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Microwave Zeeman Spectrum of Atomic Fluorine*†

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A paramagnetic resonance absorption spectrum has been observed in the products of a radio frequency electrodeless discharge in fluorine gas. The spectrum consists of eight lines, widely spaced over a magnetic field range 2000–6000 gauss, which can be identified with $\Delta M_F=\pm 1$ transitions in the ground $^2P_{\frac{3}{2}}$ level of the F^{19} atom. Analysis of the spectrum yields $-g_J(\mathrm{F};{}^2P_{\frac{3}{2}})/g_p=438.4839\pm 0.0003$, $\Delta\nu(\mathrm{F};{}^2P_{\frac{3}{2}})=4020.01\pm 0.02$ Mc/sec, $-a'''(\mathrm{F};{}^2P)/h=446\pm 10$ Mc/sec, where a''' is the coupling constant of the off-diagonal hyperfine interaction in the ^2P term and g_p is the g factor of protons in a cylindrical sample of mineral oil.

1. INTRODUCTION

THE theory of the linear Zeeman effect for many-electron atoms has recently been extended[1–5] to include relativistic contributions, calculated to order $\alpha^2\mu_0 H$. For simple atomic states this allows the calculation of atomic g factors, in terms of the theoretical magnetic properties of the free electron, to a precision of one part per million or so. Since atomic g factors are susceptible to equally precise measurement by paramagnetic resonance methods, direct tests of the over-all theory are possible.

In certain cases more detailed tests can be made. Measurements of[6] $g_J(\mathrm{H};{}^2S_{\frac{1}{2}})/g_p$, and of[7] g_p/g_l, (g_p the proton g factor) have led to a fairly direct test of the theoretical value of g_s/g_l, the ratio of the electron spin g factor to its orbital g factor. Also a direct measurement of g_s/g_l has been made on the free electron.[8] Both of these experiments are in good accord with theory, but they are not of sufficient accuracy to determine the α^2 term for the electron spin magnetic moment. On the other hand, the measured[9] ratio $g_J(\mathrm{He};{}^3S_1)/g_J(\mathrm{H};{}^2S_{\frac{1}{2}})$, which is insensitive to the precise value of the electron spin magnetic moment, provides a rigorous test of the relativistic Zeeman theory. This experiment is in excellent accord with theory.[10]

For more complex states of many-electron atoms, the confrontation of theory with experiment may be less clear cut, chiefly because of imperfect knowledge of atomic wave functions; a precise g-factor calculation requires knowledge of the radial, as well as the angular, dependence of the wave function. At present, this limits precise comparisons to the ground states of fairly light atoms, where relativistic effects are small and LS coupling prevails. One such atom, O^{16}, has already been thoroughly investigated, both in theory[2–4] and experiment.[11,12] Unfortunately, there is reason to believe that g factors calculated with even the best Hartree-Fock oxygen functions are of considerably poorer quality than the experimental results, and this robs the comparison of theory with experiment of much of its significance.

The self-consistent field method should give better wave functions for fluorine, which is one step nearer than oxygen to a closed-shell electron configuration. Together with the essentially pure LS coupling expected in the ground ^2P term, this may permit a calculation of the fluorine g factors which approaches the desired precision of $\pm 10^{-6}$. Because of the largely orbital magnetism of the ^2P term, it should then be possible to extract a particularly precise value of g_s/g_l for the electron from a measured ratio of the form $g_J(\mathrm{F})/g_J(\mathrm{H})$.

2. ENERGY LEVELS

Observed microwave Zeeman spectra are often complicated by quadratic and higher-order Zeeman effects, as well as by hyperfine structure (hfs). In such cases the linear Zeeman effect, and hence the atomic g factor, must be extricated from the observed spectrum by comparing it with a detailed energy level calculation. In favorable cases the accuracy of this calculation will be checked by the observed spectrum itself; i.e., to the extent that the number of lines exceeds the number of unknown atomic constants used in the calculation, the requirement of internal consistency must be satisfied.

The ground term of the fluorine atom is an inverted ^2P, the metastable $^2P_{\frac{1}{2}}$ level lying about 400 cm^{-1} above the ground $^2P_{\frac{3}{2}}$ level. The only stable isotope of fluorine,

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[1] W. Perl, Phys. Rev. **91**, 852 (1953).

[2] A. Abragam and J. H. Van Vleck, Phys. Rev. **92**, 1448 (1953).

[3] K. Kambe and J. H. Van Vleck, Phys. Rev. **96**, 66 (1954).

[4] F. R. Innes and C. W. Ufford, Phys. Rev. **111**, 194 (1958).

[5] V. W. Hughes, *Recent Research in Molecular Beams* (Academic Press, Inc., New York, 1959), p. 65.

[6] S. H. Koenig, A. G. Prodell, and P. Kusch, Phys. Rev. **88**, 191 (1952); R. Beringer and M. A. Heald, *ibid.* **95**, 1474 (1954); J. S. Geiger, V. W. Hughes, and H. E. Radford, *ibid.* **105**, 183 (1957); B. D. Lambe, Princeton thesis (1959) reports $-g_J/g_p$ (spherical sample of distilled H_2O) $=658.215909\pm 0.000044$.

[7] S. Liebes, Jr. and P. Franken, Phys. Rev. **116**, 633 (1959); J. H. Gardner, *ibid.* **83**, 996 (1951); W. A. Hardy, Bull. Am. Phys. Soc. **4**, 37 (1959) reported value: $-2g_l/g_p(H_2 \text{ gas})=657.4676 \pm 0.0010$.

