PHYSICAL REVIEW VOLUME 107, NUMBER 3 AUGUST 1, 1957

Radio-Frequency Zeeman Effect in O_2†*

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(Received March 7, 1957)

The molecular-beam magnetic resonance method has been used to study the Zeeman effect of the rotational states of O_2. The ratio of the g-value of the rotational magnetic moment to that of the electron-spin moment was found to be $g_K/g_S=+(6.08\pm0.74)\times10^{-5}$. The ratio of the g-value of the unpaired-electron spin moments in O_2 to that of the free-electron spin moment was found to be $g_S(O_2)/g_s(\text{free})=1-(190\pm13)\times10^{-6}$.

INTRODUCTION

A THEORETICAL treatment of the Zeeman effect of the rotational states of oxygen was first given by Schmid, Budó, and Zemplén[1] in 1936. Recently microwave absorption techniques have been applied to the problem by Beringer and Castle[2] and by Tinkham and Strandberg.[3] The latter authors have extended the theory to keep pace with improvements in experimental accuracy, as has Henry.[4]

The work to be presented here is a molecular-beam magnetic resonance study of the Zeeman effect in oxygen, undertaken to determine the rotational moment of the ground state of O_2, and to examine the total electron spin moment. The O_2 ground state is $^3\Sigma$, with two unpaired electrons giving a total spin of one. Problems of detector sensitivity restricted our observations to the first 4 rotational states, $K=1$, 3, 5, and 7. Each rotational state is split into a triplet by the difference in the electron spin-spin energy for the three configurations of the spin and rotational momenta: parallel, antiparallel, or perpendicular ($J=K+1$, $J=K-1$, $J=K$ where $\mathbf{J}=\mathbf{K}+\mathbf{S}$ is the total angular momentum). Zeeman transitions of the type $\Delta J=\Delta K=0$, $\Delta M_J=\pm1$ were observed both at low fields, where all lines arising within a particular J state are unresolved (i.e., only the linear Zeeman energy is significant), and at higher fields, where the ΔM_J lines are resolved. In part of the experiment a transition in the hyperfine structure of atomic hydrogen was observed along with the oxygen transitions to determine the ratio of the spin g-value of the electron in atomic hydrogen to that of the unpaired electrons in O_2.

THEORY

In order to obtain a theory of the Zeeman effect sufficiently accurate to describe the details of the spectrum observable by the present method, it is necessary to rederive the rotational fine-structure terms along with the Zeeman terms.[5] This is done in the general framework of the lambda-doubling theory of Van Vleck.[6] The calculation is straightforward, and we shall limit our remarks to a discussion of the initial Hamiltonian and to those results of the theory which are pertinent to the experiment.

The customary molecular notation is used in which **J**, **L**, **S**, and **K** are the total, orbital, spin, and end-over-end rotation angular momentum vectors. The projections of these vectors on the molecular axis, z, are Ω for **J**, Λ for **L**, and Σ for **S**. Since **K** has no z component, $\Omega=\Lambda+\Sigma$. The projection of **J** on the external field direction is M_J.

The Hamiltonian for the rotational energy, fine structure, and Zeeman effect for the $^3\Sigma$ ground state of $O^{16}O^{16}$ is a sum of terms as follows:

(1) rotational kinetic energy, $\hbar^2K^2/2\mathfrak{g}$, and spin-orbit interaction, $A(\mathbf{L}\cdot\mathbf{S})$. If we write $\mathbf{K}=\mathbf{J}-\mathbf{L}-\mathbf{S}$, $\hbar^2/2\mathfrak{g}=B$, and expand, these terms give

$$\begin{aligned}\mathcal{H}_1=B(\mathbf{J}^2-J_z^2)+B(\mathbf{L}^2-L_z^2)+B(\mathbf{S}^2-S_z^2)+AL_zS_z\\+(A+2B)(S_xL_x+S_yL_y)-2B(J_xL_x+J_yL_y)\\-2B(J_xS_x+J_yS_y);\end{aligned}$$

(2) spin-spin interaction of the unpaired electrons[7]:

$$\mathcal{H}_2=2\lambda_1(S_z^2-\mathbf{S}^2),$$

where λ_1 is a constant;

(3) spin-nuclear rotation interaction:

$$\mathcal{H}_3=\mu_1\mathbf{S}\cdot\mathbf{K},$$

where μ_1 is a constant;

(4) external field interaction with the orbital electron moment:

$$\mathcal{H}_4=\mu_0\mathbf{L}\cdot\mathbf{H},$$

where μ_0 is the Bohr magneton;

(5) external field interaction with the electron spin:

$$\mathcal{H}_5=g_S\mu_0\mathbf{S}\cdot\mathbf{H},$$

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† This work has been supported in part by the Office of Naval Research.

