Hyperfine Structure of the Metastable $(4p)^5(5s)\ ^3P_2$ State of $_{36}Kr^{83}$†

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The hyperfine structure (hfs) of the metastable $(4p)^5(5s)\ ^3P_2$ state of $_{36}Kr^{83}$ ($I=9/2$) has been measured by the atomic beam magnetic resonance method. The zero magnetic field intervals are: $f(11/2 \leftrightarrow 13/2) = 1830.7236(5)$ Mc/sec, $f(9/2 \leftrightarrow 11/2) = 1341.8217(2)$ Mc/sec, $f(7/2 \leftrightarrow 9/2) = 956.5583(2)$ Mc/sec, and $f(5/2 \leftrightarrow 7/2) = 656.0844(30)$ Mc/sec.

The four frequencies (after correction for second-order hyperfine interaction) are expected to be linearly related to only three interaction constants: A', B', and C' (respectively dipole, quadrupole, and octupole). The fit is satisfactory if, and only if, second-order hyperfine interaction is taken into account. The quadrupole and octupole moments of $_{36}Kr^{83}$ are $\Omega = -0.18(6)$ nm b (nuclear magneton barn) and $Q = +0.270(13)$ b. These values include no polarization corrections or corrections for any effects of configuration mixing.

I. INTRODUCTION

THE investigation to be described extends to $_{36}Kr^{83}$ the study of hyperfine interactions in atomic metastable states. Similar studies have been made on $_{10}Ne^{21}$, $_{54}Xe^{129,131}$, $_{80}Hg^{199,201}$, $_{48}Cd^{111,113}$, $_{30}Zn^{67}$, $_{12}Mg^{25}$, and $_{4}Be^{9}$.[1–7] The experimental arrangement is virtually identical to that previously described (Fig. 1).[6]

Kr^{83}, with a spin of 9/2, is the only stable isotope of krypton with nonzero spin. The present experiment was performed with naturally occurring krypton, in which the concentration of Kr^{83} is about 11.5%.

The $^3P_2$ state of krypton belongs to the configuration $(4p)^5(5s)$. (We neglect configuration interaction.) For an isotope with $I \geq 3/2$, the $p_{3/2}$ hole gives dipole, quadrupole, and octupole interactions. The $s_{1/2}$ electron gives a dipole interaction roughly twice as large as that of the $p_{3/2}$ hole. The Zeeman pattern of the four zero-field intervals is shown in Fig. 2; it is appropriate to a $^3P_2$ state, $I=9/2$, $\mu<0$. The sign of μ is taken from previous optical hfs measurements.[8] Previous measurements of the hfs of the $^3P_2$ state of Kr^{83} are displayed in Table I, together with the measurements from the present experiment.

Among atomic beam experiments performed to date which have yielded octupole moments, the present one is unique in that J, as well as I, exceeds $\frac{3}{2}$. For $I=9/2$, $J=2$, there are four hfs frequencies to be measured. However, the highest allowed order of hyperfine interaction is limited by the highest j value of any one electron (3/2 for the p hole); hence, there can only be dipole, quadrupole, and octupole interactions. Any hexadecapole interaction would remain negligibly small even if impurities in the $^3P_2$ state occurred. There are four frequencies governed by only three interaction constants, so that a check on the interpretation of the observed frequencies is available.

From the shell-model assignment for Kr^{83} one can calculate an expected octupole moment according to the theory of Schwartz,[9] which attributes the octupole moment to the single unpaired nucleon. Kr^{83} has 36 protons (even Z) and 47 neutrons, so that it falls 3 below the closed shell of 50 neutrons. These 3 are $1g_{9/2}$ neutrons. The assumption that two are paired gives one $1g_{9/2}$ neutron, consistent with $I=9/2$. Then $l=4$ $=I-1/2$, or $I=l+1/2$. Schwartz gives expressions for $\Omega/\mu_N r^3$ for a single neutron of given I, l, and g_s. We find the theoretical value $\Omega=-0.435$ nm b (nuclear magneton barn). The value is theoretical in the sense of a Schmidt limit. We have taken the free-particle value $g_s=-3.83$.[10]

II. EXPERIMENTAL ARRANGEMENT

A. Vacuum and Gas-Handling Systems

The vacuum apparatus was essentially the same as that described in reference 6. The pumping speed of the source chamber was approximately doubled. This reduces scattering due to the static gas pressure in the system, and it reduces fluctuations in the scattering of the beam caused by irregular operation of the diffusion pumps.[11] The inert gas was passed through powdered titanium packed into a stainless-steel tube and heated to 800°C. The krypton apparently contained an unknown contaminant which poisoned the thoriated tungsten filament in the exciter. The titanium removed

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[1] G. M. Grosof, P. Buck, W. Lichten, and I. I. Rabi, Phys. Rev. Letters **1**, 214 (1958).

[2] M. N. McDermott and W. Lichten, Phys. Rev. **119**, 134 (1960).

[3] W. L. Faust, M. N. McDermott, and W. Lichten, Phys. Rev. **120**, 469 (1960).

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[6] W. L. Faust and M. N. McDermott, Phys. Rev. **123**, 198 (1961).