[8] A. A. Schupp, R. W. Pidd, and H. R. Crane, Phys. Rev. **121**, 1 (1961).

[9] C. Drake, V. W. Hughes, A. Lurio, and J. White, Phys. Rev. **112**, 1627 (1958).

[10] W. Perl and V. W. Hughes, Phys. Rev. **91**, 842 (1953).

[11] E. B. Rawson and R. Beringer, Phys. Rev. **88**, 677 (1952).

[12] H. E. Radford and V. W. Hughes, Phys. Rev. **114**, 1274 (1959).

F^{19}, has a nuclear spin $I=\frac{1}{2}$ and a nuclear magnetic moment close to that of the proton. The magnetic dipole hfs interaction should be strong, due jointly to the large nuclear g factor and, as implied by the doublet splitting, a rather large value of $\langle r^{-3}\rangle$. The observed paramagnetic resonance spectrum has, in fact, a decided intermediate field character, and its interpretation requires energy level solutions in which the hfs interaction is placed on an equal footing with the external magnetic interaction, even in calculating perturbations arising from the presence of the neighboring doublet component. That is, off-diagonal (in J) matrix elements of the hfs interaction, as well as the more usual off-diagonal magnetic interaction matrix elements, must be retained in the calculation. Clendenin[13] has performed this sort of calculation relativistically for the case of an atom with a single valence electron which moves in a central field. Of special interest here is his result for an l doublet with $I=\frac{1}{2}$:

$$W-W_0=-\frac{\Delta W}{2(2j+1)}+g_j\mu_0HM_F \pm\frac{\Delta W}{2}\left(1-\frac{4M_Fx}{2j+1}+x^2+\Gamma\right)^{\frac{1}{2}}+\Lambda, \quad (1)$$

where

$$\Gamma=\frac{4}{\delta}\left\{-M_Fa'''y\pm\left[\frac{M_F{}^2(\Delta W)}{j+\frac{1}{2}}y^2 -a'''[l(l+1)-M_F{}^2]xy-M_F(\Delta W)xy^2\right]\right\},$$

$$\Lambda=\frac{1}{\delta}\left\{-\frac{(k+1)(2l+1)(a''')^2}{4} \pm\{M_Fa'''(\Delta W)y+(\Delta W)^2[l(l+1)-M_F{}^2]y^2\}\right\},$$

$$x=(g_j-g_I)\mu_0H/\Delta W, \quad y=\frac{N\mu_0H}{(2l+1)\Delta W},$$

$$N=\int_0^\infty G_{l+\frac{1}{2}}G_{l-\frac{1}{2}}dr,$$

$$\Delta W=(j+\tfrac{1}{2})[a_j-|k+1|(a''')^2/\delta].$$

This represents an expansion of the doublet energies in powers of $1/\delta$, where δ is the doublet splitting, in which quadratic and higher-order terms are neglected. The quantities a_j and a''' are, respectively, the diagonal and off-diagonal (in j) hfs coupling constants; $a_{l+\frac{1}{2}}$ is commonly written as a', and $a_{l-\frac{1}{2}}$ as a''. The quantities $G_{l+\frac{1}{2}}$ and $G_{l-\frac{1}{2}}$ are large component relativistic radial wavefunctions. Further discussion of (1) is given in reference 13.

The relativistic nature of the solution, which restricts it to the one-electron central field case, enters (1) explicitly only through the quantity N, the nonrelativistic analog of which is the normalization integral of a Schrödinger radial function. Otherwise, the solution is applicable to a general Russell-Saunders L doublet with $I=\frac{1}{2}$. For the rather light fluorine atom, where relativistic effects should be small, we set N equal to unity and, on substituting $l=1$, assume that (1) gives the doublet energies correctly to terms linear in $1/\delta$. Third-order perturbation theory indicates that terms quadratic in $1/\delta$ have a relative size of about 1 part in 10^7. Although not wholly negligible, such contributions are smaller than the experimental uncertainties, and may safely be ignored.

The propriety of this use of a one-electron formula to describe the energy levels of the fluorine atom, with five valence electrons, is discussed further in Sec. 4. In the last analysis the justification is *a posteriori*: Eq. (1) fits the observed spectrum.

3. THE EXPERIMENT

The paramagnetic resonance absorption spectrum of the fluorine atom was sought in the products of a radiofrequency electrodeless discharge in low-pressure fluorine gas. Aside from minor modifications in the gas-handling system made necessary by the corrosive nature of fluorine, the apparatus and conduct of the experiment were those of the earlier work on oxygen.[12]

3.1. Apparatus

The spectrometer employs a TE_{011} cylindrical transmission cavity excited at its resonant frequency of 9100 Mc/sec by a dc-stabilized klystron. A bolometer detector is used, and signal amplification is at 30 cps, the magnetic field modulation frequency. A static magnetic field perpendicular to the cavity axis is provided by an 8-in. electromagnet, powered by submarine storage cells and controlled by a proton resonance feedback circuit.

The absorption sample was a fast moving stream of gas, contained in a quartz tube which could be inserted axially through the microwave cavity. Just upstream of the cavity, the gas tube passed through a radiofrequency coil resonant at 40 Mc/sec which was coupled to a 50-watt power oscillator. With this arrangement, a deep red glow discharge, showing strong optical lines of the neutral fluorine atom, could be excited in the fluorine gas stream at a pressure of a few mm of Hg.[14] Pressure broadening of the microwave absorption lines required, however, that the total pressure in the cavity be somewhat less than 100μ Hg; this pressure differential was maintained by interposing a drilled aluminum plug in the quartz tube.