* Submitted by J. M. Hendrie in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science at Columbia University.

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[1] Schmid, Budó, and Zemplén, Z. Physik **103**, 250 (1936).

[2] R. Beringer and J. G. Castle, Jr., Phys. Rev. **81**, 82 (1951).

[3] M. Tinkham and M. W. P. Strandberg, Phys. Rev. **97**, 937 and 951 (1955).

[4] A. F. Henry, Phys. Rev. **80**, 396 (1950).

[5] The treatment of the Zeeman theory of O_2 by Tinkham and Strandberg, reference 3, is carried to the same order of approximation as the present work, although in a somewhat different form.

[6] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

[7] This form of the spin-spin interaction differs from the usual form, $\lambda_1(3S_z^2-\mathbf{S}^2)$ only in a diagonal constant. M. Mizushima and R. M. Hill, Phys. Rev. **93**, 745 (1954), also have used the form $2\lambda_1(S_z^2-\mathbf{S}^2)$.

where g_S is the g-value for the total electron spin in the pertinent molecular state[8];

(6) external field interaction with the nuclear rotation:

$$\mathcal{H}_6 = g_K{}^n \mu_0 \mathbf{K}\cdot\mathbf{H},$$

where $g_K{}^n$ is the g-value for that part of the rotational moment due to the rotational motion of the two oxygen nuclei.

Of the terms in $\mathcal{H}_1$, the first, $B(\mathbf{J}^2-J_z{}^2)$, has the expectation value $B[J(J+1)-\Omega^2]$, which will be recognized as the rotational energy of the symmetric top.[9] The expectation value of $B(\mathbf{L}^2-L_z{}^2)$ is a constant for a given electronic state, and is generally added to the electronic energy. The terms $B(\mathbf{S}^2-S_z{}^2)+AL_zS_z$, with the diagonal value $B[S(S+1)-\Sigma^2]+A\Lambda\Sigma$, give the principal part of the spin multiplet splitting within a given electronic state of the molecule. The AL_zS_z is of course, the magnetic interaction of the electron spin and orbital moments. For the $^3\Sigma$ state of O_2, $\Lambda=0$, and the $A\Lambda\Sigma$ term is not present. The remaining parts of $\mathcal{H}_1$ are off-diagonal, appearing as perturbations of the principle terms above, and giving rise to the fine structure effects of rotational distortion of the spin multiplet spacing, lambda doubling, and rho tripling of the rotational levels. The Hamiltonian $\mathcal{H}_1$ was used in a discussion of $^3\Pi$ and $^3\Sigma$ state fine structures by Hebb,[10] whose work was later expanded by Schlapp[11] to obtain accurate expressions for the oxygen fine structure.

The terms $\mathcal{H}_2$ and $\mathcal{H}_3$ were treated by Kramers.[12] The spin-spin term leads to the largest effect in the tripling of the oxygen rotational levels. Development of the theory shows that the off-diagonal elements of $\mathcal{H}_1$ contribute terms to the fine structure of precisely the same form as $\mathcal{H}_2$ and $\mathcal{H}_3$, and that it is impossible to separate these terms by an analysis of the field-free spectrum. The Zeeman energies of interaction of the external field with the magnetic moments associated with $\mathbf{S}$, and the nuclear rotation part of $\mathbf{K}$, $\mathcal{H}_5$ and $\mathcal{H}_6$, are straightforward. The interaction of the electron orbital moment with the external field, $\mathcal{H}_4$, leads to two separate terms in the energy expressions. The first is the usual electronic contribution to the rotational moment arising from a component of $\mathbf{L}$ developed along $\mathbf{K}$ by rotational distortion of the electron orbital motions.[13] This contribution has a g-value, $g_K{}^e$, which is added to that of the nuclear rotation, $g_K{}^n$, to obtain the g-value of the total rotational moment of the molecule, g_K. The second term involves a component of $\mathbf{L}$ arising from perturbation of the orbital electron motions by the spin magnetic fields, with g-value g_p. Both g_K and g_p are much smaller than g_S. Not included in the terms above are any effects of centrifugal distortion.

Matrix elements of the Hamiltonian are calculated in the Hund's case "a" representation, and the resulting matrix diagonalized to a sufficient accuracy to match the experiment.