[7] A closely related experiment upon the $c(1\sigma_g, 1\pi_u)\ ^3\Pi_u$ metastable state of the hydrogen *molecule* has been described by W. Lichten, Phys. Rev. **120**, 848 (1960).

[8] F. Bayer-Helms, Z. Physik **154**, 175 (1959). See also Table I.

[9] C. Schwartz, Phys. Rev. **97**, 380 (1955).

[10] See, however, Sec. V-D of the present paper and Fig. 3 and footnote 22 under that section.

[11] See Sec. IV of the present paper.

the contaminant so that we obtained a higher and more dependable emission current.

B. Rf Equipment

A modified Airborne Instruments cavity oscillator type 124A with a type 2C39A triode was used to excite resonances for all four of the zero-field hfs intervals.

For precise frequency measurements, several discrete frequencies were made available by a Gertsch FM-4 frequency multiplier driven by a quartz crystal controlled frequency standard. A beat frequency (typically 30 Mc/sec), produced between the transition-inducing oscillator signal and one of these discrete frequencies, was measured with a Hewlett-Packard counter type 524C/D or with a Gertsch FM-3 frequency meter.

The shielded π and $\pi-\sigma$ hairpins described in reference 6 were used, as described in Table II.

C. Inhomogeneous Fields and the Homogeneous Field

The deflecting fields, A and B, were operated at approximately 2000 G, corresponding to $x=17$, where $x\equiv g_J\mu_0 H/A$.

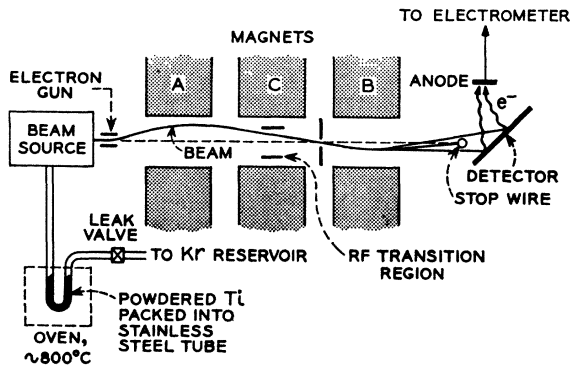

FIG. 1. Schematic diagram of the apparatus. Two trajectories are shown for atoms which undergo transitions, and one for an atom which does not. The rf equipment is not shown.

The homogeneous field C was operated in the range from 0.3 to 1.0 G for the measurement of the interval $f(5/2\leftrightarrow 7/2)$. For the other intervals it was necessary to use fields in the range from 1.5 to 3.0 G in order to resolve thoroughly the Zeeman structure (which has many closely spaced lines; see Fig. 2), given linewidths