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[13] W. W. Clendenin, Phys. Rev. 94, 1590 (1954). The formula presented in this paper contains serious typographical errors, which have been corrected in Eq. (1) above. Minor changes in notation have also been made.

[14] No attempt was made to measure fluorine gas pressures accurately; here, as later, pressures were estimated from measured flow rates and calculated pumping speeds.

Fluorine was fed to the discharge through a variable leak (a flattened copper tube) from a steel storage tank which contained electrolytically generated fluorine[15] at a pressure of one atmosphere. Valves were of the bellows type, with Teflon gaskets; connections were made with brass piping. The entire storage system was purged with fluorine gas before the final filling. The low-pressure part of the gas system, past the variable leak, was made of Pyrex glass except in the vulnerable region of the glow discharge, where quartz was used to minimize contamination of the gas stream. Stopcock grease and neoprene O-rings gave satisfactory service at pressures below 1 mm Hg. The vacuum pumps were protected by a charcoal trap in which the fluorine was removed by chemical reaction.

3.2. The Spectrum

A cursory search over the magnetic field range 4000–6000 gauss disclosed six strong, widely separated microwave absorption lines. Their positions were in harmony with the energies (1) provided the values $g_J \simeq \frac{4}{3}$ (the Landé g factor of a $^2P_{\frac{3}{2}}$ level) and $\Delta W/h \simeq 4000$ Mc/sec were used to calculate the expected magnetic field spectrum. The results of this rough calculation are shown in Fig. 1, which is a plot of the magnetic field dependence of the energies (1) for a $^2P_{\frac{3}{2}}$ level. The eight predicted $\Delta M_F = \pm 1$ transitions are indicated by arrows, and the abscissas of the six arrows labelled *a* through *f* are consistent with the six observed lines. The transitions *g* and *h* would be forbidden at strong fields; at the intermediate fields indicated in Fig. 1 their line intensities should be, respectively, about $\frac{1}{8}$ and $\frac{1}{5}$ that of the strong lines. On more careful search at their predicted positions, lines *g* and *h* were in fact found, and with their expected intensities.

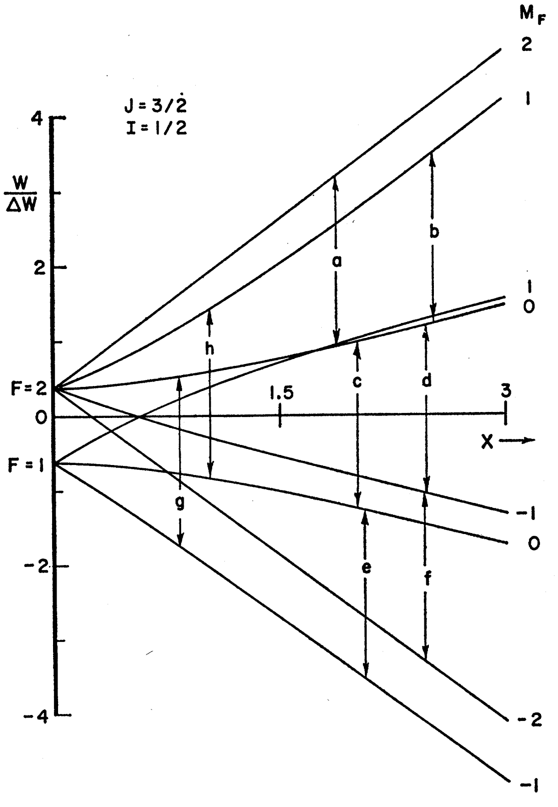

Fig. 1. Energy diagram appropriate to the $^2P_{\frac{3}{2}}$ level of fluorine. Transitions corresponding to observed lines are labelled *a* through *h*. $x = (g_J - g_I)\mu_0 H/\Delta W$.

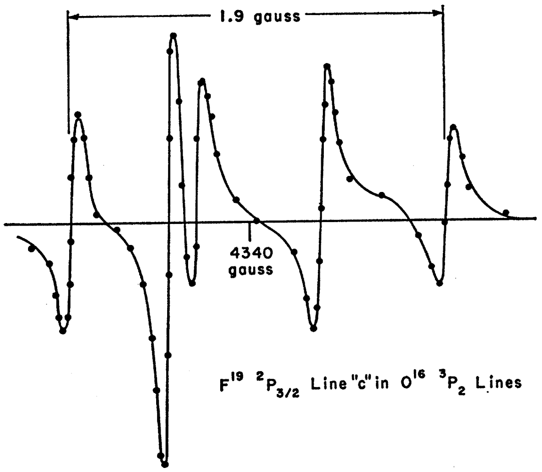

Fig. 2. A fluorine line (second from left) obscured by the oxygen impurity spectrum.

At no time were further absorption lines found which could be assigned to transitions in the metastable $^2P_{\frac{1}{2}}$ level. This is not surprising, since the calculated $^2P_{\frac{1}{2}}$ transition probabilities are some five times smaller than that of the least favorable $^2P_{\frac{3}{2}}$ transition (corresponding to line *g*). Even neglecting population differences, this alone would place any $^2P_{\frac{1}{2}}$ absorption signals well below the spectrometer noise level. Other lines did, however, appear: four are shown in the experimental record of Fig. 2, together with one of the strong fluorine lines which is accidentally coincident at this observing frequency. The spacings and mean g factor of this quartet identifies it positively with the $^3P_2$ state of atomic oxygen. The two lines of the $^3P_1$ oxygen spectrum, which occupy flanking positions 5 gauss to either side of the $^3P_2$ quartet, were also present. From the relative signal intensities of Fig. 2, the concentration of oxygen atoms in the microwave cavity may be estimated as roughly one-half that of fluorine atoms. This should not, however, be taken as a reliable measure of the oxygen impurity in the inlet gas, since the radiofrequency discharge system worked somewhat better for oxygen than for fluorine. Also, fluoridation of the walls of the discharge tube may have released a significant amount of oxygen to the gas stream; in the region

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[15] Sold by Allied Chemical and Dye Corporation in cylinders containing 7 lb of gas at 400 psi.

