic susceptibility obeys Curie's law in the range from room temperature down to liquid helium temperature; a slight deviation from Curie's law begins only below 4°K.[2]

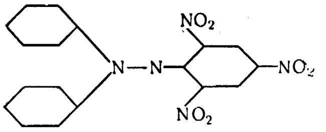

FIG. 1. Structure of the DPPH molecule.

In solid DPPH the electron resonance line is narrow; its width (1.5 — 2 oe) is much smaller than that which would be produced by a dipole interaction between electrons in different molecules. This phenomenon is explained[1] by the presence of a strong intermolecular exchange interaction which narrows the line. In dilute solutions the width of the DPPH electron resonance line increases and it splits into five hyperfine components, spaced about 10 oe apart.[3] In the work of Hutchinson et al.,[3] this hyperfine (h. f.) structure is attributed to the presence of an interaction between the nuclear spin I and the electron spin S of the form

$$\mathcal{H}_{\text{h.f.}} = \sum_i h a_i \mathbf{I}_i \mathbf{S},$$

with $a_1 \approx a_2$ for the two central nitrogen atoms, and $a_i \ll a_1, a_2$ for all the other coupling constants. On the other hand, Weissman[4] showed that if the exchange is strong the dipole-dipole interaction between the electron and nuclear spins averages to zero, and the only term contributing to the Hamiltonian is the Fermi contact interaction, proportional to the electron spin density[5] at the position of the particular nucleus.

Behrson,[6] using a simple molecular orbital method, made a rough calculation of the spin density in the DPPH molecule and obtained a result in agreement with experiment, namely $a_1 = a_2$. Besides this, his calculation led to the conclusion that there should be an observable interaction between the unpaired electron and the protons in ortho and para positions in the phenyl rings; this interaction will shift the resonance of these protons to lower frequency (in a given external field). At the same time, the protons in meta positions in the phenyl and picryl groups, according to this calculation, are not coupled to the unpaired electron and should give an unshifted proton line.

The first experimental indication that the DPPH molecule has at least two non-equivalent groups of protons was obtained by Berthet and Riemann,[7] who studied the proton resonance in DPPH at a field of ~6500 oe and a temperature of 77° K. Similar measurements were made somewhat more carefully later by Gutowsky et al.[8] The latter authors carried out a more exact calculation of the coupling constants using the localized-pair method, which gives the possibility of a negative spin density.[5] According to this calculation, the proton spectrum in DPPH should have four lines: the ortho and para protons in the phenyl groups should, as before, give two closely spaced lines shifted to the low-frequency side (in a given external field), while the meta protons in the phenyl and picryl groups should give lines shifted to the high-frequency side.

The present work is a study of the proton resonance in DPPH, mostly at liquid helium temperatures, where the high values of H/T needed to resolve the individual lines can be obtained. The proton resonance spectrum of DPPH was found to contain, besides the expected lines, an intense unshifted line; the origin of this unshifted line is not understood. This shows that our picture of the state of the unpaired electron in the molecule is apparently incomplete.

APPARATUS AND SAMPLES

The proton resonance was detected with a regenerative detector of the type used by Pound and Knight;[9] after narrow-band amplification and synchronous detection, the signal was recorded by an ÉPP-09 recording potentiometer. The coil was wound directly on a thin-walled glass ampoule 6 mm in diameter containing about 0.15 cm^3 of sample which was placed in a Dewar; the coil was connected to the electronic apparatus by a specially constructed coaxial cable.

The 935-oe magnetic field was obtained with a permanent magnet; the other fields were obtained with an electromagnet[10] fed by a motor generator with an electronic current stabilizer. The field was measured by a separate proton resonance system. The modulating field was supplied by supplementary windings on the magnet poles. The modulation frequency was 30 cps, amplitude ~1.5 oe. The time constant of the phase detector was 10 sec and a sweep through the whole frequency range took about 30 — 40 min.

Two polycrystalline DPPH preparates were used as samples: one prepared in A. E. Arbuzov's laboratory, the other obtained in France.* Both samples gave nearly the same results.