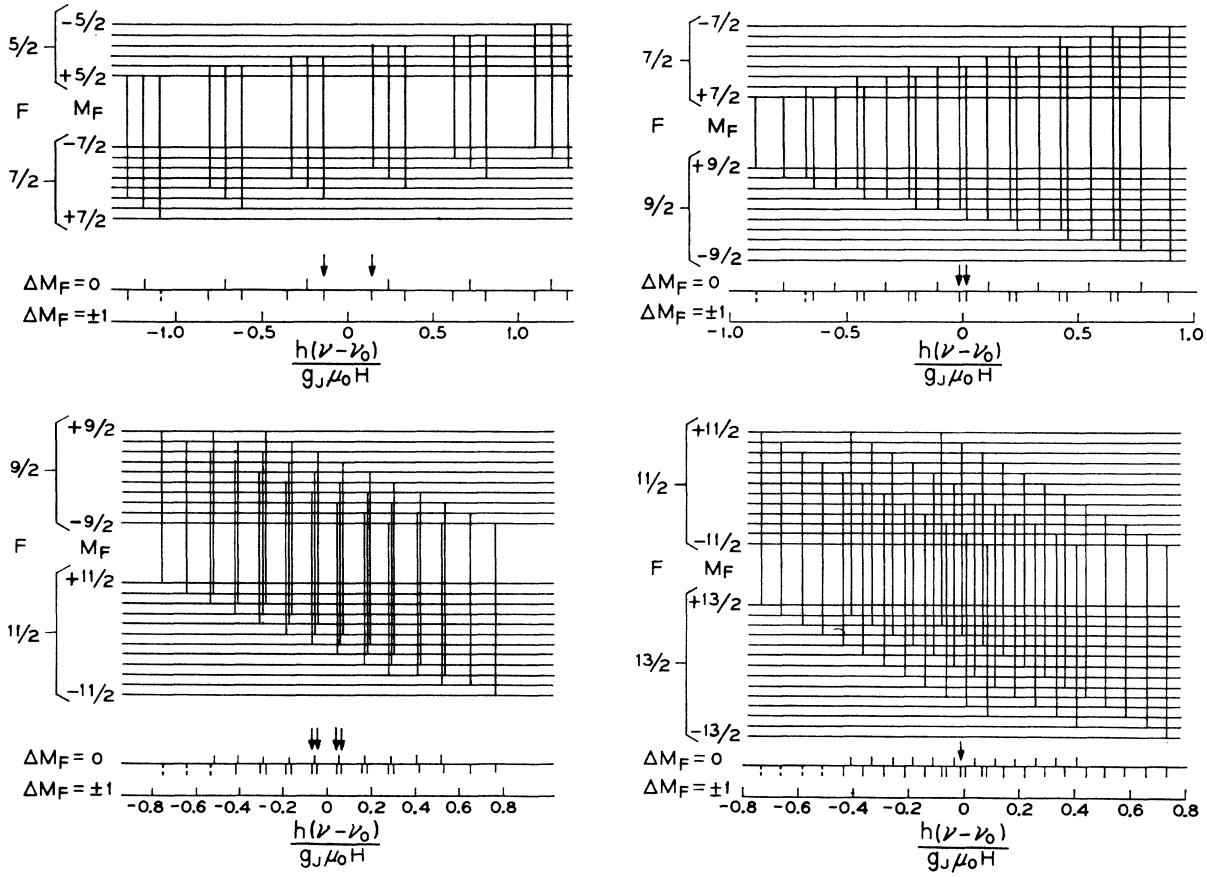

FIG. 2. The Zeeman spectrum, for $I=9/2$, μ_I negative, a $^3P_2$ state. The magnetic splittings of the several F levels are not drawn in proportion to the g_F values. The components used for precise measurements of the zero-field intervals are identified by arrows. Components drawn with broken lines correspond to $\Delta M_J=0$ at high field, so that they are generally not observable.

TABLE I. Measurements on $_{36}Kr^{83}$.

Investigators	Method	I	μ (nm)	Q (barns)	Ω (nm b)
Kopfermann and Wieth-Knudsen[a]	Fabry-Perot		negative		
Korsching[b]	Fabry-Perot, densitometry	9/2 (from intensities)	−1.0	+0.19 +0.26	
Koch and Rasmussen[c]	Fabry-Perot, enriched sample	9/2 (from splitting)			
Brun, Oeser, Staub, and Telschow[d]	Nuclear magnetic resonance		±0.96706(4)		
Rasmussen and Middelboe[e]	Fabry-Perot, separated isotopes	9/2 (confirmed)		+0.22(2)	
Bayer-Helms[f]	Fabry-Perot, enriched sample, densitometry	9/2 (confirmed)	negative	+0.25(17)	
Kuiper and Friedburg[g]	Atomic beam of metastables, discharge source, enriched sample	9/2 (confirmed)		+0.251(5)	
Present work	Atomic beam of metastables, electron gun source, natural abundance	9/2 (confirmed)		+0.270(13)[i]	−0.18(6)

Frequencies for the $^3P_2$ state (Mc/sec)

	$f(5/2\leftrightarrow7/2)$	$f(7/2\leftrightarrow9/2)$	$f(9/2\leftrightarrow11/2)$	$f(11/2\leftrightarrow13/2)$
Kuiper and Friedburg[g]			1341.820(10)	1830.714(10)
Present work	656.0844(30)	956.5583(2)	1341.8217(2)	1830.7236(5)

g_J factor for the $^3P_2$ state of Kr

Kuiper and Friedburg[h]	1.5009(1)	
Present work	1.5011(2)	(two measurements only)

[a] H. Kopfermann and N. Wieth-Knudsen, Z. Physik **85**, 353 (1953).
[b] H. Korsching, Z. Physik **109**, 349 (1938).
[c] J. Koch and E. Rasmussen, Phys. Rev. **76**, 1417 (1949).
[d] E. Brun, J. Oeser, H. H. Staub, and C. G. Telschow Helv. Phys. Acta **27**, 173A (1954).
[e] E. Rasmussen and V. Middelboe, Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd. **30**, No. 13 (1955).
[f] F. Bayer-Helms, Z. Physik **154**, 175 (1959).
[g] H. Friedburg and H. Kuiper, Naturwissenschaften **48**, 69 (1961).
[h] H. Friedburg and H. Kuiper, Naturwissenschaften **18**, 487 (1957).
[i] The disparity between this value of Q and those of references f and g is not due to any disparity between measured quantities (i.e., B); rather it is to be attributed to a different choice of $a_{3/2}$ or of $1/r^3$ in the relation between Q and B (see Sec. V-D).

of about 16 kc/sec. One gauss corresponds to $x\simeq10^{-2}$, so that all observations were made in a field in which the Zeeman effect was nearly linear. Nevertheless, quadratic and third-order[12] corrections were considered. The quadratic corrections were between 0.3 and 10 kc/sec in magnitude. There is a nonzero third-order correction only for the interval $f(11/2\leftrightarrow13/2)$, for the present data. The other intervals were determined exclusively by measurement of symmetric pairs of Zeeman components [two lines of the form $(F, M_F\leftrightarrow F', M_{F'})$ and $(F, -M_F\leftrightarrow F', -M_{F'})$]; and it develops that there is no third-order correction for a zero-field interval determined from the average of such a pair. We expect that all odd-order terms are zero. For the $f(11/2\leftrightarrow13/2)$ interval there was no third-order correction greater than 0.2 kc/sec, considerably less than the stated uncertainty.