TABLE I. Energies of the ${}^2P_{\frac{3}{2}}$ transitions $(F,M_F) \leftrightarrow (F', M_F-1)$. $x=(g_J-g_I)\mu_0H/\Delta W$, $z=3a'''/\mu_0H$.

Transition	Line	$h\nu$
$(2,2) \leftrightarrow (1,1)$	a	$g_J\mu_0H+\frac{\Delta W}{2}[1-x+(1-x+x^2)^{\frac{1}{2}}]+\left[1+z+\frac{x-\frac{1}{2}+z(x+1)}{(1-x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$
$(2,1) \leftrightarrow (2,0)$	b	$g_J\mu_0H-\frac{\Delta W}{2}[(1+x^2)^{\frac{1}{2}}-(1-x+x^2)^{\frac{1}{2}}]+\left[1-z\left(1+\frac{2x}{(1+x^2)^{\frac{1}{2}}}\right)+\frac{x-\frac{1}{2}+z(x+1)}{(1-x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$
$(1,1) \leftrightarrow (1,0)$	c	$g_J\mu_0H+\frac{\Delta W}{2}[(1+x^2)^{\frac{1}{2}}-(1-x+x^2)^{\frac{1}{2}}]+\left[1-z\left(1-\frac{2x}{(1+x^2)^{\frac{1}{2}}}\right)-\frac{x-\frac{1}{2}+z(x+1)}{(1-x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$
$(2,0) \leftrightarrow (2,-1)$	d	$g_J\mu_0H-\frac{\Delta W}{2}[(1+x+x^2)^{\frac{1}{2}}-(1+x^2)^{\frac{1}{2}}]-\left[1+z\left(1-\frac{2x}{(1+x^2)^{\frac{1}{2}}}\right)-\frac{x+\frac{1}{2}-z(x-1)}{(1+x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$
$(1,0) \leftrightarrow (1,-1)$	e	$g_J\mu_0H+\frac{\Delta W}{2}[(1+x+x^2)^{\frac{1}{2}}-(1+x^2)^{\frac{1}{2}}]-\left[1+z\left(1+\frac{2x}{(1+x^2)^{\frac{1}{2}}}\right)+\frac{x+\frac{1}{2}-z(x-1)}{(1+x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$
$(2,-1) \leftrightarrow (2,-2)$	f	$g_J\mu_0H-\frac{\Delta W}{2}[1+x-(1+x+x^2)^{\frac{1}{2}}]-\left[1-z+\frac{x+\frac{1}{2}-z(x-1)}{(1+x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$
$(2,0) \leftrightarrow (1,-1)$	g	$g_J\mu_0H+\frac{\Delta W}{2}[(1+x^2)^{\frac{1}{2}}+(1+x+x^2)^{\frac{1}{2}}]-\left[1+z\left(1-\frac{2x}{(1+x^2)^{\frac{1}{2}}}\right)+\frac{x+\frac{1}{2}-z(x-1)}{(1+x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$
$(2,1) \leftrightarrow (1,0)$	h	$g_J\mu_0H+\frac{\Delta W}{2}[(1+x^2)^{\frac{1}{2}}+(1-x+x^2)^{\frac{1}{2}}]+\left[1-z\left(1-\frac{2x}{(1+x^2)^{\frac{1}{2}}}\right)+\frac{x-\frac{1}{2}+z(x+1)}{(1-x+x^2)^{\frac{1}{2}}}\right]\frac{(1/9)(\mu_0H)^2}{\delta}$

of the glow discharge the quartz surface was visibly attacked.

Because of the interference from the oxygen lines, no precise measurements were attempted on line *c*. Line *g* was also neglected because of its low intensity. A typical recording of one of the remaining six lines is shown in Fig. 3. Abscissas represent proton resonance frequencies measured in the same volume of magnetic field as occupied by the fluorine gas sample. The spectrometer displays in a point-by-point way an approximate first derivative of the absorption line. The experimental points have been fitted roughly by the pure derivative of a Lorentz line; deviations from a good fit are of the sort that can be accounted for by the broadening and symmetrical distortion of the line caused by modulation of the magnetic field. The width between peaks of the quasi-derivative line is 60 mgauss. This corresponds, after subtraction of the calculated modulation broadening,[16] to a Lorentz half-width of 35 mgauss (7 parts in 10^6). In this and other recordings of the fluorine lines, pressure effects were the major source of line broadening; at pressures so low that the lines were barely detectable, their widths were found to approach the limiting value set by the magnetic field inhomogeneity over the sample volume: about 15 mgauss.

