

Hyperfine Structure of the 9161-cm⁻¹ ²D_{5/2} State of Au¹⁹⁷ and the Nuclear Electric-Quadrupole Moment*

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The hfs of the 5d⁹6s² ²D_{5/2} metastable atomic state at 9161 cm⁻¹ in Au¹⁹⁷ has been studied by the atomic-beam magnetic-resonance technique. The results, in conventional notation, are $g_J=1.20000(2)$, $A=+80.236(3)$ Mc/sec, $B=-1049.781(11)$ Mc/sec, and $C=+0.0004(4)$ Mc/sec. A detailed comparison of these results with those of Blachman and Lurio on the ²D_{3/2} member of the same term indicates that configuration interaction is very small in the ²D term. The nuclear electric-quadrupole moment is calculated to be $Q(\text{Au}^{197})=+0.59\pm 0.12$ b.

I. INTRODUCTION

IN recent years, a number of authors have studied the magnetic hfs of the 3d¹⁰4s ²S_{1/2} atomic ground state of Au in the isotopes $A=190-199$. Detailed information on the nuclear spins, nuclear magnetic-dipole moments, and magnetic-dipole hyperfine-interaction constants has thereby been obtained in the nuclear ground state of these isotopes. In addition, the hfs of Au¹⁹⁷ (the only stable Au isotope) has been studied^{1,2} in the 3d⁹4s² ²D_{3/2} metastable atomic state at 21435 cm⁻¹. By means of the electric-quadrupole hyperfine interaction in this state, the nuclear electric-quadrupole moment has been estimated. The results of the present experiment make possible a comparison of the dipole and quadrupole hyperfine interactions in both members of the 3d⁹4s² ²D term.

II. APPARATUS

The present experiment was performed with a conventional flop-in atomic-beam magnetic-resonance apparatus which has been previously described.³ The Au was evaporated from a graphite oven heated by electron bombardment. The beam was detected with an electron-bombardment universal detector equipped with a mass spectrometer which discriminated strongly against all ions for which $A\neq 197$. In examining rf resonances, the radiofrequency was swept stepwise through the frequency interval of interest. The counts registered in the electron multiplier were fed, after amplification and scaling by a factor of 10, to a multi-channel scaler whose address was advanced in coordination with the frequency advance. Radiofrequency power for inducing the two higher $\Delta F=\pm 1$ hyperfine transitions at 0.7 and 1.0 Gc/sec was obtained from a phase-locked, voltage-tuned magnetron.

The transitions examined were all of the normal type, for which $m_J(A)=-m_J(B)=\pm\frac{1}{2}$, where $m_J(A)$ and

$m_J(B)$ represent the magnetic quantum numbers associated with the electronic angular momentum \mathbf{J} in the strong, inhomogeneous A and B magnets, respectively.

Population of the metastable ²D_{5/2} state at 9161 cm⁻¹ was achieved solely on the basis of the Boltzmann distribution. At about 1500°C where Au has a vapor pressure of 10⁻¹ mm Hg, the Boltzmann factor for the ²D_{5/2} state is 0.00059. Since the transitions examined connect pairs of magnetic substates, the signal intensity in the ²D_{5/2} state is only $0.00059\approx 1/1700$ of that for the ²S_{1/2} ground state, and consequently a counting time of about 15 min was normally required to collect enough data for a reasonable resonance curve.

III. THEORY OF THE EXPERIMENT

The 3d⁹4s² ²D_{5/2} state at 9161 cm⁻¹ in Au is far removed⁴ from all other states. The Hamiltonian which describes the hyperfine interaction in such a state of a free atom is⁵

$$\mathcal{H} = A\mathbf{I}\cdot\mathbf{J} + BQ_{op} + C\Omega_{op} + g_J\mu_0 H(J_z + \gamma I_z),$$

where electron-nuclear 2^l-pole interactions through $l=3$ have been retained. The parameters A , B , and C are, respectively, the magnetic-dipole, electric-quadrupole, and magnetic-octupole hyperfine-interaction constants. Empirically determined values of these parameters may be compared with theoretical expectations. The quantities \mathbf{I} and \mathbf{J} are the operators for the nuclear spin and the total electronic angular momentum, respectively, and I_z and J_z are their projections on the axis of the external magnetic field H . The electric-quadrupole and magnetic-octupole operators are denoted by Q_{op} and Ω_{op} , g_J is the electronic g factor, μ_0 the Bohr magneton, and $\gamma=g_I/g_J$ is the ratio of the nuclear to the electronic g factor.