[12] A. K. Mann and P. Kusch, Phys. Rev. **77**, 427 (1949), give an expression for the quadratic energy $W^2(F, M)$. It can be shown that the third-order energy is given by $W^3(F, M) = \Sigma\ [\beta_2(F, M; F', M)/W_F - W_{F'}][g_J\mu_0H(g_{F'}/g_J - g_F/g_J)M]$, (sum over $F'=F-1, F+1$) where $\beta_2(F, M; F', M) = |\langle F, M|g_J\mu_0\mathbf{I}\cdot\mathbf{H}|F', M\rangle|^2/(W_F - W_{F'})$. Since $\beta_2(F, M; F', M)$ is a quadratic energy term, it should be possible simply to extract a value for it from Mann and Kusch. However, the expressions of Mann and Kusch for the quadratic energy neglect terms of the order $(g_I\mu_NH)(g_J\mu_0H)/(W_F - W_{F'})$.

III. MEASUREMENT OF RESONANCE FREQUENCIES

The procedure for taking resonance curves was essentially the same as that described in reference 6, for the xenon experiment. Symmetric pairs of Zeeman components with small field-dependence were used in determinations of the zero-field intervals whenever this was practicable, since such a measurement is relatively insensitive to inhomogeneities in the static field C. (See Fig. 2; note the pairs symmetric about the zero-field frequency.) For $f(11/2\leftrightarrow13/2)$ there were no symmetric pairs such that each component gave an acceptable signal level. Instead, we measured a π line with a linear field dependence of $-1/143g_J\mu_0H$ (see Fig. 2), such a small value that there could be no noticeable distortion due to a slightly inhomogeneous field. We measured $g_J\mu_0H$ by observing the $\Delta J=0$, $\Delta M_J=\pm1$ π resonance of the isotopes of even N ($I=0$).

For each of the zero-field intervals, correct identification of the component lines was ensured not only by observing most of the lines, but also by checking that the precisely measured lines had the proper magnetic field dependence.

The signal-to-noise ratio was between 5 to 1 and 10 to 1 for the interval $f(11/2\leftrightarrow13/2)$. For the intervals $f(9/2\leftrightarrow11/2)$ and $f(7/2\leftrightarrow9/2)$ it was 20 to 1 or better.

TABLE II. Results for the hfs intervals from individual runs.

Lines used[a]	Hairpin, π or $\pi-\sigma$	Static field, $g_J\mu_0H/h$ (kc/sec)	Frequency observed (Mc/sec)	Standard deviation of mean (kc/sec)	Number of resonance curves taken
$f(11/2\leftrightarrow13/2)$					
$(11/2, +9/2\leftrightarrow13/2, +7/2), -1/143$	$\pi-\sigma$	3656	1830.7228		1
and $\Delta M_J=\pm1$. (The "number of		4003	1830.7234	0.3	2
resonance curves taken" refers,		4548	1830.7240	0.1	2
for this interval, to the $\Delta F=\pm1$		5016	1830.7238	0.2	3
line only.)					
$f(9/2\leftrightarrow11/2)$					
$(9/2, \pm3/2\leftrightarrow11/2, \pm1/2), \pm9/143$	π	4987	1341.8215	0.12	4
		5446	1341.8217	0.05	6
$(9/2, \mp5/2\leftrightarrow11/2, \mp3/2), \pm23/429$	π	5446	1341.8218	0.03	6
$f(7/2\leftrightarrow9/2)$					
$(7/2, \pm1/2\leftrightarrow9/2, \mp1/2), \pm1/77$	π	5038	956.5584	0.04	6
		3313	956.5581	0.04	6
$f(5/2\leftrightarrow7/2)$					
$(5/2, \mp1/2\leftrightarrow7/2, \mp3/2), \pm1/7$	$\pi-\sigma$	794	656.0869	0.35	4
		1006	656.0852	0.2	6
	π	662	656.0826	0.1	5
		1955	656.0828	0.2	6

[a] Transitions will be specified by the notation $(F, M_F\leftrightarrow F', M_F')$ and by the linear field-dependence factor $(g_FM_F-g_F'M_F')/g_J$.

For the interval $f(5/2\leftrightarrow7/2)$ it was 20 to 1 at best and 4 to 1 at worst. A typical linewidth was 16 kc/sec.

IV. DISCUSSION OF ERRORS

The greatest source of random fluctuations among the various determinations of the zero-field intervals was probably the limited signal-to-noise ratio of the individual points on the resonance curves. We believe that the greatest source of noise was irregular action of the diffusion pumps. The static gas pressure, then, fluctuated; and the scattering of the beam fluctuated in turn. The fluctuation in that portion of the beam which failed to refocus on the stop wire in the absence of rf (about 10%, due to imperfect trajectories) constituted noise. Effects of drift of the homogeneous field were uniformly small because the Zeeman components measured were chosen for very small field-dependence. The existence of such components is a favorable feature of the spectrum, which has the rather large number of fifty components.

The possible sources of systematic error are described in references 2 and 6. The most significant would be expected to be the hairpin errors (Millman and Doppler shifts, discussed in reference 6 for our hairpins) and failure of the symmetric pair method to eliminate completely the effects of inhomogeneities in the static field. The latter failure is possible because the trajectories of the atoms involved in the two transitions of a pair do not take them through exactly the same region of the static field in the hairpin. The effect should be especially small for lines of small field-dependence. It is interesting that the Millman shift is zero for σ lines, and it is equal and opposite for the two components of a π symmetric pair; there is thus no net error from this source in either case in a determination of a zero-field interval from a symmetric pair.