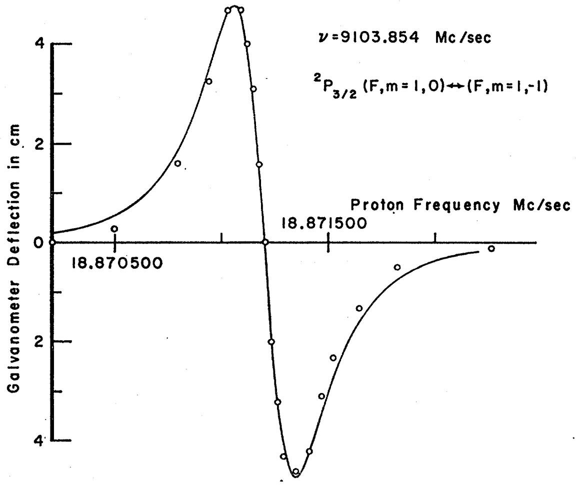

FIG. 3. A fluorine line. Experimental points are fitted roughly with the derivative of a Lorentz absorption line, neglecting field modulation broadening effects.

3.3. Analysis of the Spectrum

It is convenient to expand the root appearing in (1) in powers of $\Gamma/[1-4M_Fx/(2j+1)+x^2]$. We discard all terms of second and higher order in $1/\delta$, and write in Table I the energies of the eight $\Delta M_F=\pm1$ transitions in the ${}^2P_{\frac{3}{2}}$ level.

In each of these eight equations, five constants characteristic of the fluorine ${}^2P$ term appear: $g_J({}^2P_{\frac{3}{2}})$, $\Delta W({}^2P_{\frac{3}{2}})$, a''', g_I, and δ. Of these, only g_I and δ have been measured in other experiments; to deduce g_J from the observed spectrum, one must therefore find simultaneous values of ΔW and a'''. The small relative size of the terms involving $(\mu_0H)^2/\delta$ suggests a trial and error method, in which the coefficients of these terms are evaluated numerically from rough experimental values

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[16] R. Beringer and J. G. Castle, Jr., Phys. Rev. 78, 581 (1950).

of g_J and ΔW, together with trial values of a'''. The transition energy equations for lines a and f may then be solved explicitly for g_J and ΔW in terms of ν, H, and the fundamental constants h and μ_0. The latter are eliminated by expressing H through the proton resonance relation

$$h\nu_p = -g_p\mu_0 H.$$

Then on substituting the measured microwave frequency ν and the proton resonance frequencies ν_p measured at the centers of lines a and f, one may calculate precise values of $\Delta\nu = \Delta W/h$ and the ratio g_J/g_p.

By adjusting a''' (and recalculating $\Delta\nu$ and g_J/g_p with each adjustment), a set of values for the three constants were eventually found which predicted, within experimental error, the measured positions of all eight lines of the fluorine spectrum.

3.4. Results

The numerical results depend somewhat on the values of the doublet splitting δ and the nuclear g-factor ratio g_I/g_p used in the analysis. For δ we have used the value -404.0 cm^{-1} (the negative sign accounts for the inverted fine structure) found from the vacuum ultraviolet spectrum of FI.[17] The tolerable error in this number, within which our results are unaffected, is about 1 cm^{-1}; the number of figures quoted would indicate that the actual uncertainty is somewhat less. The ratio g_I/g_p has been measured in several nuclear magnetic resonance experiments, all of which agree to the necessary precision of 1 part in 10^4. We have used the value $g_I/g_p = 0.940814 \pm 0.000009$ measured in aqueous HF.[18] A molecular beam experiment has shown the sign of the ratio to be positive.[19]

TABLE II. Experimental data on g_J/g_p and $\Delta\nu$.[a]

Data set	$-g_J/g_p$	$\Delta\nu$ (Mc/sec)
1	438.48367	4019.973
2	.48403	19.986
3	.48433	20.021
4	.48380	20.027
5	.48422	20.011
6	.48382	20.032
7	.48415	20.033
8	.48371	20.010
9	.48439	20.014
10	.48365	20.018
11	.48345	20.012
12	.48442	19.996
13	.48384	19.981
14	.48382	20.012
15	.48389	20.000
16	.48341	19.998

[a] Mean value: $-g_J/g_p = 438.48391 \pm 0.00008$; $\Delta\nu = 4020.007 \pm 0.004$ Mc/sec.

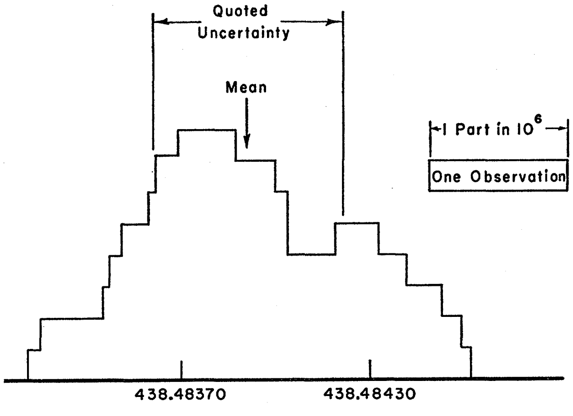

FIG. 4. Histogram of 16 determinations of the fluorine ${}^2P_{\frac{3}{2}}$ g-factor ratio.

Table II contains the results of sixteen observations of each of the lines a and f, obtained from the analysis described in Sec. 3.3. These measurements were all of about the same quality, so the calculated values of $\Delta\nu$ and g_J/g_p have been assigned equal weights in taking mean values. The histograms of Figs. 4 and 5 present the results in graphic form. The total spreads in these distributions can be accounted for by estimated errors in measuring the magnetic field and in tuning the klystron to the cavity resonance frequency. The relative errors in $\Delta\nu$ and g_J/g_p differ by a factor of about six, but this only reflects the relative sizes of magnetic and hyperfine energies at the magnetic field strength used.