We note that the empty ampoule gave a weak proton line, probably due to protons in the insulation on the windings, in the glue applied to the windings, and in the walls of the ampoule; the intensity of this line did not exceed 1 — 2% of the intensity of the DPPH line.

RESULTS

Figure 2 shows typical traces of the absorption line in a 935-oe field at temperatures of 4.2°, 2.5°, and 1.55° K. Figure 3 shows integral curves for the 935-oe field and various temperatures; similar curves for 2000 oe are shown in Fig. 4. Each integral curve is the average of 4 or 5 traces taken on different days.

From Figs. 3 and 4 it is clear that the proton spectrum of DPPH has four components, one remaining at the position of the unshifted proton line, one shifted to lower frequency and two shifted to higher frequencies. The width of the central line is practically independent of H/T, while the satellite widths increase with increasing H/T.

Figure 5 shows the dependence of the shift on H/T for each of the satellites. The linear dependence of the shift on H/T shows that it is caused by the paramagnetism of the unpaired electron.

Table I gives the relative intensities of the satellite for various fields and temperatures. The relative intensity of a line is defined to be the ratio of its area to the total area of the whole integral curve. The accuracy of these measurements is determined

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*We take this opportunity to thank V. M. Chibrykin, who furnished us with these samples.

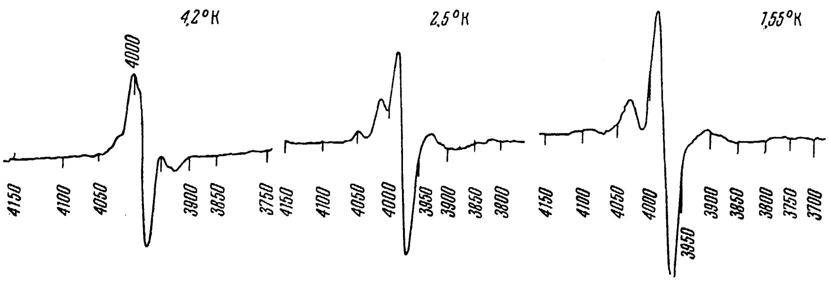

FIG. 2. Trace of the derivative of the proton absorption lines in DPPH at 935 oe at temperatures 4.2°, 2.5°, and 1.55° K.

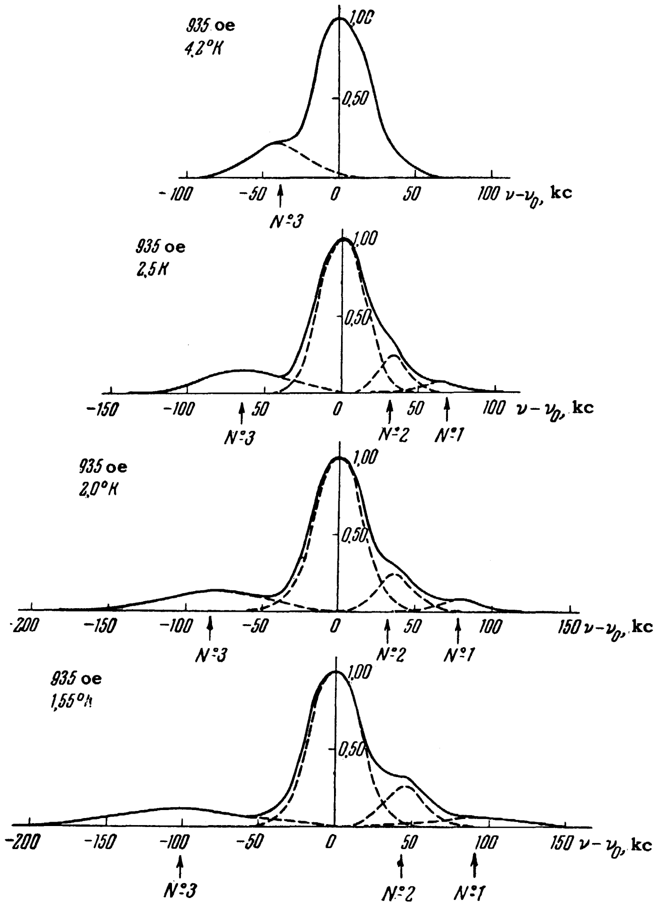

FIG. 3. Proton line in DPPH at 935 oe.

from the scatter in the different integral curves obtained in different runs. Besides this scatter, there is also an arbitrariness in splitting the full curve up into its components; as a result, the probable error in the intensities is 15 — 20%.