The frequency standard was believed to be accurate to at least one part in 10^8, so that there should be no significant error from that source. However, we must point out that, whereas for the various measured values of the intervals $f(11/2\leftrightarrow13/2)$, $f(9/2\leftrightarrow11/2)$, and $f(7/2\leftrightarrow9/2)$, differences from the mean are random, unrelated to date of observation, magnitude of magnetic field, etc., this is not true of the interval $f(5/2\leftrightarrow7/2)$ (see Table II). The first two runs, taken on the same day, give the mean value 656.0860 Mc/sec. The latter two, taken on another day, give the mean value 656.0827 Mc/sec. The discrepancy of 3.3 kc/sec is rather large compared to the standard deviations belonging to the individual runs. The two runs taken on the first day show a discrepancy of 1.7 kc/sec; this might be taken to imply that the data of that day were at fault. It is possible that there was some erratic behavior of the frequency standard on that day.

V. RESULTS AND DISCUSSION

A. Zero-Field Intervals

The final values for the zero-field intervals are presented in Table I, together with the previous results of Kuiper and Friedburg. The stated uncertainties are not less than three standard deviations.

B. Second-Order Corrections

Although first-order perturbation theory is generally adequate for obtaining the magnetic dipole and electric quadrupole interaction constants from the energy intervals, earlier work[2,6,9] has shown that, in all cases thus far investigated, a second-order treatment results in sizable corrections to the magnetic octupole interaction as derived from the first-order theory. For a state $|^3P_2, F\rangle$, belonging to an sp configuration, an

expression[13] for the part of the second-order hyperfine energy $W_F{}^2$ associated with the states $|{}^3P_1, F\rangle$, $|{}^3P_0, F\rangle$, and $|{}^1P_1, F\rangle$ of that same configuration was given in reference 2 (Hg experiment). The expression for $W_F{}^2$ and the definitions of quantities involved in reference 2 are valid for the general case intermediate between L-S and j-j coupling and for arbitrary I; they apply directly to the $|{}^3P_2, F\rangle$ states of Kr^{83}. The expression does not allow for any effect of configuration interaction upon the second-order corrections. The constants necessary for the evaluation of $W_F{}^2$ are c_1, c_2, a_s, $a_{3/2}$, $b_{3/2}$, ξ, and η. Note that $c_1'=c_2$ and $c_2'=-c_1$.[14]

For krypton, c_1 and c_2 values were calculated in several ways: from the fine structure, from the measured $g|{}^3P_1\rangle=1.242$, and from the measured $g|{}^1P_1\rangle=1.259$.[15] (For the good j-j coupling of krypton, the states are better described as $|s_{1/2}, p_{3/2}, J=1\rangle$ and $|s_{1/2}, p_{1/2}, J=1\rangle$, respectively.) The following values are consistent with the results of each of those calculations: $c_1=+0.9881(5)$, $c_2=+0.154(3)$.

The values of $a_{3/2}$ and a_s were calculated as follows: a'' and a''' were assumed to be governed by $a''/a'=5\theta(1-\delta)_{1/2}(1-\epsilon)_{1/2}$[16] and $a'''/a'=-\frac{5}{16}\xi$. With a'' and a''' thus eliminated in favor of a', the equations of Breit and Wills,[14]

$$4A(|{}^3P_2\rangle)=a_s+3a', \tag{1a}$$

$$4A(|{}^1P_1\rangle)=(2c_2'^2-c_1'^2)a_s+5c_1'^2a'+2c_2'^2a''+4c_1'c_2'\sqrt{2}a''' \tag{1b}$$

can be solved for a' (and a_s) in terms of known quantities. $A(|{}^3P_2\rangle)=-8.15\times10^{-3}$ cm^{-1} and $A(|{}^1P_1\rangle)=-24.66\times10^{-3}$ cm^{-1}.[8] If we replace the equation for $A(|{}^1P_1\rangle)$ by the similar relation for $A(|{}^3P_1\rangle)$ (in which the c quantities become unprimed), we have, from the (poorly) known value of $A(|{}^3P_1\rangle)$, another means to calculate a' and a_s. The former method gives $a'=-6.070\times10^{-3}$ cm^{-1} and the latter gives $a'=-6.55\times10^{-3}$ cm^{-1}. Kopfermann[17] gives a way to calculate a' from the fine structure, and we find from this method $a'=-6.37\times10^{-3}$ cm^{-1}. We have chosen $a'=-6.3(3)\times10^{-3}$ cm^{-1} [or $-189(9)$ Mc/sec]. Then a_s is taken from Eq. (1a) above; we find $a_s=-13.7(9)\times10^{-3}$ cm^{-1} [or $-411(27)$ Mc/sec].