Figure 6 shows the consistency of these mean values with other lines of the spectrum. The comparisons are made by calculating the transition frequencies ν_{calc} from the measured proton resonance frequencies ν_p and the experimental values of $\Delta\nu$, g_J/g_p and a''', and then comparing with the measured microwave frequency. The results of several observations of each line are

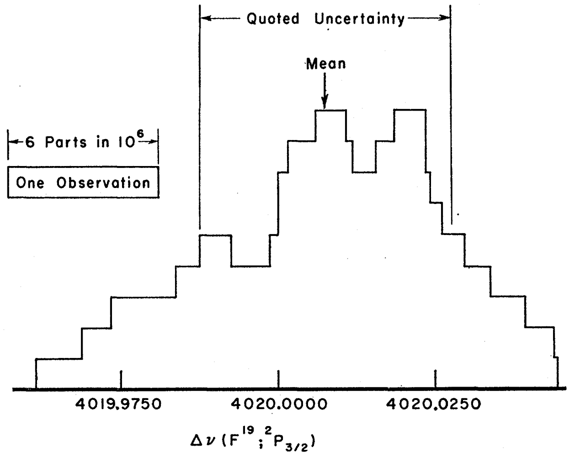

FIG. 5. Histogram of 16 determinations of the fluorine ${}^2P_{\frac{3}{2}}$ hyperfine structure interval.

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[17] B. Edlén, Z. Physik **98**, 445 (1936).

[18] T. Kanda, Y. Masuda, R. Kusaka, Y. Yamagata, and J. Itoh, Phys. Rev. **83**, 1066 (1951).

[19] S. Millman and P. Kusch, Phys. Rev. **60**, 91 (1941).

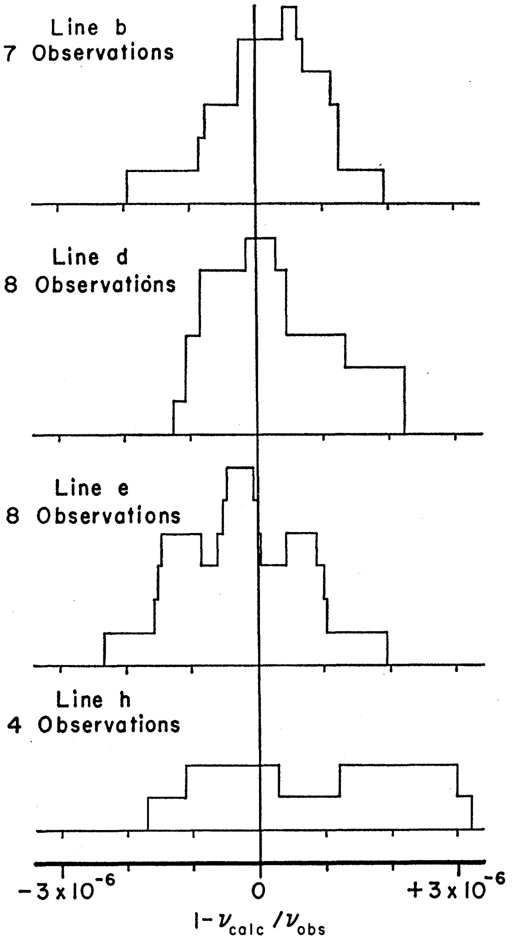

FIG. 6. Histograms illustrating the consistency of the fluorine spectrum with the energy formula (1).

plotted in the form of histograms. The average deviations from perfect fit are a few parts in 10^7 for each of the lines *b*, *d*, and *e*; experimental uncertainties were larger for line *h* because of its low intensity. The appropriate value of a''' was in fact chosen to make the grand average deviation from perfect fit for lines *b*, *d*, and *e* essentially zero; the good fit to line *h* can be regarded as additional confirmation of the results, especially of the value of $\Delta\nu$, to which it is particularly sensitive.

We take as primary experimental results:

$$-g_J(\mathrm{F};{}^2P_{\frac{3}{2}})/g_p=438.4839\pm0.0003,$$
$$\Delta\nu(\mathrm{F};{}^2P_{\frac{3}{2}})=4020.01\pm0.02\ \mathrm{Mc/sec},$$
$$-a'''(\mathrm{F};{}^2P)/h=446\pm10\ \mathrm{Mc/sec},$$

where g_p refers to protons in a cylindrical sample of mineral oil of length-to-diameter ratio 5/1. The uncertainties quoted with g_J/g_p and $\Delta\nu$ are four times the statistical standard errors in the respective means, and they include about 80% of the individual measurements. The uncertainty in a''' is a conservative estimate based on the fitting process described above. On combining the measured values of $\Delta\nu$ and a''', we find the hfs coupling constant for the ${}^2P_{\frac{3}{2}}$ level to be $a'(\mathrm{F};{}^2P_{\frac{3}{2}})/h=2009.99\pm0.01$ Mc/sec.

4. DISCUSSION

To interpret the fluorine spectrum, we have used theoretical energy levels which were originally calculated for a single relativistic *p* electron in a central field. This is not so drastic a misrepresentation as it may seem, for the form of Eq. (1) is determined almost entirely by angular momentum considerations. A careful calculation of the eigenvalues of the nonrelativistic operator

$$\mathcal{H}=\mathcal{H}_0+g_J\mu_0\mathbf{J}\cdot\mathbf{H}+g_I\mu_0\mathbf{I}\cdot(\mathbf{H}+\mathbf{H}_e),\qquad(2)$$

in any pure ${}^2P$ term with $I=\frac{1}{2}$, would reproduce (1) exactly but for the relativistic correction *N*. The symbol $\mathbf{H}_e$ in (2) represents the magnetic field produced at the nucleus by the atomic electrons; the magnetic dipole hfs interaction must be written in this way (instead of the approximate form $a\mathbf{I}\cdot\mathbf{J}$) to preserve matrix elements off-diagonal in *J*.