It is clear that in a fixed magnetic field, the satellite relative intensities are independent of temperature in the helium temperature range, but they decrease noticeably in going from 935 oe to 2000 oe. In a further increase in field to 5000 oe the satellites continue to become weaker, but not so rapidly; in this field it is difficult to measure the shifts and intensities with any accuracy.

In a field of about 5000 oe, measurements were also made at 77° K. Here the resonance line is asymmetric, like that observed in references 7 and 8. Because the shifts are so small, it is hopeless to try to split the line into its components. One can only conclude that the satellite intensities apparently increase on going from helium temperatures to nitrogen temperature.

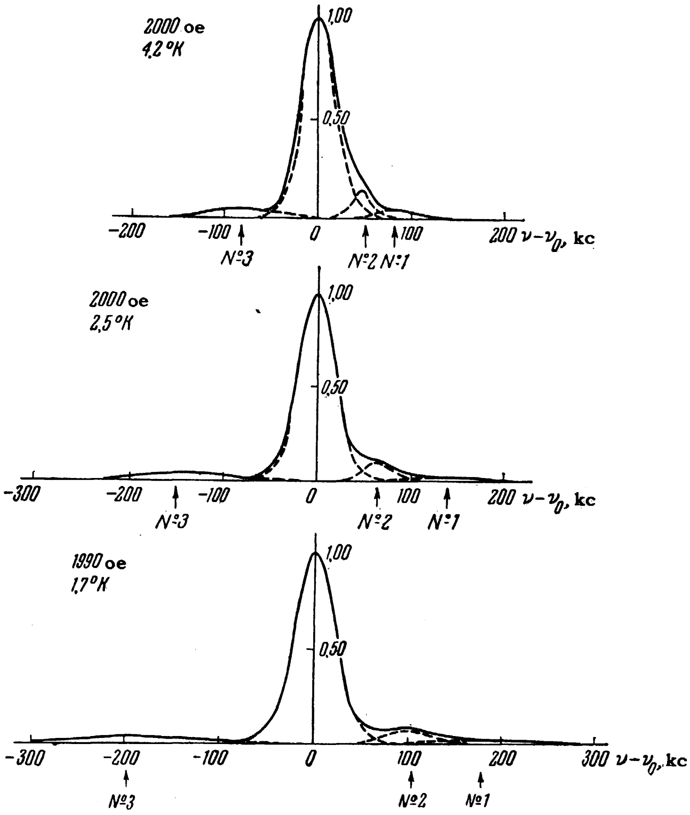

FIG. 4. Proton line in DPPH at 2000 oe.

DISCUSSION OF THE RESULTS

From Table I it is clear that the intensities of the lines are in the ratios 1 : 2 : 3 : 11 at 935 oe and 1 : 2 : 3 : 25 at 2000 oe. Thus, while the satellite intensities maintain a constant ratio, the relative intensity of the central line increases with increasing field. Moreover, the central line is so intense that if the weakest line (No. 1) is assumed to be produced by one proton, then all 12 protons in the DPPH molecule are not sufficient to produce the observed intensity of the central line.