In order for a transition to be observed in the present apparatus, it must satisfy the refocusing condition $m_J(A)=-m_J(B)=\pm\frac{1}{2}$ as well as the selection rules $\Delta F=0, \pm 1$; $\Delta m_F=0, \pm 1$. Those transitions that satisfy these requirements cannot be specified, in principle,

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¹ W. von Siemens, Ann. Physik **13**, 158 (1953).

² A. G. Blachman and A. Lurio, Bull. Am. Phys. Soc. **8**, 9 (1963).

³ W. J. Childs, L. S. Goodman, and D. von Ehrenstein, Phys. Rev. **132**, 2128 (1963); W. J. Childs and L. S. Goodman, *ibid.* (to be published).

⁴ C. E. Moore, Natl. Bur. Std. (U. S.) Circ. 467, 1958, Vol. III, p. 188.

⁵ N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956), pp. 272 and 277.

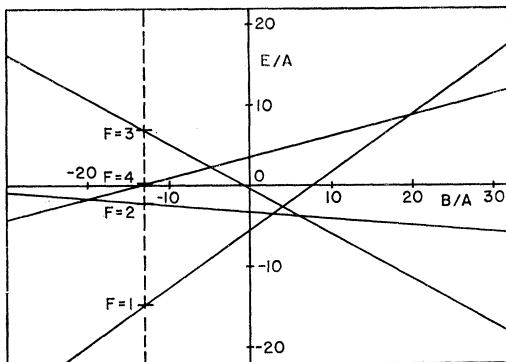


FIG. 1. The zero-field energy levels of the $^2D_{5/2}$ state of Au^{197} plotted against B/A . The plot is for the case $A > 0$ and $C \approx 0$. The "normal" ordering, i.e., that given by the interval rule, occurs for $B/A = 0$. The actual ordering is given by the dashed line, which corresponds to the value $B/A \approx -13$.

without knowledge of the relative magnitudes and signs of the ratios B/A and C/A . The magnetic-octupole interaction is always so much smaller than the magnetic-dipole interaction, however, that the ratio C/A need not be considered for this purpose. The transitions meeting the requirements listed above are uniquely specified (for a given sign of A) by the value of B/A . In Au^{197} , the nuclear spin $I = \frac{3}{2}$ may combine with the total electronic angular momentum $J = \frac{5}{2}$ to form four zero-field hyperfine states characterized by the total angular-momentum quantum numbers $F = 4, 3, 2,$ and 1 . When the octupole interaction is ignored, it follows from the Hamiltonian that at zero field

$$E/A = \mathbf{I} \cdot \mathbf{J} + (B/A)Q_{\text{op}}.$$

In Fig. 1, these values are plotted against B/A for each of the four levels. It is seen that the zero-field level ordering, which (with the "no-cross" rule) determines which transitions are observable, depends only on B/A . The experimental value $B/A = -13.084$ is represented by a dashed line in the figure. It can thus be seen that if $A > 0$ (an assumption justified below), the $F = 4$ level lies below the $F = 3$; but otherwise the ordering is "normal." Figure 2 shows schematically the magnetic-field dependence of all the magnetic substates of these four zero-field levels. Zero field is at the left and (very) strong field at the right. The single-quantum transitions that are expected to be observable are labeled α through ζ ; all have been observed. Several multiple-quantum transitions were also seen.

IV. PROCEDURE

The theoretical transition frequencies for transitions $\alpha, \beta,$ and γ have almost no dependence on the parameters $A, B,$ and C at small values of the external field H , and can thus be calculated simply with fair accuracy. Searches for these transitions at low field quickly revealed them. They were followed up in field, as shown in Table I, through 125 G. A computer program, adapted

TABLE I. Summary of observations on the $^2D_{5/2}$ metastable state of Au^{197} . The observed resonance frequency of the $(2, -1 \leftrightarrow 2, -2)$ transition in the $^2S_{1/2}$ ground state of Au^{197} is given in column 2. Column 1 gives the field intensity deduced from this observation. The last four columns give the data for the $^2D_{5/2}$ state, and the difference between the observed and calculated frequency. The values of $A, B, C,$ and g_J used in the calculation are those reported in this paper.

