the field under adiabatic fast passage conditions. At 300°K. $T_1 \simeq 10^{-3}$ sec., at 77°K. $T_1 \simeq 5 \times 10^{-3}$ sec., at 4.2°K. $T_1 \simeq 4$ min., at 1.2°K. $T_1 \simeq 20$ min. The magnetization was observed in each case at a field of 3200 oersteds; at 4.2 and 1.2°K. the field to which the magnetization was being equilibrated was 8000 oersteds. The concentration of triphenylmethyl was approximately 0.1 mole %.

In view of the remarkably long relaxation times at low temperature estimation of the static susceptibility from measurements of the inductance at a single frequency is not possible unless the frequency is lower than $\sim 10^{-3}$ cycle per second.

WASHINGTON UNIVERSITY
SAINT LOUIS, MISSOURI S. I. WEISSMAN
BELL TELEPHONE LABORATORIES, INC. G. FEHER
MURRAY HILL, NEW JERSEY E. A. GERE

RECEIVED SEPTEMBER 6, 1957

A NOVEL DEUTERIUM ISOTOPE EFFECT IN NUCLEAR RESONANCE SPECTROSCOPY

Sir:

I have observed a relatively large and hitherto unreported deuterium isotope effect in nuclear spin resonance (NSR) spectroscopy. By comparison of the fluorine NSR spectrum of *n*-C_3F_7D with that of *n*-C_3F_7H I have found that the fluorine nuclei in the $-CF_2D$ group are 0.60 ± 0.05 p.p.m. more shielded than those in the $-CF_2H$ group. This difference in shielding value ("chemical shift") should be of theoretical interest, inasmuch as the molecular wave function is not substantially altered. Qualitatively it may be seen that the direction of the shift indicates a *greater electron-donating power for deuterium than for hydrogen.* The atomic volume of deuterium in covalent compounds is well known to be smaller than that of hydrogen,[1,2] a fact which, by elementary particle-in-a-box considerations, requires a greater escaping tendency for the electrons.

The samples of *n*-C_3F_7H and *n*-C_3F_7D were prepared by decarboxylation of *n*-$C_3F_7CO_2Na$ (dried at 110°) in the presence of a slight excess of, respectively, H_2O and D_2O. The reactions were carried out at 200° for 2.5 hours in a stainless steel rocking autoclave; decarboxylation was quantitative, and the trace of C_3F_6 formed was readily removed by low-temperature distillation. The *n*-C_3F_7D was shown by infrared spectroscopy to contain less than 1% of *n*-C_3F_7H; however, one sample upon mere passage through a small P_2O_5–"Ascarite" (NaOH-on-asbestos) tube was found to contain 4 to 5% of the hydride.

The NSR spectra were determined with a Varian Associates V-4300 High Resolution spectrometer operating at 40 megacycles per second. The *n*-C_3F_7H and *n*-C_3F_7D were examined separately and also in mixture, by which means it was shown that the peaks due to the CF_3CF_2- group suffered no displacement larger than 3–5 c.p.s. upon isotopic substitution. Shielding *S*-values in parts-per-million, defined[3] by the equation $S = 10^6 (H_{\text{obs.}} - H_{\text{CFBr}_3})/H_{\text{CFBr}_3}$, are: for the CF_3 group, 94.6 p.p.m.; for the central CF_2 group, 145.4 p.p.m.; for the CF_2H group 150.2 p.p.m.; and for the CF_2D group, 150.8 p.p.m. The positions of the multiplet centers of the latter two groups were measured relative to the central CF_2 group in order that relative errors might be no greater than ± 0.05 p.p.m.; errors in the *S*-values are ± 0.1 to 0.2 p.p.m.

The CF_2H fluorine resonance is a doublet, with $J(CF_2H)$ being 51.5 ± 1 c.p.s., in good agreement with the value 50.2 ± 1 c.p.s. found for the triplet proton resonance. The doublet proton line in *n*-$C_6H_{13}F$ has $J(CH_2F) = 47.4 \pm 1$ c.p.s., and in $CHFBrCH_2Br$ has $J(CHFBr) = 49 \pm 2$ c.p.s.[4] The CF_2D fluorine resonance is an equal triplet, the extreme peaks being separated by 14.5 ± 2 c.p.s. The ratio $J(CF_2H)/2J(CF_2D)$ is thus 3.5 ± 0.5, the expected value being 3.26, the ratio of the nuclear moments of H and D. Both the CF_2H and CF_2D fluorine peaks show further splitting into triplets having *J*-values of 4.0–4.5 c.p.s. For the internal CF_2 group a quadruplet with splitting about 4.7 ± 1 c.p.s. is observed in *n*-C_3F_7H but *only a triplet* with splitting approximately 4.9 c.p.s. in *n*-C_3F_7D; this indicates that $J(HC-CF_2)$ is about the same as $J(F_2C-CF_2)$ in *n*-C_3F_7H, the smaller $J(DC-CF_2)$ not being observed.

Acknowledgment.—I thank Dr. B. F. Murphey for use of the NSR equipment, and Wm. B. Barte and Geo. N. Filipovich for assistance.

CONTRIBUTION NO. 127
CENTRAL RESEARCH DEPARTMENT
MINNESOTA MINING AND MANUFACTURING COMPANY
ST. PAUL 6, MINNESOTA GEORGE VAN DYKE TIERS

RECEIVED AUGUST 22, 1957

---

(1) J. A. Dixon and R. W. Schiessler, THIS JOURNAL, **76**, 2197 (1954).

(2) C. K. Ingold, *et al.*, *J. Chem. Soc.*, 920 (1936); 235 (1946).

(3) G. V. D. Tiers, presented at the Nuclear Resonance Symposium at the 132nd A.C.S. Meeting, New York, 1957, and shortly to be submitted for publication. Virtually all carbon-bonded fluorine atoms yield positive *S*-values (*i.e.*, greater shielding of the fluorine nucleus) by the above equation, and accordingly $CFBr_3$ (b.p. 107°, f.p. below −80°) is suggested as a desirable and convenient primary standard for fluorine NSR spectroscopy.

(4) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953), find $J = 48$ and 53 c.p.s. for H and F in CH_2F_2.