

FIG. 2. Neutron yield from beryllium.

true that a ( $p\alpha, \alpha n$ ) process might contribute a small neutron yield especially where the ( $p, \alpha$ ) reaction is highly exothermic. However, the neutron yield from ( $p\alpha, \alpha n$ ) processes would be small compared to the corresponding ( $pd, dn$ ) reaction because of the higher potential barrier and shorter range of the alpha-particle. From these considerations, it seems unlikely at present that the neutron yield below the threshold would affect the ( $p, n$ ) studies of other elements.

\* Assisted by joint program of the ONR and AEC.

- <sup>1</sup> Sherr, Blair, Kratz, Bailey, and Taschek, *Phys. Rev.* **72**, 662 (1947).
- <sup>2</sup> G. T. Hunter and H. F. Richards, *Phys. Rev.* **76**, 1445 (1949).
- <sup>3</sup> H. T. Richards and R. V. Smith, Report of Chicago Meeting of American Physical Society, 1949 (*Phys. Rev.* **77**, 752 (1950)).
- <sup>4</sup> W. A. Fowler and C. C. Lauritsen, *Phys. Rev.* **76**, 314 (1949).
- <sup>5</sup> Thomas, Ruben, Fowler, and Lauritsen, *Phys. Rev.* **75**, 1612 (1949).

In Fig. 2 the correct cross-section scale is between 0 and  $0.5 \times 10^{-24}$  cm<sup>2</sup>. Private communication.

## Chemical Shifts in the Magnetic Resonance of F<sup>19</sup>

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 August 3, 1950

SEVERAL instances have been reported recently<sup>1-4</sup> of the dependence of nuclear magnetic resonance frequencies on the nature of the chemical compound containing the nuclei. This "chemical effect," or magnetic shielding, has been discussed theoretically<sup>5</sup> but the complexity of the calculations permits their application only to the simplest molecules. We are presently making an experimental survey of the wide variety of existent polyatomic fluorine compounds to determine the influence of structural factors. Initial observations suggest that, in the simpler covalent compounds, the magnetic shielding of an F<sup>19</sup> nucleus chemically bound to another element is related to the position of that element in the periodic table. For elements in a given period

the shielding decreases with increasing atomic number, while for elements in the same group the shielding increases with increasing atomic number. Also, in complex fluorides the shielding depends on the inductive effects of neighboring chemical bonds. Measurements of the influence of temperature on the magnetic shielding in several compounds over a total range of 225° revealed no dependence larger than the experimental error.

Observations were made using conventional equipment,<sup>6</sup> and a permanent magnet with field of 6375 gauss. The magnetic shielding in an "unknown" was determined, at a fixed frequency of 25-54 Mc, by alternately measuring the field biasing current necessary to center the resonance on an oscilloscope, first for the unknown and then for another, reference compound. Only samples were interchanged; the coil containing the samples remained fixed throughout. With field inhomogeneities less than 0.1 gauss, sharp lines in liquids permitted measurements of differences in the resonance field to a probable error of  $\pm 0.01$  gauss or  $\pm 1.5$  p.p.m. of the external field. The temperature dependence was investigated by having the sample in a cryostat and a reference sample outside as parts of a dual system excited by the same oscillator. Resonances were viewed on either a dual oscilloscope or a standard oscilloscope with a manual switch. Samples which are gases at room temperature were observed with a similar arrangement.

In Fig. 1(A) are the results for the simpler fluorides, suggesting the periodicity of the magnetic shielding. Data for the N<sup>14</sup> magnetic resonance<sup>3</sup> in NO<sub>2</sub><sup>-</sup>, CN<sup>-</sup>, and NH<sub>4</sub><sup>+</sup> and also<sup>7</sup> for B<sup>11</sup> in BCl<sub>3</sub>, BBr<sub>3</sub> and B(OCH<sub>3</sub>)<sub>3</sub> follow the same rules. Observations on the P<sup>31</sup> magnetic resonance<sup>7</sup> in PCl<sub>3</sub>, PBr<sub>3</sub>, PI<sub>3</sub>, P<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> follow the period rule but the magnetic shielding in PCl<sub>3</sub> is slightly greater than in PBr<sub>3</sub>, counter to the group trend for F<sup>19</sup>. Figure 1(B) lists the data for various complex fluorides, discussion of which will be given in a later article.