It is necessary to carry the energy expressions only to terms quadratic in the field at the comparatively low fields at which the measurements were made. The rotational triplet energies are of the form

$$\begin{aligned} W_{J=K,\,K\mp1} = {} & (W^0)_{J=K,\,K\mp1} \\ & + (W^1)_{J=K,\,K\mp1} + (W^2)_{J=K,\,K\mp1}. \end{aligned} \qquad (1)$$

The field-free energies are

$$\begin{aligned} (W^0)_{J=K} &= B'x-2\lambda-\mu, \\ (W^0)_{J=K\mp1} &= B'(x+1)-3\lambda-\tfrac{3}{2}\mu\pm[S(J)]^{\frac{1}{2}}, \end{aligned} \qquad (2a)$$

and the linear Zeeman energies are

$$(W^1)_{J=K} = [g_S+(x-1)g_K]\mu_0 HM_J/x,$$

$$\begin{aligned} (W^1)_{J=K\mp1} = \Bigg\{ & g_S\left[\frac{1}{2x}\pm\frac{T(J)}{2x[S(J)]^{\frac{1}{2}}}\right] \\ & +g_K\left[\frac{2x-1}{2x}\mp\frac{T(J)}{2x[S(J)]^{\frac{1}{2}}}\right] \\ & \pm g_p\left[\frac{2(B'-\mu/2)}{[S(J)]^{\frac{1}{2}}}\right]\Bigg\}\mu_0 HM_J, \end{aligned} \qquad (2b)$$

where the various parameters are defined as follows, consistent with the notation of Hebb[10]:

$$x = J(J+1),$$

$$T(J) = \lambda-[4J(J+1)+1](B'-\tfrac{1}{2}\mu),$$

$$S(J) = \lambda^2-2\lambda(B'-\tfrac{1}{2}\mu)+[4J(J+1)+1](B'-\tfrac{1}{2}\mu)^2,$$

[with the special case $[S(0)]^{\frac{1}{2}}=-\lambda+(B'-\frac{1}{2}\mu)$]

$$B' = B-8\textstyle\sum_\Pi[|(\Pi|BL_y|\Sigma)|^2/(E_\Pi-E_\Sigma)],$$

$$\lambda = \lambda_1+\textstyle\sum_\Pi[|(\Pi|AL_y|\Sigma)|^2/(E_\Pi-E_\Sigma)],$$

$$\mu = \mu_1+8\,\mathrm{Re}\textstyle\sum_\Pi[(\Sigma|BL_y|\Pi)(\Pi|AL_y|\Sigma)/(E_\Pi-E_\Sigma)],$$

$$\begin{aligned} g_K = g_K{}^n+g_K{}^e = g_K{}^n & \\ +8\,\mathrm{Re}\textstyle\sum_\Pi & [(\Sigma|BL_y|\Pi)(\Pi|L_y|\Sigma)/(E_\Pi-E_\Sigma)], \end{aligned}$$

$$g_p = 4\,\mathrm{Re}\textstyle\sum_\Pi[(\Sigma|AL_y|\Pi)(\Pi|L_y|\Sigma)/(E_\Pi-E_\Sigma)].$$

The sums are taken over all permutations of the electronic quantum numbers which yield nondegenerate molecular Π states. The parameters λ, μ, and B' show the mixing of Π states in the Σ ground state (manifested as off-diagonal matrix elements of $\mathcal{H}_1$ in the spin-spin and spin-nuclear rotation interactions, and in the rotational kinetic energy term). The energies E_Σ

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[8] The convention throughout this paper is to take the g-value of an angular momentum vector as *minus* the ratio of the moment in Bohr magnetons to the angular momentum in units of $\hbar$. Thus g_s (free electron) $=+2.00229$.

[9] F. Reiche and H. Rademacher, Z. Physik **39**, 444 (1926); **41**, 453 (1927) and R. de L. Kronig and I. I. Rabi, Nature **118**, 805 (1926); Phys. Rev. **29**, 262 (1927).

[10] M. H. Hebb, Phys. Rev. **49**, 610 (1936).

[11] R. Schlapp, Phys. Rev. **51**, 342 (1937).

[12] H. A. Kramers, Z. Physik **53**, 422 and 429 (1929).