To the extent, then, that relativistic effects and possible deviations from *LS* coupling can be absorbed by the constants g_J, $\Delta\nu$, and a''', Eq. (1) should be adequate for purposes of deriving these constants from the fluorine spectrum. The excellent internal consistency of the spectrum, shown by Fig. 6, should dispel any remaining doubt on this point. We consider the histograms of Fig. 6 as sufficient evidence that the results of this experiment are subject only to errors of measurement, not of interpretation.

The most troublesome experimental errors are those caused by nonuniformity of the magnetic field over the absorption sample. By repeated careful shimming of the electromagnet, these errors were made as small as possible and were given a more-or-less random distribution. The success of this effort, as judged by the shapes of the histograms in Figs. 4 and 5, was something less than complete. Nevertheless, any errors arising therefrom should be well inside the quoted uncertainties. Errors from imperfect tuning of the klystron to the cavity resonant frequency are probably comparable with magnetic field errors, but it is much easier to give them a random distribution. The value of g_J/g_p is determined mostly by the ratio of a microwave to a proton resonance frequency; both frequencies were measured by comparison with the same laboratory frequency standard consisting of a crystal oscillator and multiplier chains, and so errors in the calibration of the standard are relatively unimportant. The value of $\Delta\nu$ does depend on an absolute frequency measurement, but the required accuracy was easily maintained by checking the laboratory standard occasionally against WWV. Of other conceivable systematic errors, the most serious might be a pressure shift of the resonance lines. A full investigation of pressure effects in fluorine would be difficult; we were content to observe that there was no significant line shift as the gas flow rate was varied within practical limits. The possible existence of a pressure shift too small to be detected in this way is accounted for by the experimental uncertainties quoted in Sec. 3.4.

The measured ratio g_J/g_p is best compared with theory by combining it with the analogous ratio measured in the ground state of atomic hydrogen: $-g_J(\mathrm{H};{}^2S_{\frac{1}{2}})/g_p=658.2167\pm0.0006$. This is the mean result of two paramagnetic resonance measurements[6]—one made by the atomic beam method, the other with the same apparatus used here. Small corrections for shape-dependent diamagnetism of the proton samples are included in this figure.[12] The experimental ratio of g factors is then

$$g_J(\mathrm{F};{}^2P_{\frac{3}{2}})/g_J(\mathrm{H};{}^2S_{\frac{1}{2}})=\tfrac{2}{3}-(497\pm1)\times10^{-6}.$$

The Landé g factors alone would give a theoretical ratio of $\frac{2}{3}$; it is the deviation from this ratio that concerns us here.

The detailed Zeeman theory of light atoms includes four known sources of g-factor perturbations: the electron spin g-factor anomaly, the relativistic Zeeman effect, deviation from pure LS coupling, and the effect of nuclear motion about the center of mass. The last of these can be calculated by the method of Abragam and Van Vleck,[2] based on the earlier work of Phillips[20]; we find the contribution to the fluorine g factor to be less than 10^{-6} and hence negligible. Deviation from LS coupling can alter an ideal g factor through its admixture of states of different L and S, and hence different g factors. In the fluorine ${}^2P$ term, which is the only term of the ground $2p^5$ configuration, deviation from LS coupling can come about only through combined electrostatic and magnetic admixture of non-LS coupled states from excited configurations. Corresponding g-factor contributions appear only on reaching the fourth order of a perturbation calculation and, although important in heavy atoms, decrease rapidly with atomic number[21]; we estimate that the fluorine ${}^2P$ g factors are affected by at most a few parts in 10^7. The relativistic and diamagnetic g-factor corrections are difficult to evaluate for complex atoms, and we have made only an approximate calculation, following the method of Abragam and Van Vleck which neglects exchange effects.[3] The relativistic correction, which involves $\langle T\rangle_{2p}$, the mean kinetic energy of a $2p$ electron, was computed with self-consistent field wavefunctions for fluorine given by Brown[22] and amounts to $\Delta g=-(16/15)(\langle T\rangle_{2p}/mc^2)=-176\times10^{-6}$. The diamagnetic corrections include the Lamb correction and the orbit-orbit correction and in the notation of Abragam and Van Vleck are given by:

$$\Delta g_{\mathrm{Lamb}}=-(2/9)\alpha^2(\langle W\rangle_{2p}-\tfrac{1}{5}\langle V\rangle_{2p})$$

and

$$\Delta g_{\text{orbit-orbit}}=-(2/9)\alpha^2(\langle W\rangle_{2p}+\langle V\rangle_{2p}).$$

The quantities $\langle W\rangle_{2p}$ and $\langle V\rangle_{2p}$ were evaluated using Slater analytic wavefunctions[23] and were found to have the values $\langle W\rangle_{2p}=2.85$ and $\langle V\rangle_{2p}=0.40$ in atomic units. Hence it follows that $\Delta g_{\mathrm{Lamb}}=-33\times10^{-6}$ and $\Delta g_{\text{orbit-orbit}}=-39\times10^{-6}$. When added to the nonrelativistic g factor of a ${}^2P_{\frac{3}{2}}$ state, this gives the theoretical result: $g_J(\mathrm{F};{}^2P_{\frac{3}{2}})=g_s/3+2g_l/3-248\times10^{-6}$. If this is combined with the theoretical hydrogen g factor[24] $g_J(\mathrm{H};{}^2S_{\frac{1}{2}})=g_s(1-\alpha^2/3)$, and the theoretical values[25] $g_s=2(1.0011596)$ and $g_l=1$ are inserted, the result is $g_J(\mathrm{F};{}^2P_{\frac{3}{2}})/g_J(\mathrm{H};{}^2S_{\frac{1}{2}})=\frac{2}{3}-498\times10^{-6}$. This ratio is consistent with the experimental results.