Calibration data		Transition	ΔF	$\nu(^2D_{5/2})$ (Mc/sec)	$\nu(\text{obs}) - \nu(\text{calc})$ (kc/sec)
H (G)	$\nu(^2S_{1/2})$ (Mc/sec)				
5.000	3.511	β	0	5.999(6)	7
5.000	3.511	γ	0	7.690(6)	0
10.000	7.034	β	0	12.075(5)	3
10.000	7.034	γ	0	15.366(6)	2
10.005	7.037	α	0	10.487(7)	2
15.006	10.573	α	0	15.720(6)	5
20.000	14.116	α	0	20.930(5)	0
20.000	14.116	β	0	24.489(7)	-2
20.000	14.116	γ	0	30.672(5)	1
25.000	17.676	β	0	30.825(10)	-3
25.000	17.676	γ	0	38.300(20)	-7
30.000	21.247	α	0	31.365(4)	3
35.000	24.832	α	0	36.583(7)	7
35.000	24.832	β	0	43.752(7)	4
35.000	24.832	γ	0	53.554(7)	4
40.000	28.428	α	0	41.801(6)	9
45.000	32.037	α	0	47.014(5)	1
50.000	35.659	α	0	52.254(9)	12
50.000	35.659	β	0	63.722(6)	7
50.000	35.659	γ	0	76.372(7)	12
60.000	42.939	α	0	62.741(5)	-1
65.000	46.598	α	0	68.029(6)	9
70.000	50.270	α	0	73.324(9)	0
75.000	53.954	γ	0	114.248(6)	-7
125.000	91.504	α	0	134.951(5)	0
125.000	91.504	β	0	171.615(10)	-1
125.000	91.504	γ	0	188.294(6)	-3
550.000	467.946	α	0	816.370(15)	-10
1.000	0.701	δ	1	518.750(17)	1
1.000	0.701	ϵ	1	711.918(8)	0
1.000	0.701	ζ	1	1000.444(10)	0

from the Berkeley program⁶ HYPERFINE 4-94, was used to provide a best least-squares fit to the data by varying the four parameters $A, B, C,$ and g_J . From these values, the zero-field hyperfine intervals $E(F) - E(F-1)$ were then calculated. The three observable $\Delta F = \pm 1$ transitions $\delta, \epsilon,$ and ζ were then searched for and found at a field of 1 G. The appearance of transition ζ as observed at 1 G is shown in Fig. 3. This resonance is selected for display because it is typical of the results obtained on the 9161-cm^{-1} state; many observations were better and many were not so good.

After the $\Delta F = \pm 1$ transitions were observed, the resonance frequency of transition α was measured at 550 G in an effort to reduce the uncertainty in the value of g_J .

The magnetic-field strength at which each observation was made was determined by observing the $(F, m_F \leftrightarrow F', m_{F'}) = (2, -1 \leftrightarrow 2, -2)$ transition in the $^2S_{1/2}$ atomic ground state of Au^{197} . The value obtained for g_J in the metastable $^2D_{5/2}$ state is therefore depend-

⁶ This program was kindly supplied by Professor H. A. Shugart, University of California, Berkeley, California.

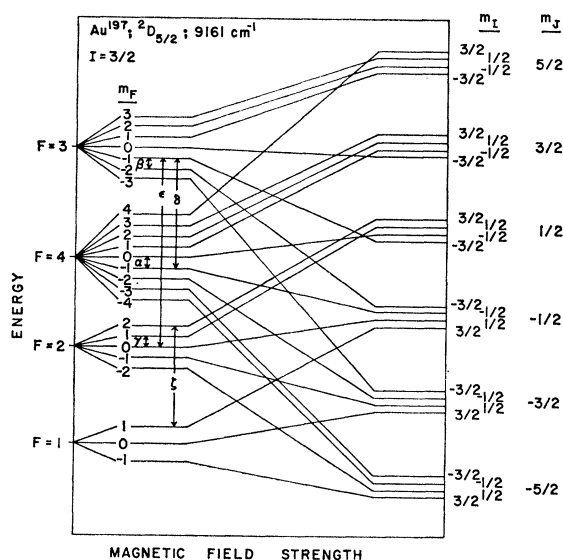


FIG. 2. A schematic plot of the magnetic-field dependence of the hyperfine energy levels of the $^2D_{5/2}$ state of Au^{197} . Those transitions that were observed are indicated.

ent on the value⁷ $g_J(^2S_{1/2}) = 2.0033045(40)$ used in setting the field.