A. Simple Fluorides	B. Complex Fluorides
0.0000 BeF <sub>2</sub> aq.	
	0.0013 HF aq. conc.
	0.0020 CH <sub>2</sub> F <sub>2</sub> liq.
	0.0025 BF <sub>3</sub> etherate
	0.0030 HBF <sub>4</sub>
0.0046 BF <sub>3</sub> liq.	
0.0048 SiF <sub>6</sub> <sup>2-</sup> aq. satd. soln.	
0.0058 F <sup>-</sup> aq. satd. KF	0.0057 1,4-difluorobenzene
	0.0062 1,3-difluorobenzene
	0.0063 1,3,5-trifluorobenzene
	0.0073 1,2,3,4-tetrafluorobenzene
0.0080 CF <sub>4</sub> liq.	
0.0093 SbF <sub>3</sub> aq. satd.	0.0088 CHF <sub>3</sub> liq.
0.0102 PF <sub>6</sub> <sup>-</sup> aq. satd. NH <sub>4</sub> PF <sub>6</sub>	0.0097 CF <sub>3</sub> CO <sub>2</sub> H
	0.0105 mNH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -CF <sub>3</sub>
	0.0106 C <sub>6</sub> H <sub>5</sub> -CF <sub>3</sub> & mCl-C <sub>6</sub> H <sub>4</sub> -CF <sub>3</sub>
	0.0107 CH <sub>3</sub> CF <sub>3</sub> liq. & oCl-C <sub>6</sub> H <sub>4</sub> -CF <sub>3</sub>
	0.0110 CF <sub>3</sub> -CCl <sub>2</sub> -CCl <sub>2</sub> -& mNO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -CF <sub>3</sub>

FIG. 1. Magnetic shielding of the F<sup>19</sup> nucleus. The F<sup>19</sup> resonance in BeF<sub>2</sub> is at the highest external field, thus exhibiting the largest magnetic shielding. Values given are percentage decrease in resonance field relative to BeF<sub>2</sub>. [Except for BF<sub>3</sub> etherate, values in this list for compounds previously reported by Dickinson (reference 2) agree with his values when allowance is made for the difference in external magnetic fields, and a field calibration correction factor (reference 7) of 0.64 is applied to his values. Observations included Co, Cu, Fe, H, (NH<sub>4</sub>), Mg, and Zn salts, which differed among themselves only slightly in excess of experimental error.]

Multiple resonances were found in several fluorocarbons containing fluorine atoms in differing structural positions. 2,3,5-trifluorobenzotrifluoride,  $C_6H_2F_3-CF_3$ , has a double resonance, one with shielding of 0.0115 percent and the other of 0.0047 percent, which in itself is rather broad and may be double. The perfluorolube oil (du Pont) resonance is a triplet with a strong center line at 0.0055 percent and shoulders at 0.0098 and 0.0002 percent. The resonance in  $n-C_3F_7CO_2H$  is a doublet at 0.0053 and 0.0095 percent. Several binary mixtures were examined, including  $CF_3-CCl=CCl_2$  with 1,4-difluorobenzene, 1,3,5-trifluorobenzene, and 1,2,4,5-tetrafluorobenzene. In these mixtures two resonances appeared at field values identical with those of the separate compounds.

The temperature independence of magnetic shielding was observed in perfluorolube oil from 240 to 400°K, in  $BF_3$  etherate from 175 to 375°K, in  $CF_3CO_2H$  from 235 to 370°K, and in a mixture of 1,2,4,5-tetrafluorobenzene and  $CF_3-CCl=CCl_2$  from 225 to 400°K. In the mixture only the separation of the resonance lines was followed.

Measurements are in progress on additional simple fluorides to provide more adequate information for detailed theoretical consideration. Also, we wish to report preliminary observations on the magnetic shielding of the proton resonance which in mineral oil apparently occurs at a field 0.02 to 0.05 gauss higher than in benzene,  $CF_3CO_2H$ ,  $HBF_4$ ,  $CHCl_3$ , concentrated HCl and  $HNO_3$ .

We wish to thank R. E. McClure and S. B. Yochelson for their assistance with the equipment, and R. L. Poynter for his help with a number of measurements. We are also indebted to Dr. G. C. Finger of the State Geological Survey for many of the compounds.

Equipment was provided largely through a Grant-in-Aid from Research Corporation. We also wish to express our appreciation to the Arnold Engineering Company, Marengo, Illinois, for their cooperation in the design and construction of the large permanent magnet essential to the research.

\* Supported in part by the ONR.

<sup>1</sup> W. D. Knight, Phys. Rev. **76**, 1259 (1949). This report, while mainly concerned with resonance shifts attributed to conduction electrons in metals, mentions observed chemical effects in phosphorus compounds.

<sup>2</sup> W. C. Dickinson, Phys. Rev. **77**, 736 (1950).

<sup>3</sup> W. C. Proctor and F. C. Yu, Phys. Rev. **77**, 717 (1950).

<sup>4</sup> J. E. Mack, Rev. Mod. Phys. **22**, 64 (1950), Section IIIC2.

<sup>5</sup> N. F. Ramsey, Phys. Rev. **78**, 699 (1950). E. Hylleraas and S. Skavlem, Phys. Rev. **79**, 117 (1950).

<sup>6</sup> Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

<sup>7</sup> W. C. Dickinson, private communication; we have confirmed his values for  $PCl_3$ ,  $PBr_3$ , and  $H_3PO_4$  and also observed  $PI_3$  and  $P_4$ .