The uncertainties in the values of the constants of this theory which have not yet been discussed are not significant. The values taken are $b_{3/2}=B=-452.1720$ Mc/sec (-15.08×10^{-3} cm^{-1}), $\xi=1.0172$, $\eta=1.048$; $\theta=1.156$, $(1-\delta)_{1/2}=1.000$, $(1-\epsilon)_{1/2}=1.000$. θ, ξ, and η are proportional to the value taken for C''/C' (notation of reference 9); we adopted the value -1.014.

If the second-order energy is calculated with these constants and subtracted from the measured hfs intervals (higher orders being neglected), a set of frequencies are obtained which we call the corrected or first-order frequencies $f^{(1)}(F\leftrightarrow F')$. They are

$$f^{(1)}(11/2\leftrightarrow13/2)=1830.7292(11)\text{ Mc/sec}\quad[\text{correction}+0.0056(10)\text{ Mc/sec}],$$
$$f^{(1)}(9/2\leftrightarrow11/2)=1341.8273(20)\text{ Mc/sec}\quad[\text{correction}+0.0056(20)\text{ Mc/sec}],$$
$$f^{(1)}(7/2\leftrightarrow9/2)=956.5576(22)\text{ Mc/sec}\quad[\text{correction}-0.0007(22)\text{ Mc/sec}],$$
$$f^{(1)}(5/2\leftrightarrow7/2)=656.0739(33)\text{ Mc/sec}\quad[\text{correction}-0.0105(14)\text{ Mc/sec}].$$

C. Interaction Constants

These frequencies are linearly related to a set of interaction constants, each of which is in turn related to a nuclear moment. It is true that for a pure electronic state ($s_{1/2}$, $p_{3/2}$, $J=2$), such as we assume, there can be no interaction at all with a nuclear hexadecapole moment. Nevertheless, for $I>3/2$, $J>3/2$, one can calculate the coefficients for the dependence of the $f^{(1)}$'s upon a fictitious interaction constant, A_4'. (See reference 9 for a discussion of interaction constants in general.) We expect then that the measured $f^{(1)}$'s should be consistent with $A_4'=$ zero. The relations are[18]:

$$f^{(1)}(11/2\leftrightarrow13/2)=-(13/2)A'-(13/24)B'-(13/3)C'-(65/9)A_4', \tag{2a}$$

$$f^{(1)}(9/2\leftrightarrow11/2)=-(11/2)A'+(0)B'+(11/2)C'+(385/18)A_4', \tag{2b}$$

$$f^{(1)}(7/2\leftrightarrow9/2)=-(9/2)A'+(5/16)B'+(13/14)C'-(65/2)A_4', \tag{2c}$$

$$f^{(1)}(5/2\leftrightarrow7/2)=-(7/2)A'+(7/16)B'-(13/2)C'+(455/18)A_4'. \tag{2d}$$

These relations assume that A' is negative, as determined by the previous optical measurements. Solution of the 4×4 Eqs. (2) gives

$$A'=-243.9693(2)\text{ Mc/sec},$$
$$B'=-452.1698(29)\text{ Mc/sec},$$
$$C'=-0.00079(25)\text{ Mc/sec},$$
$$A_4'=+19(50)\times10^{-6}\text{ Mc/sec}.$$

[13] See errata, Sec. VI of the present paper.

[14] Our convention on the definitions of a factors is essentially that of G. Breit and L. A. Wills [Phys. Rev. 44, 470 (1933)], rather than that of Schwartz (reference 9), but with the following identifications: $a_{3/2}\equiv a'$, $a_{1/2}\equiv a''$. The use of this notation invites confusion with Schwartz' notation, but it is used in this paper in order to retain consistency with references 2 and 6. ξ and η are from the notation of Schwartz.

[15] Charlotte E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 11, p. 170.

[16] This relation was given in reference 2 (recall $a_{3/2}\equiv a'$, $a_{1/2}\equiv a''$).

[17] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958), p. 131.

[18] The primes are used, in comformity with past notation (references 2 and 6), to correspond to $f^{(1)}$'s; unprimed interaction constants correspond to f's (*not* corrected for second-order hfs).

The hexadecapole terms in the $f^{(1)}$'s are then [see Eqs. (2) above] -0.14, $+0.41$, -0.62, and $+0.48$ kc/sec; all are small compared to the uncertainties in the $f^{(1)}$'s. If we reject the data of the first run for $f(5/2\leftrightarrow 7/2)$, then $C'=-0.00068(20)$ Mc/sec and $A_4'=+3(45)\times 10^{-6}$ Mc/sec.

The corresponding interaction constants uncorrected for second order are

$$A=-234.96900(9)\text{ Mc/sec},$$
$$B=-452.1572(21)\text{ Mc/sec},$$
$$C=-0.00161(18)\text{ Mc/sec},$$
$$A_4=+49(26)\times 10^{-6}\text{ Mc/sec}.$$

The corrections are significant only for C (and for A_4). The hexadecapole terms in the f's are -0.36, $+1.07$, -1.63, and $+1.26$ kc/sec. If we reject the data of the first run for $f(5/2\leftrightarrow 7/2)$, then $C=-0.00150(10)$ Mc/sec, and $A_4=+34(10)\times 10^{-6}$ Mc/sec. The hexadecapole interaction constant which the second-order corrections themselves introduce, $A_{4\text{ corr}}$, may be calculated directly from the *quadrupole-quadrupole part* of the second-order corrections; we find $A_{4\text{ corr}}=-30\times 10^{-6}$ Mc/sec. This is approximately the value required to cancel A_4, provided we have rejected the first run for $f(5/2\leftrightarrow 7/2)$.