V. RESULTS AND DISCUSSION

The zero-field hyperfine intervals in the $5d^96s^2^2D_{5/2}$ state were obtained from the $\Delta F = \pm 1$ observations in Table I by the computer program. The results are

$$|E(F=4) - E(F=3)| = 518.880 \pm 0.017 \text{ Mc/sec,}$$

$$|E(F=3) - E(F=2)| = 713.101 \pm 0.008 \text{ Mc/sec,}$$

$$|E(F=2) - E(F=1)| = 1000.304 \pm 0.010 \text{ Mc/sec.}$$

These results may be compared with the eigenvalues of the zero-field Hamiltonian to obtain values of the magnetic-dipole, electric-quadrupole, and magnetic-octupole hyperfine-interaction constants A , B , and C , respectively. In practice, the computer program made a simultaneous least-squares fit to all the data of Table I, with A , B , C , and g_J treated as free parameters. (The value of g_J has been measured precisely previously.⁸) The values obtained are

$$A = +80.236 \pm 0.003 \text{ Mc/sec,}$$

$$B = -1049.781 \pm 0.011 \text{ Mc/sec,}$$

$$C = +0.0004 \pm 0.0004 \text{ Mc/sec,}$$

$$g_J = 1.20000 \pm 0.00002.$$

Although B/A is found to be negative and C/A to be

positive, the absolute sign of A was not measured. That $A > 0$ is inferred from the close agreement of the measured $|A|$ with the theoretical estimate of A discussed below.

The Electronic g Factor g_J

The $^2D_{5/2}$ metastable atomic state at 9161 cm^{-1} in $Au I$ arises from the single-hole configuration $5d^96s^2$ with s and l aligned to give the maximum $J = j = l + \frac{1}{2}$. There are no other states of the same J within the configuration to be mixed by the spin-orbit interaction. Because there is no spin-orbit mixing within the configuration, any perturbation of the g factor by the electrostatic interaction with other configurations should also be very small. The Russell-Saunders g value of $6/5$ must be modified by both the Schwinger and the Breit-Margenau (relativistic) corrections which, in this case, very nearly cancel. The Breit-Margenau correction was made by use of relativistic self-consistent Hartree wave functions calculated by Cohen⁹ for $Pt (Z=78)$ and $Hg (Z=80)$. The final theoretical prediction for the g value is 1.20009. The experimental value, which is determined relative to the g value of the ground-state $g_J(Au^{198}, 5d^{10}6s; ^2S_{1/2}) = 2.0033045(40)$,⁷ is found to be $g_J(Au^{197}, 5d^96s^2; ^2D_{5/2}) = 1.20000 \pm 0.00002$. The very slight remaining difference (-0.00009 ± 0.00002) between the experimental and calculated g values of the $^2D_{5/2}$ state is probably due to the diamagnetic correction¹⁰ and possibly also to configuration interaction with configurations in which there is some spin-orbit mixing of the $J = \frac{5}{2}$ states. The remaining discrepancy is very small, and neither effect has been calculated.

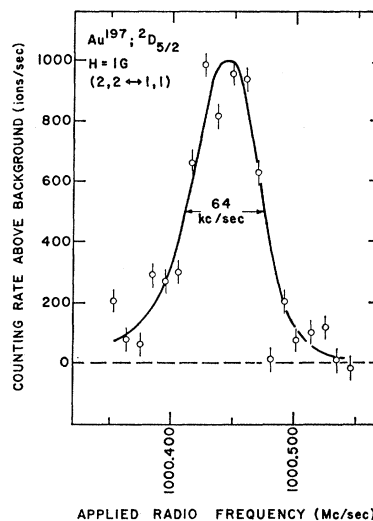


FIG. 3. Transition ξ in the $^2D_{5/2}$ state of Au^{197} , as observed at 1G. The $(2, -1 \leftrightarrow 2, -2)$ transition in the $^2S_{1/2}$ atomic ground state, which is about 1700 times as intense, was used for field calibration.

