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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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 $\frac{1}{2}$. 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 $\chi_{aa} = -73.3 \pm 0.3$ megacycle/second and $\chi_{bb} = 39.8 \pm 0.2$ megacycle/second. The quan-

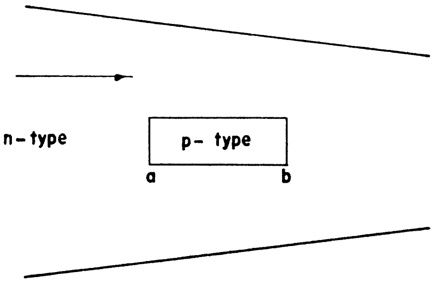

FIG. 1. $6_{24} \rightarrow 6_{33}$ multiplet of CH_2CFCl.

TABLE I. Molecular parameters for the isotopic species of CH_2CFCl.*

	$(a+c)/2$	$(a-c)/2$	κ
CH_2CFCl^{35}	7065.00	3616.62	−0.542724
CH_2CFCl^{37}	7030.91	3650.42	−0.568678

* The number of significant figures quoted appears to be justified by the very close agreement of the five transitions of $J<6$ for the Cl^{35} species. This would indicate that the deviations of about a megacycle in the $J \gtrsim 6$ transitions, which are consistent in sign, may be accounted for in terms of centrifugal distortion.

TABLE II. CH_2CFCl^{35} transitions.

Transition	Frequency calculated (Mc)	Frequency observed
$1_{01} \rightarrow 2_{12}$	21,026.7	21,026.70
$2_{12} \rightarrow 3_{03}$	20,214.2	20,214.29
$6_{43} \rightarrow 7_{34}$	22,420.4	22,419.13
$2_{12} \rightarrow 2_{21}$	21,699.7	21,699.70
$3_{13} \rightarrow 3_{22}$	24,362.3	24,362.48
$5_{05} \rightarrow 5_{14}$	24,601.4	24,601.24
$6_{15} \rightarrow 6_{24}$	20,392.4	20,391.51
$6_{24} \rightarrow 6_{33}$	24,896.3	24,895.46
$7_{16} \rightarrow 7_{25}$	25,657.3	25,656.30
$7_{25} \rightarrow 7_{34}$	23,897.8	23,896.29
	CH_2CFCl^{37} transitions	
$1_{01} \rightarrow 2_{12}$	20,822.8	20,822.8
$8_{54} \rightarrow 9_{45}$	22,848.8	22,852.40
$2_{12} \rightarrow 2_{21}$	21,902.5	21,902.50
$3_{13} \rightarrow 3_{22}$	24,427.4	24,427.38

tities χ are products of eQ and $(\partial^2 V/\partial a^2)$ and $(\partial^2 V/\partial b^2)$, the appropriate components of the molecular field gradient at the Cl nucleus. a and b are the principal axes of least and intermediate moments of inertia, respectively.

The assignments were initially made solely on the basis of the observed multiplet structure. Particularly helpful in this regard were certain of the Q-branch transitions of $J>2$, which appear as quadruplets of lines with a ratio of certain component separations which is determined only by the J value involved. Figure 1 shows the $6_{24} \rightarrow 6_{33}$ multiplet; the ratio of the differences A and B agreeing with that calculated from the first-order formulas for a $6 \rightarrow 6$ transition. Although a P or R branch transition gives rise to a similar quadruplet, the ratio of spacings depends on the quadrupole coupling factors of the two levels involved and will not usually be confused with that expected for any Q-branch transition. The amount of the separation depends, however, on the magnitude of the individual coupling factors, so that, due to limitations of resolution, some of the transitions may appear as singlet or doublet lines.

Because the a axis is very nearly parallel to the C−Cl bond, one may calculate with reasonable assurance -74.4 ± 2 mc/sec. as the value of the quadrupole coupling along the bond.

The corresponding deuterated compound is now being prepared, with whose results we hope to determine the structure of the molecule.

We wish to express our gratitude to Dr. M. Prober of this laboratory for the preparation of the compounds used in this investigation. We also wish to thank Miss V. G. Thomas for her assistance with the numerical computations involved in this work.