An alternative to the admission of a nonzero A_4' is to find best-fit values of A', B', C' from Eqs. (2) with $A_4'\equiv 0$. They are[19] (using all data here)

$$A'=-243.9693(2)\text{ Mc/sec},$$
$$B'=-452.1697(36)\text{ Mc/sec},$$
$$C'=-0.00080(28)\text{ Mc/sec}.$$

Substitution of these values into Eqs. (2) gives that set of frequencies fitting three constants which best fit the corrected frequencies:

$$f^{(1)}(11/2\leftrightarrow 13/2)=1830.7291(26)\text{ Mc/sec},$$
$$f^{(1)}(9/2\leftrightarrow 11/2)=1341.8268(19)\text{ Mc/sec},$$
$$f^{(1)}(7/2\leftrightarrow 9/2)=\ 956.5581(30)\text{ Mc/sec},$$
$$f^{(1)}(5/2\leftrightarrow 7/2)=\ 656.0736(25)\text{ Mc/sec}.$$

The rms deviation from the measured $f^{(1)}$'s is 0.35 kc/sec. The corresponding rms deviation for the frequencies without second-order correction (fit again by three constants) is 1.1 kc/sec.

Perhaps the following is the best way to investigate the degree of failure of a three-constant fit, in view of the fact that the measured $f^{(1)}$'s are not all equally reliable: With the first three frequencies we solve Eqs. (2a, b, c) (taking $A_4'=0$) for A', B', C'. Then Eq. (2d) gives a value for $f^{(1)}(5/2\leftrightarrow 7/2)$ (the frequency measured least reliably) which can be compared with the measured value, 656.0739(33) Mc/sec. The value predicted from Eq. (2d) is 656.0719(26) Mc/sec, so that the discrepancy is 2.0 kc/sec with an uncertainty of 4.2 kc/sec. A similar treatment of the frequencies without second-order hfs correction gives a discrepancy of 5.7 kc/sec with an uncertainty of 3.0 kc/sec. If the first run for $f(5/2\leftrightarrow 7/2)$ is rejected, the discrepancy is 0.3 ± 3.1 kc/sec for the corrected frequencies and 4.0 ± 1.6 kc/sec for the uncorrected frequencies. From these considerations, or from the earlier observation that $A_4+A_{4\text{ corr}}=A_4'\simeq$zero, we infer that the second-order corrections are necessary for a good fit with three constants. And the A_4 value measured can be taken to represent an observed displacement of energy levels, which is of hexadecapolar symmetry, but which is due to the quadrupole-quadrupole term in the square of the second-order hfs matrix elements. These have the form [$f(F)\times$dipole constants$+g(F)\times$quadrupole constants].

D. Calculation of the Nuclear Octupole and Quadrupole Moments

We calculate the nuclear octupole moment from the relation[20] $\Omega=(7g_I/Z^2)(F_{3/2}/T)(c_{3/2}/a_{3/2})a_0^2\times 10^{24}$ nm b

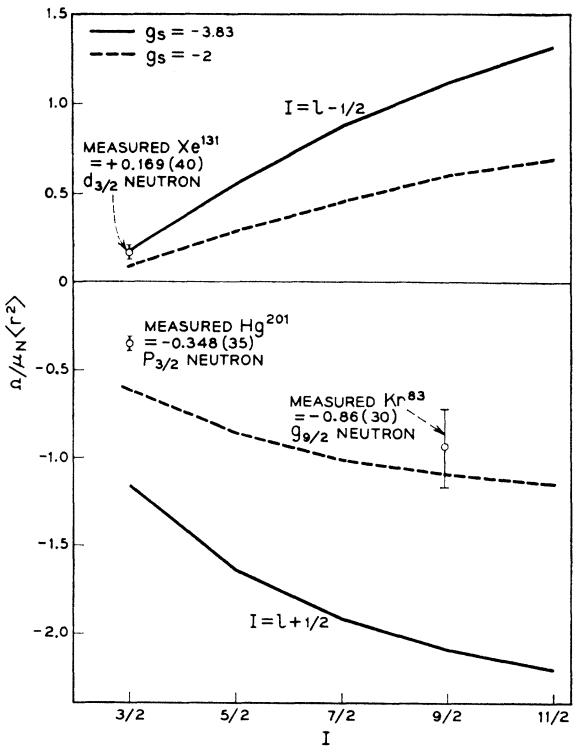

FIG. 3. Schmidt limit diagram for odd-neutron nuclei, according to the theory of Schwartz,[9] who gave the corresponding diagram for odd-proton nuclei. The g_s factors taken are the free-particle value and the Dirac value.

[19] These best-fit values were found by a method which gave equal weighting to each of the measured frequencies, rather than by a more thorough treatment accounting for the unequal probable errors. The intention is merely to show that values of A', B', and C' derived by such a method do not differ appreciably from those obtained by solution of the 4×4.