⁷ P. A. Vanden Bout and V. Ehlers (private communication, 1965). This value, measured for Au^{198} , is presumably correct for Au^{197} .

⁸ S. Penselin, quoted by I. Lindgren, in *Perturbed Angular Correlations*, edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1964), p. 399.

⁹ S. Cohen, University of California Radiation Laboratory Report Nos. UCRL-8389, 1958 and UCRL-8635, 1959 (unpublished).

¹⁰ P. K. Lindgren, University of California Radiation Laboratory Report No. UCRL-9184, 1960 (unpublished).

The Magnetic-Dipole Hyperfine Interaction

The $5d^96s^2$ electron configuration in Au I produces only the 2D term. The hfs of both members (${}^2D_{5/2}$ and ${}^2D_{3/2}$) of the fine-structure doublet have now been measured,² and it is instructive to consider them together. In the absence of configuration interaction, the magnetic-dipole hyperfine-interaction constant $A({}^2D_J)$ for these single-hole states may be expressed¹¹ as

$$A({}^2D_J) = [L(L+1)/J(J+1)] 2\beta\beta_N(\mu_I/I) \\ \times \langle r^{-3}(5d_j) \rangle \times F_r(L, J, Z_i) (1-\delta)(1+\epsilon),$$

where $l=L=2$, $j=J$, β and β_N are the Bohr and nuclear magnetons, respectively, μ_I is the nuclear magnetic dipole moment, and $I=\frac{3}{2}$ is the nuclear spin. The quantity $F_r(d_j, Z_i)$ is a Casimir relativistic correction factor (tabulated by Kopfermann¹²) dependent on L , J , and an effective nuclear charge Z_i which is normally about $Z-10$ or $Z-11$ for d electrons. The terms $(1-\delta)$ and $(1+\epsilon)$ are further corrections for the distribution of charge and magnetic moment within the nuclear volume. They are negligible except for s and $p_{1/2}$ electrons.

The value of $\langle r^{-3}(5d_j) \rangle$ should be nearly independent of j and may be approximated by $\langle r^{-3}(5d) \rangle$ which can be extracted¹³ from the observed fine-structure splitting of the $5d^96s^2$ 2D term. When the result $\langle r^{-3}(5d) \rangle = 11.8 a_0^{-3}$, and the known values⁸ of μ_I and I are used in the expression above, it is predicted¹⁴ that

$$A({}^2D_{5/2})_{\text{calc}} = +77 \text{ Mc/sec},$$

$$A({}^2D_{3/2})_{\text{calc}} = +190 \text{ Mc/sec}.$$

The very close agreement between these predicted values and the measured values²

$$A({}^2D_{5/2})_{\text{obs}} = +80 \text{ Mc/sec},$$

$$A({}^2D_{3/2})_{\text{obs}} = +200 \text{ Mc/sec},$$

is a strong indication that configuration interaction,

¹¹ B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (John Wiley & Sons, Inc., New York, 1965), pp. 130 and 138. Note that the j -dependent part of the numerator of Eq. (5-68) should read $2j-1$, as, for example, in Eq. (30.11) on p. 154 of Ref. 12.

¹² H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958), pp. 445-448.

¹³ R. E. Trees, *Phys. Rev.* **92**, 308 (1953).

¹⁴ In these calculations and in those that follow, the effective nuclear charge Z_i is taken to be $Z-10$, as recommended by Trees (Ref. 13). There are at least two methods of estimating the proper value of Z_i . The first involves requiring the A factor calculated by use of the $\langle r^{-3} \rangle$ value from the fine-structure splitting to be equal to the observed A factor. This is achieved by varying the only remaining parameter Z_i . The average result obtained for the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ states in this way is $Z-13$. The principal disadvantage of this approach, in addition to the assumption of the purity of the state, is that the radial dependence of the spin-orbit interaction $r^{-1}(dU/dr)$ is only approximated by r^{-3} with an effective charge. The other method of obtaining $\langle r^{-3} \rangle$ is to choose that value of Z_i for which the ratios $[B({}^2D_{5/2})/B({}^2D_{3/2})]_{\text{calc}}$ and $[A({}^2D_{5/2})/A({}^2D_{3/2})]_{\text{calc}}$ are equal to the observed values. This method gives $Z-6$. The average of the two methods, $Z_i=Z-9.5$, is in close agreement with the findings of Kopfermann (Ref. 12), Wybourne (Ref. 11), and Trees (Ref. 13).