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Erratum: A Theory of Pressure Absorption

[Phys. Rev. **76**, 1268 (1949)]

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SOME numerical values must be corrected as follows: The experimental intensity of the Q-branch of O_2 band near 1556 cm^{-1} is 4.4×10^6 cm^{-1} instead of 4.0×10^8 cm^{-1}, at 1 atm. Thus $\beta^2 + (11/30)\gamma^2$ in (6) must be assumed to be 1.9×10^{-52} in order to explain the above experimental results.

The estimation of the intensity ratio of the quadrupole absorption to the pressure absorption must be revised as follows,

$$1 : \left(\frac{c}{\nu}\right)^2 \frac{n}{R_0{}^8}\left(\beta^2 + \frac{11}{30}\gamma^2\right) \doteqdot 1 : 10^4.$$

Coherent Scattering of X-Rays by Atoms with More Than One Electron According to the One-Electron Theory and the Positron Theory

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THERE is no doubt that the "one-electron theory" and the "positron theory" cannot give identical expressions for the *coherent scattering* of x-rays by atoms. Recently Halpern and Hall[1] announced the results of this calculation, which exhibited this fact, but from the very beginning it is clear that the one-electron theory cannot give rise, for example, to the terms due to vacuum polarization. The real problem consists therefore in determining the order of magnitude of the differences in the results of the two theories.

On the other hand, it is evident that these differences may be separated into two classes from the beginning: Those which are encountered for the atom with many electrons as well as for the hydrogen atom and those which are specific to the atom with many electrons, and which are due, if they exist, to the interactions between electrons. The terms of the first class are to be looked for in the "one-particle parts" (in the sense defined by Schwinger[2]), the other in the two- and many-particle parts. It is these latter terms we tried to find.

Let N be the number of electrons, $\varphi_1\varphi_2\cdots$ the wave functions of a single electron in the field of the nucleus. Let

$$\psi(x) = \sum a_n \varphi_n \exp(itE)_n$$

be the matter field, H the coupling between the matter field and the transverse electromagnetic field, and H^c the Coulomb interaction of the electrons. We introduce S and T by

$$\partial S/\partial t = H, \quad \partial T/\partial t = \tfrac{1}{2}i[S, H] - H_{\text{self}}{}^{\text{tr}} \text{ and } \epsilon(t) = \pm 1 \text{ if } t \gtrless 0.$$

H^c shall be treated as a perturbation. To the one-particle parts of $\frac{1}{2}i[S, H]$ which give to the well-known terms (Waller):

$$\sum_{Z}\sum_{i=1}^{N} \varphi_i{}^*(\boldsymbol{\alpha}\cdot\mathbf{A}_0)\varphi_z\varphi_z{}^*(\boldsymbol{\alpha}\cdot\mathbf{A}_1)\varphi_i/(E_z - E_i \pm |k|), \tag{1}$$

we must add the two-particle terms of

$$\tfrac{1}{2}i^2[S, (S, H^c - H^c{}_{\text{self}})] + i(T, H^c - H_{\text{self}}{}^c)$$
$$= -\tfrac{1}{4}\int \{[H^c(t) - H_{\text{self}}{}^c(t), H(t')], H(t'')\}\epsilon(t-t')\epsilon(t'-t'')dt'dt''.$$

As the calculation shows, this is equivalent to replacing in (1) the function φ by $\varphi + \varphi'$, where φ_i', for instance, is given by

$$\varphi_i' = \sum_{\lambda \neq i} \sum_{j \neq i}^{N} \varphi_\lambda \frac{\langle \lambda j | H^c - H_{\text{self}}{}^c | ij \rangle}{E_i - E_\lambda}.$$

In other words, the scattering due to the ith electron is to be calculated for an electron moving in the field of the nucleus and the mean field of the other electrons. But this is exactly the result of the one-electron theory, if the interaction between electrons is treated as a perturbation.

Thus, we are led to the following conclusion: If there is a non-negligible difference between the results of the one-electron theroy and the positron theory, this difference cannot be attributed to the interaction of the electrons within the atom.

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