[20] This expression was given in reference 2 and again in reference 6. It applies for $I\geq 3/2$ with a $p_{3/2}$ electron or hole.

and we obtain $\Omega=-0.18(6)$ nm b. The value $T/F_{3/2}=0.77$ has been obtained from Schwartz.[21] $c_{3/2}=C'=-0.79(28)$ kc/sec.[14] If we reject the data for the first run for $f(5/2\leftrightarrow 7/2)$, then $C'=-0.68(20)$ kc/sec and $\Omega=-0.15(4)$ nm b. The principal source of error in Ω is the error in $c_{3/2}$. In this value of $c_{3/2}$ there has been made no correction for configuration mixing of the $|^3P_2\rangle$ state. The measured Ω lies between the Schmidt limits, and it has the sign anticipated; but it is smaller than expected for $g_s=-3.83$ (see Fig. 3).[21a] Williams[22] has recently given a discussion of the octupole moments of a number of nuclei and of the g factors.

We calculate the nuclear quadrupole moment from the relation[23] $Q=-(8/3)(b_{3/2}/a_{3/2})(F_{3/2}/R)(g_I m/M_p)(\mu_0^2/e^2)\times 10^{24}$ b, and we obtain $Q=+0.270(13)$ b. The value $R/F_{3/2}=1.028$ has been taken from Schwartz.[21] $b_{3/2}=B'=-452$ Mc/sec. The source of error in Q is the error in $a_{3/2}$[14] (see footnote i of Table I). We have included no correction for the effect of polarization of the electron core, as discussed by Sternheimer.[24]

E. g_J Factor for the Krypton Metastable $^3P_2$ State

The ratio $g_J(^3P_2$ krypton$)/g_J(^3P_2$ argon) was measured by observations of the $\Delta M_J=\pm 1$, $\Delta J=0$ transitions (frequency $g_J\mu_0 H$) for the even isotopes of each gas in the same magnetic field. The result of two measurements is $g_J(^3P_2$ krypton$)/g_J(^3P_2$ argon$)=1.00007(10)$. If the known value $g_J(^3P_2$ argon$)=1.500964(8)$ is used,[25] there follows $g_J(^3P_2$ krypton$)=1.5011(2)$; this result is considered to confirm that of Friedburg and Kuiper (see footnote h, Table I), $g_J(^3P_2$ krypton$)=1.5009(1)$.

VI. ERRATA ON PREVIOUS PAPERS

The expression for $W_F{}^2$ in reference 2 should be multiplied by the factor 1/16. The expression relating Q and $b_{3/2}$ in reference 6 should be multiplied by the factor (-1). (See footnote 23 of the present paper.)

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Finally, we wish to thank Professor P. Kusch for advice and for personal encouragement toward the completion of this project.

[21] C. Schwartz, Phys. Rev. **105**, 173 (1957).
[21a] *Note added in proof.* See final paragraph of Introduction.
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[23] A similar expression was given in reference 2 and again in reference 6 (see errata, Sec. VI of the present paper). The expression applies for $I\geq 1$, with a plus sign for a $p_{3/2}$ electron and with a minus sign for a $p_{3/2}$ hole.
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Nonlinear Effects in Spectra of the Iron Group

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As known for the last ten years, calculations made with the linear theory agree poorly with the experimental results for the $3d^6$ configuration of Fe III, compared with the agreement obtained for the $3d^54s$ configuration of that spectrum. It is shown that effects of $3s3d^64s$ on $3s^23d^54s$ satisfy the necessary conditions for linear behavior, consistent with the close agreement obtained in the latter configuration of Fe III. Corresponding effects of $3s3d^7$ on $3s^23d^6$ are not linear. When they are included in the calculation, close agreement is obtained in the $3d^6$ configuration as well; the mean error is reduced from ± 364 cm^{-1} to ± 66 cm^{-1}. An additional parameter, γ, is introduced to define this nonlinear effect. The value of γ obtained from the experimental data by use of least squares is confirmed reasonably well by the value calculated from Watson's self-consistent field results. The parameters of the linear theory are changed considerably when this nonlinear effect is accounted for.

THE present work continues calculations initiated in a recent paper.[1] Introductory material, and most of the references essential to the present work, are contained in A. Excepting the work in A, since the introduction of the linear theory ten years ago,[2–4] the parameters of the theory have been studied purely in

* Deceased.
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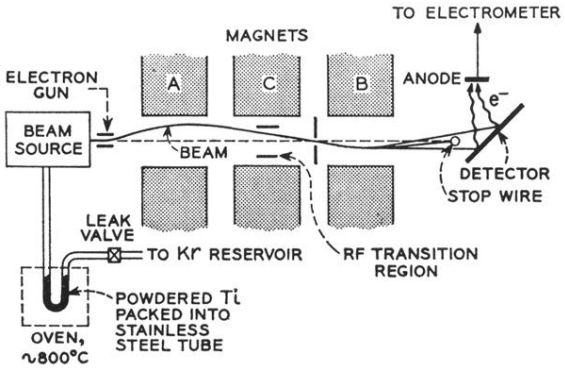

FIG. 1. Schematic diagram of the apparatus. Two trajectories are shown for atoms which undergo transitions, and one for an atom which does not. The rf equipment is not shown.