including core polarization, plays a very minor role in the 2D term. Still more striking evidence of this is found by taking the ratio of the calculated A factors and comparing it with the ratio of the observed ones. The ratio of the calculated values is

$$\left(\frac{A({}^2D_{5/2})}{A({}^2D_{3/2})} \right)_{\text{calc}} = \frac{3 F_r(d_{5/2}, Z_i) \langle r^{-3}(5d_{5/2}) \rangle}{7 F_r(d_{3/2}, Z_i) \langle r^{-3}(5d_{3/2}) \rangle} \\ = 0.4040 \frac{\langle r^{-3}(5d_{5/2}, Z_i) \rangle}{\langle r^{-3}(5d_{3/2}, Z_i) \rangle} \approx 0.4040$$

whereas the ratio of observed values [in which the value $A({}^2D_{3/2}) = +199.842$ Mc/sec is taken from Lurio²] is

$$[A({}^2D_{5/2})/A({}^2D_{3/2})]_{\text{obs}} = 80.236/199.842 = 0.4015.$$

The dependence of the calculated ratio on Z_i is less than 1% over the expected range of values of Z_i . The ability of the theory to predict this ratio to within better than 1% offers very strong evidence that interconfiguration mixing in the 2D term makes a negligible contribution to the A factors.¹⁵ The admixture of configurations with s - d excitations (the Sternheimer effect¹⁶) may, however, be important in the quadrupole interaction.

The very small degree of core polarization (admixture with configurations with s - s' excitations) in the 2D term may be compared with the situation in the $5d^{10}6s^2S_{1/2}$ atomic ground state. The observed magnetic-dipole hyperfine-interaction constant $A({}^2S_{1/2})_{\text{obs}} = +3050$ Mc/sec¹⁷ may be compared with the calculated value $A({}^2S_{1/2})_{\text{calc}} = +3360$ Mc/sec.¹⁸ The difference is probably due to admixture with configurations of the type $ns5d^{10}6s^2$ and $ns5d^{10}6sn's$, where $n < 6$ and $n' > 6$.

The Electric-Quadrupole Hyperfine Interaction

The electric-quadrupole hyperfine-interaction constant B for the state $5d^96s^2$ 2D may be written¹¹

$$B(5d^96s^2 {}^2D_J) = -e^2 Q [(2J-1)/2(J+1)] \\ \times \langle r^{-3}(5d_j) \rangle R_r(L, J, Z_i),$$

where Q is the nuclear electric-quadrupole moment and $R_r(L, J, Z_i)$ is another relativistic correction factor tabulated by Kopfermann.¹² The negative sign arises from the fact that the configuration involves a single hole rather than a single electron. The ratio of the B factors for the two states of the 2D term is thus

$$\left(\frac{B({}^2D_{5/2})}{B({}^2D_{3/2})} \right)_{\text{calc}} = \frac{10 R_r(d_{5/2}, Z_i) \langle r^{-3}(5d_{5/2}) \rangle}{7 R_r(d_{3/2}, Z_i) \langle r^{-3}(5d_{3/2}) \rangle} \\ = 1.185 \frac{\langle r^{-3}(5d_{5/2}) \rangle}{\langle r^{-3}(5d_{3/2}) \rangle} \approx 1.185,$$

¹⁵ B. G. Wybourne, Ref. 11, pp. 149-151.

¹⁶ R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950); **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957).

¹⁷ G. Wessel and H. Lew, *Phys. Rev.* **92**, 641 (1953).