Of major concern in a more careful calculation of relativistic effects would be the quality of the atomic wave functions used. For instance, an accuracy of $\pm10^{-6}$ in the theoretical g factor would require knowledge of $\langle T\rangle_{2p}$ to about $\frac{1}{2}\%$. This makes severe demands of a self-consistent field wave function, and independent experimental tests of the wave function are necessary if one is to put confidence in a g factor calculated out as far as 10^{-6}. Appropriate tests are provided by the observed fine and hyperfine structure since they, like $\langle T\rangle_{2p}$, depend strongly on the behavior of the wave function near the nucleus.

Brown's self-consistent field, although the result of a simplified Hartree-Fock calculation, still predicts the fine structure fairly well: The calculated spin-orbit doublet splitting is 428.9 cm^{-1}, which differs from the observed splitting by 6%. By way of contrast, the corresponding discrepancy for oxygen, using an elaborately calculated Hartree-Fock field, is 10%.[3]

The fluorine hfs is potentially valuable as a test of wave functions because the theory of the hfs may be cross checked among the three measurable coupling constants which, except for negligible relativistic corrections, are[13,26] $a'=-16g_I\mu_0^2\langle r^{-3}\rangle/15$, $a''=5a'$, and $a'''=-5a'/16$, where the mean value of r^{-3} is taken over the $2p$ wave function. The measured ratio a'''/a' actually differs from the theoretical value $-\frac{5}{16}$ by some 30%; obviously, the theory must be refined before the hfs can serve as a test of wave functions.

Such hfs perturbations have been observed in many atoms, and they are generally thought to be caused by configuration mixing. In particular, Fermi and Segrè[27] have shown that a configuration having unpaired s electrons, which have a large magnetic interaction with

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the nucleus, can strongly affect the hfs of other configurations to which it is electrostatically coupled. Koster[28] has made detailed calculations of this effect on the hfs of the ${}^2P$ ground term of gallium, including only the excited configuration which results from promoting a $4s$ electron to a $5s$ orbital. Schwartz[29] has calculated the relative contributions of this "$s \rightarrow s'$ mixing" to the three hfs constants of a general ${}^2L$ term.

With the assumption that $s \rightarrow s'$ mixing in fluorine—i.e., an admixture of $2s2p^5ns$ configurations to the ground $2s^22p^5$—is the major source of hfs perturbation, Schwartz's analysis may be applied to the measured ratio a'''/a' to determine β', the fractional contribution by s electrons to the measured hfs constant a'. For a ${}^2P$ term, and neglecting small relativistic corrections, the theoretical hfs constants a', a'', and a''' must now be multiplied by, respectively, the correction factors $(1+\beta')$, $(1-\beta'/5)$, and $(1-16\beta'/5)$. Thus the theoretical ratio a'''/a' becomes $-5(1-16\beta'/5)/16(1+\beta')$. On equating this to the measured ratio, one finds $\beta'=0.074$; that is, if s electrons alone are responsible for the hfs perturbation, they account for 7.4% of the observed value of a'. Because of the extremely strong coupling of the unpaired $2s$ electron with the nucleus, the actual admixture of $2s2p^5ns$ configurations required is reasonably small: The formulas given by Koster suggest that such configurations need contribute less than 1% to forming the ${}^2P$ states in fluorine.

Through its adjustment of the theoretical $2p^5$ coupling constants, Schwartz's analysis allows one to deduce a consistent value of $\langle r^{-3}\rangle$ from the spectrum. Its value is $6.78a_0^{-3}$, only 1.5% smaller than that given by integration with Brown's wave function. Unfortunately, at least from our point of view, this serves less as a test of the wave function than of the assumption of $s \rightarrow s'$ mixing. A measurement of the ${}^2P_{\frac{1}{2}}$ hfs interval would clarify the situation, since the ratio a''/a' is also predicted by Schwartz's analysis; the value of β' deduced here would require the ratio to be 4.59 instead of the uncorrected value 5.

Configuration mixing has no effect on an atomic g factor comparable to its perturbation of hfs, because the interaction responsible—the electrostatic repulsion between electrons—can mix only states of the same angular momenta; the coupling of the ground term can be altered only through additional spin-dependent interactions in the excited configurations. Corresponding g-factor perturbations do not occur in lower than fourth order, and thus can be negligible while the second-order hfs perturbations are large. There is another way, however, in which excited configurations can enter a ground-state g factor—through the relativistic corrections. Here, as in hfs, the configurations containing unpaired s electrons are probably the worst offenders, since s electrons have large kinetic energies as well as large magnetic interactions with the nucleus. We estimate from the observed hfs perturbation that relativistic g-factor corrections calculated for a pure $2p^5$ configuration may be in error by as much as 1% through neglect of $s \rightarrow s'$ mixing alone.[30]

Note added in proof. For a discussion of the theoretical g value for fluorine refer also to J. S. M. Harvey, R. A. Kamper, and K. R. Lea, Proc. Phys. Soc. (London) **76**, 979 (1960).

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