We wish to thank J. K. Galt for assistance in setting up the proton resonance equipment, and S. Millman for several valuable discussions.

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Hyperfine Structure and Exchange Narrowing of Paramagnetic Resonance†

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November 21, 1949

THE free radical α, α-diphenyl β-picryl hydrazyl, $(C_6H_5)_2N-NC_6H_2(NO_2)_3$, shows the strongest and narrowest electronic paramagnetic resonance absorption so far reported. This resonance was observed by its effect on the transmission of microwaves (frequency approximately 24,000 mc) through a TE_{01} cavity with a small amount of the free radical placed approximately on the axis of the cavity. The microwave frequency was tuned to give maximum transmission through the cavity while the cavity was in place between the pole pieces of an electromagnet. With an amount of the free radical as small as 2 mg the transmitted power was reduced by a factor of three when the magnetic field was of the proper value (approximately 8600 oersteds) to give resonance. The half-width of the resonance at half-maximum absorption was 1.45 oersteds. Because of its sharpness and intensity, this resonance may be of value for stabilizing or measuring magnetic fields in cases where the signal produced by the proton resonance is not sufficiently strong.

The electronic g-value was obtained by measuring the electron's resonant frequency and the proton frequency in the same magnetic field. The ratio of proton to electron frequencies obtained was 15.178×10^{-4} which, combined with results of Taub and Kusch,[1] gives a g-value of 2.0042 ± 0.0004. The g-value and line width obtained are in fair agreement with the results of Holden, Kittel, Merritt, and Yager,[2] who have made measurements parallel to those presented here and with whom we have enjoyed very helpful discussions.

The unusually narrow line-width observed is evidently due to exchange narrowing[3] since spin-spin interactions alone would lead one to expect a half-width of approximately 50 oersteds. The free radical was dissolved in concentrations of 3.0 and 1.5 weight percent in benzene and the resonance width examined. With these dilutions exchange effects should be negligible, and indeed the resonance half-widths (half-widths at half-maximum) were greater than in the solid, being 7.5 and 5 oersteds respectively for the two solutions. These latter widths are, as closely as can be calculated, just those to be expected from spin-spin interactions. Motion of the molecules in solution gives no appreciable narrowing of the line at the frequencies used since the relaxation time is 10^{-10} sec. or larger.

Gaseous NO has been examined by Beringer and Castle[4] with a somewhat similar technique. They find associated with the electronic resonance a hyperfine structure due to coupling between the N^{14} and electronic magnetic moments. If the odd electron in NO is considered to be on the nitrogen atom in an essentially atomic $2p$ state, the expected interaction is approximately $75\,I\cdot J$ megacycles/sec. Here the average inverse cube of the electron's distance from the nucleus has been taken from a previous estimate for nuclear quadrupole effects.[5] The experimental results give an interaction of $31\,I\cdot J$ mc, indicating that the probability of finding the odd electron on the nitrogen atom is approximately $\frac{1}{3}$. This is what may be expected if the electron participates in a 3-electron bond.[6]

The free radical examined here is in a $^2\Sigma$ electronic state and the odd electron might be assumed to be in a $2p$ orbit on the nitrogen atom which has only two bonds. In this case hyperfine structure consisting of three equally spaced, equal intensity lines separated by 125 mc or 45 gauss may be expected. If exchange interactions between the electrons in adjacent molecules are as large as the electron-nuclear coupling, this hyperfine structure may be considerably modified or eliminated. Since the exchange effects are evidently important in the solid material, failure to find hyperfine structure is perhaps not surprising. However, in the diluted solutions of the free radical hyperfine structure of the type described was expected, but not found. What hyperfine splitting is present must be less than the line width, hence the probability of finding the odd electron on the nitrogen which formerly has only two valence bonds must be less than 0.15. In order to produce such a small hyperfine structure, this electron must either have considerable probability of being found on nuclei of zero spin such as oxygen, or perhaps circulate over a considerable region of the molecule and hence average out a large number of small interactions with nuclei.

Study of hyperfine structure in other molecules with magnetic moments of electronic origin should give considerable information about the electron distributions.

The interest and encouragement of Dr. W. V. Cohen during this investigation is appreciated. In addition we are indebted to Mr. Walter Merkle for making available the Brookhaven cyclotron magnet in which this work was carried out, and to Mr. George Brush and others of the cyclotron group for considerable assistance.

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Microwave Spectrum of CH_2CFCl

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THE microwave spectrum of the asymmetric top molecule CH_2CFCl has been observed and analyzed. The molecular parameters for both isotopic species are given in Table I. The frequencies computed with these parameters for the transitions which have been identified appear in Table II, together with the observed frequencies corrected for quadrupole effect.

The assignments of these lines were further confirmed, in every case, by the agreement (0.5 percent) of the observed quadrupole multiplet structure with that computed by first-order theory.[1] The quadrupole parameters used were $\chi_{aa}=-73.3\pm0.3$ megacycle/second and $\chi_{bb}=39.8\pm0.2$ megacycle/second. The quan-
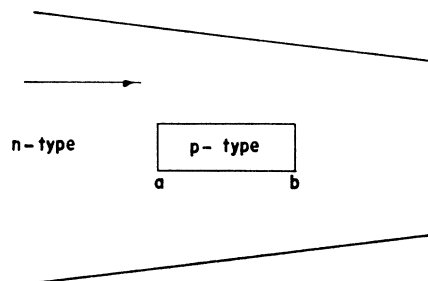

Fig. 1. $6_{24}\rightarrow6_{33}$ multiplet of CH_2CFCl.