If we neglect for the moment the existence of

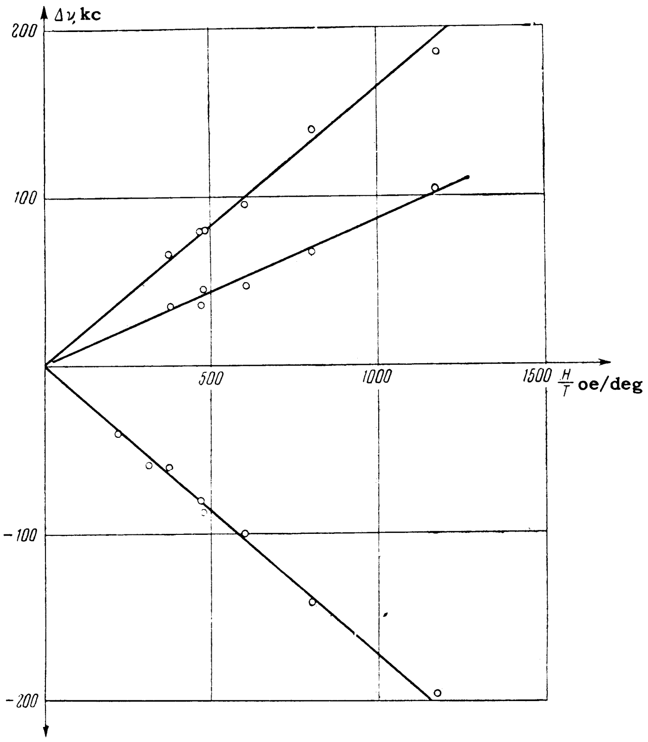

FIG. 5. Satellite shift, Δν versus H/T.

the unshifted proton line, it is easy to assign the 12 DPPH protons to the three satellites. Namely, in qualitative agreement with calculations,[8] the two protons in the picryl group can be assigned to line No. 1, the four meta protons in the phenyl groups to No. 2, and the six ortho and para protons in the phenyl groups to No. 3. In Table II are listed the values of the coupling constants a_i calculated from the slopes of the curves in Fig. 5 by the formula

$$\Delta\nu_i = a_i(\gamma_e/2\pi)(g\beta H/4kT),$$

where $\Delta\nu_i$ is the line shift, γ_e is the electron gyromagnetic ratio, and β is the Bohr magneton. In the same table, the corresponding calculated[6,8] coupling constants are listed for comparison. It is clear that the calculations using the localized pair method are in qualitative agreement with experiment.

TABLE II Coupling constants a_i

Proton position	Experiment	Theory* (ref. 6)	Theory (ref. 8)
meta (picryl)	1.74	0.0	2.2
meta (phenyl)	0.92	0.0	1.58
ortho (phenyl)	—1.84	—0.90	—3.00
para (phenyl)	—1.84	—0.90	—2.79

*Calculated according to[11] $a_i = -22.5\rho_{c_i}$, with ρ_{c_i} taken from reference 6.

Let us now return to the central line. What is its origin? Obviously, some part of its intensity may be due to the presence of nonmagnetic compounds. However, to ascribe it entirely to such an admixture is difficult on the following grounds: a) the admixture would have to be too large, since the central line constitutes 60 — 80% of the total intensity; b) two compounds synthesized in different places give identical results within the accuracy of the measurements; c) it is difficult to imagine how the magnetic field could change the relative intensities of the admixture line and the DPPH lines.

On the other hand, magnetic susceptibility data[2] show that DPPH has normal paramagnetic properties down to the lowest temperatures, and every molecule has one unpaired electron. Therefore it is apparently not possible to ascribe the central line to the pairing of some of the molecules with consequent diamagnetic behavior.

One might try to explain the central line by assuming that the DPPH molecule has two states, one having zero spin density at the positions of the hydrogen nuclei. If the energy difference between these two states increased with increasing magnetic field, then the observed dependence of relative intensity on field strength could be understood. But in this case, the relative intensity should also vary with temperature. Table I, however, shows that this does not happen.

In conclusion, we express our profound gratitude to academician P. L. Kapitza for his constant interest in this work and to A. S. Borovik-Romanov for discussions.

TABLE I Satellite relative intensities

H, oe	460	935					2000		
T, °K	1.7	4.2	3	2.5	2	1,55	4.2	2.5	1.7
I_1	—	—	—	0,06	0,05	0.06	0,03	0.03	0.03
I_2	—	—	—	0,11	0,12	0.12	0.07	0.06	0.06
I_3	0.22	0.20	0.17	0.19	0.18	0.18	0.09	0.08	0.08
$I_1 + I_2 + I_3$				0,36	0.35	0.36	0.19	0.17	0.17

Remark: I_1, I_2, I_3 are the intensities of lines No. 1, 2, and 3.

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Translated by M. Bolsterli
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