¹⁸ This calculation followed the procedure outlined on pp. 130-131 of Ref. 11.

which may be compared with the observed ratio [in which the value $B(^2D_{3/2}) = -911.075$ Mc/sec is taken from Lurio¹⁹]

$$[B(^2D_{5/2})/B(^2D_{3/2})]_{\text{obs}} = -1049.781/-911.075 = 1.152.$$

The disagreement between the calculated and observed ratios is less than 3%. (In fact, if a slight adjustment is made in the value¹⁴ used for Z_i , the ratios for both dipole and quadrupole interactions can be made to agree to within 0.2%.) The close agreement between the theoretical and experimental values of the ratio of the B factors is to be expected, however, since configuration interaction does not alter the ratio through second order.¹⁵

The Nuclear Electric-Quadrupole Moment

The value of the nuclear electric-quadrupole moment may be deduced (neglecting, for the moment, any Sternheimer correction) from the observed electric-quadrupole hyperfine-interaction constants $B(^2D_J)$ by solving the expression given for B to find

$$Q(^2D_J) = \frac{2(J+1)}{2J-1} \frac{B(^2D_J)}{e^2 R_r(L, J, Z_i)} \frac{1}{\langle r^{-3}(5d_j) \rangle}.$$

The value of $\langle r^{-3}(5d_j) \rangle$ may be taken, as above, from the observed fine-structure splitting. The $\langle r^{-3} \rangle$ values deduced from the fine-structure splitting, however, rely on approximating the actual potential with a hydrogenic field modified by an empirical screening factor. An alternative approach is to determine $\langle r^{-3}(5d_j) \rangle$ from the observed magnetic-dipole hyperfine-interaction

¹⁹ From Lurio, Ref. 2. The value $B(^2D_{3/2}) = -900 \pm 60$ Mc/sec, which W. von Siemens (Ref. 1) measured optically and from which he obtained the first estimate $Q(\text{Au}^{197}) = +0.56 \pm 0.10$ b, is remarkably close to the precise value (-911.075 Mc/sec) obtained by Lurio (Ref. 2). The difference between the Q values deduced by Lurio and by von Siemens is due partly to the latter's less accurate values of A and B for the $^2D_{3/2}$ state, and partly to his choice of $Z_i = Z-19$ in place of the present estimate of $Z-10$. The procedure he used in estimating $Z_i = Z-19$ leads to $Z-13$ when the present (improved) values of A and μ_I are used. See footnote 14 for further details.

constants to be

$$\langle r^{-3}(5d_j) \rangle = \frac{J(J+1)}{L(L+1)} \frac{A(^2D_J)}{2\beta\beta_N(\mu_I/I)} \frac{1}{F_r(L, J, Z_i)}.$$

The values of $\langle r^{-3} \rangle$ determined from the magnetic hyperfine interaction should be reliable for the 2D term since the extreme purity of the levels with respect to both spin-orbit mixing and configuration interaction has already been demonstrated. The value of $\langle r^{-3} \rangle$ obtained from the magnetic hyperfine interaction is

$$\langle r^{-3}(5d_{5/2}) \rangle = \langle r^{-3}(5d_{3/2}) \rangle = 12.3a_0^{-3},$$

which may be compared with the value $11.8 a_0^{-3}$ obtained from the fine-structure splitting.

If the value $\langle r^{-3}(5d_j) \rangle = 12.3a_0^{-3}$ is substituted in the expression above, it is found that

$$Q(^2D_{5/2}) = +0.585b,$$

$$Q(^2D_{3/2}) = +0.598b.$$

The result for the $^2D_{3/2}$ state is that given by Lurio.²

It has been pointed out above that Sternheimer shielding may be present in spite of the failure of the A factors to reveal the presence of any configuration mixing. The assignment of an uncertainty is difficult since it arises entirely from uncertainties in the theory. The uncertainty is probably less than 20%. Thus, the best value is probably

$$Q(\text{Au}^{197}) = +0.592b \pm 20\%,$$

obtained by averaging the above values of $Q(^2D_{5/2})$ and $Q(^2D_{3/2})$.

The Magnetic-Octupole Hyperfine Interaction

The magnetic-octupole interaction seen by Lurio² in the $^2D_{3/2}$ state is extremely small, but definite. As can be seen from the least-squares value of C in the present experiment, only an upper limit can be assigned to the octupole interaction in the $^2D_{5/2}$ state.

ACKNOWLEDGMENT

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