## The $\beta$ -Spectrum of $C^{14}$

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TWO of the most striking contradictions<sup>1</sup> of the predictions of the nuclear shell model are given by the  $\beta$ -spectra of  $C^{14}$  and  $P^{32}$ . Therefore, although both of these spectra have been extensively investigated, the results are of sufficient interest—and in sufficient doubt—to warrant verification. This communication and one to be published shortly will present a careful repetition of some of these investigations.

Three previous determinations<sup>2</sup> of the  $C^{14}$  spectrum have indicated that the shape is allowed. Two other measurements<sup>3</sup> made at about the same time as the former set show at least an indication of a non-linear Fermi plot. Most of these observations had in common the use of an insoluble  $BaCO_3$  source, which made the preparation of thin, uniform sources rather difficult. Feldman and Wu (using a helical focusing spectrometer) had probably the best source, since they used an aggregate thickness of only 0.015 mg/cm<sup>2</sup>, and special precautions were taken to ensure that the particle size in the precipitate was small and uniform. However, Cook *et al.* (using a shaped field spectrometer) varied the source thickness from 0.13 to 0.97 mg/cm<sup>2</sup> and concluded that, since the

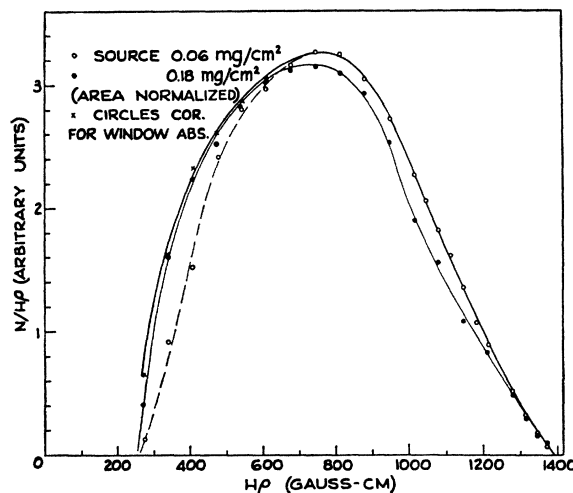


FIG. 1. Momentum distribution for  $C^{14}$ .

shape of the spectrum did not depend strongly on the thickness, their observed curvature of the Fermi plot was a real characteristic, rather than an instrumental distortion. Possibly, however, the variation in the *effective* source thickness was less than they supposed; i.e., that much of the distortion was produced not in the source aggregate but rather in the individual grains of the material. However, their result was essentially corroborated by Angus, Cockroft, and Curran, who used a proportional counter technique. In the present investigation, a double thin lens spectrometer was used, with the resolution set at 2.1 percent. Previous work with this instrument<sup>4</sup> has confirmed the negligible amount of purely instrumental distortions. The source material was  $NaHCO_3$ , converted from the 40 percent enriched  $BaCO_3$  obtained from the Isotopes Division at Oak Ridge. It was felt that the danger of losing a small amount of the activity by exchange with  $CO_2$  in the atmosphere<sup>5</sup> would be compensated by the increased accuracy made possible by the ease of deposition of a soluble source material.

Thin, uniform sources were deposited on 0.01-mg/cm<sup>2</sup> Nylon loaded with Aquadag, and immediately placed in the vacuum system to prevent further loss of activity. Figure 1 shows momentum distributions for two of the sources used (0.06, 0.18 mg/cm<sup>2</sup> approximately) with both curves normalized to the same area. These represent a graphic illustration of the thick source distortion. A window correction (for a 0.05-mg/cm<sup>2</sup> Nylon window) has been applied to the thin source curve. Figure 2 shows the Fermi plots for these two curves. The thicker source apparently results in a straight line to 80 keV where the curve deviates upward. A still thicker source (0.24 mg/cm<sup>2</sup>, not shown in Fig. 2) was straight only for the last 30 keV of the range. A dashed straight line has been drawn through the thin source points; here, however, there is a distinct indication that the upper solid curve (fitted to the experimental points) is convex to the energy axis, in agreement with reference 3. Below this region the curve is linear to 25 keV, while below this point the (corrected) curve rises. Assuming that the window correction is good, this rise probably is due to source thickness. The maximum (in Fig. 1) occurs at 45 keV, agreeing with Angus *et al.*<sup>3</sup> and the end-point energy is  $155 \pm 1$  keV, in agreement with the previous work.

While, therefore, it would seem that the shape is not quite allowed, this result is not very helpful in explaining the  $\beta$ -transition. The empirical classification is second-forbidden and the spin change is unity. Assuming that the transition is really second-forbidden the only possibility (with no parity change) is the Fermi interaction with the correction factor  $A_{-}$  in Konopinski's notation. This factor however was not applied successfully to the observed plot. Primakoff<sup>6</sup> has suggested that the ground state of  $N^{14}$  is an accidental mixture of states in such proportions that the