[13] J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. **85**, 24 (1952).

and E_{Π} are the electronic energies of the Σ state and the various Π states of the molecule. The quadratic Zeeman energies are given by

$$\begin{aligned}
(W^2)_{J=K}={}&[(g_S-g_K)\mu_0H]^2\left\{\frac{J[(J+1)^2-M_J^2]}{2(J+1)^2(2J+1)(2J+3)}\left[\frac{2J+3+\dfrac{T(J+1)}{[S(J+1)]^{\frac{1}{2}}}}{(W^0)_{J=K}-(W^0)_{J+1,\,K=J+2}}\right.\right.\\
&+\left.\frac{\left[2J+3-\dfrac{T(J+1)}{[S(J+1)]^{\frac{1}{2}}}\right]\left(1-\dfrac{g_p}{g_S}\right)+\left[1-(2J+3)\dfrac{\lambda-(B'-\frac{1}{2}\mu)}{[S(J+1)]^{\frac{1}{2}}}\right]\dfrac{g_p}{g_S}}{(W^0)_{J=K}-(W^0)_{J+1,\,K=J}}\right]+\frac{(J+1)(J^2-M_J^2)}{2J^2(2J-1)(2J+1)}\\
&\left.\times\left[\frac{2J-1+\dfrac{T(J-1)}{[S(J-1)]^{\frac{1}{2}}}}{(W^0)_{J=K}-(W^0)_{J-1,\,K=J-2}}+\frac{\left[2J-1-\dfrac{T(J-1)}{[S(J-1)]^{\frac{1}{2}}}\right]\left(1-\dfrac{g_p}{g_S}\right)-\left[1-(2J-1)\dfrac{\lambda-(B'-\frac{1}{2}\mu)}{[S(J-1)]^{\frac{1}{2}}}\right]\dfrac{g_p}{g_S}}{(W^0)_{J=K}-(W^0)_{J-1,\,K=J}}\right]\right\},
\end{aligned}$$

$$\begin{aligned}
(W^2)_{J=K\mp1}={}&[(g_S-g_K)\mu_0H]^2\left\{\frac{(J+2)[(J+1)^2-M_J^2]}{2(J+1)^2(2J+1)(2J+3)}\right.\\
&\times\left[\frac{\left[2J+1\mp\dfrac{T(J)}{[S(J)]^{\frac{1}{2}}}\right]\left(1-\dfrac{g_p}{g_S}\right)-\left[1\mp\dfrac{(2J+1)[\lambda-(B'-\frac{1}{2}\mu)]}{[S(J)]^{\frac{1}{2}}}\right]\dfrac{g_p}{g_S}}{(W^0)_{J=K\mp1}-(W^0)_{J+1,\,K=J+1}}\right]+\frac{(J-1)(J^2-M_J^2)}{2J^2(2J-1)(2J+1)}\\
&\left.\times\left[\frac{\left[2J+1\pm\dfrac{T(J)}{[S(J)]^{\frac{1}{2}}}\right]\left(1-\dfrac{g_p}{g_S}\right)+\left[1\pm(2J+1)\dfrac{\lambda-(B'-\frac{1}{2}\mu)}{[S(J)]^{\frac{1}{2}}}\right]\dfrac{g_p}{g_S}}{(W^0)_{J=K\mp1}-(W^0)_{J-1,\,K=J-1}}\right]\right\}\\
&\pm(g_S\mu_0HM_J)^2\left[\frac{4x+1-[T(J)]^2/S(J)}{8x^2[S(J)]^{\frac{1}{2}}}\right]\mp g_Sg_p(\mu_0HM_J)^2\left[\frac{1+T(J)(B'-\frac{1}{2}\mu)/S(J)}{x[S(J)]^{\frac{1}{2}}}\right]\\
&\mp g_Sg_K(\mu_0HM_J)^2\frac{8x-1}{4x^2[S(J)]^{\frac{1}{2}}}.\qquad(2\text{c})
\end{aligned}$$

The expressions (2c) include all terms of the form g_S^2, and those terms of the form g_Sg_p and g_Sg_K which contribute as much as one part in 5000 of the quadratic splitting. All terms of the form g_p^2, g_K^2, and g_pg_K have been dropped in (2c) since they are negligible at the fields used.

The mean frequency in cycles per second, $f(K,J)$, of the set of transitions of the type $\Delta M_J=\pm1$ arising in a particular state K, J is given by

$$\begin{aligned}
&f(K,J)\\
&\quad=(\mu_0H/h)[a(K,J)g_S+b(K,J)g_K+c(K,J)g_p].\qquad(3)
\end{aligned}$$

The quantities $a(K,J)$, $b(K,J)$, and $c(K,J)$, which are tabulated in Table I, are the bracket terms which appear as coefficients of g_S, g_K, and g_p in (2b). They have been evaluated for the observed transitions by use of the experimental values of λ, B', and μ given by Miller and Townes.[14] The bracketed term in (3) is of course, the total g-value, $g_J(K,J)$ of the state K, J. In much of the experiment it was convenient to measure the ratio of two transition frequencies rather than determine the magnetic field for each transition. The set (3) may be put in a useful form for comparison to the data by dividing by $f(1,1)$. The resulting ratio equations, to a sufficient accuracy, are of the form

$$\begin{aligned}
&f(K,J)/f(1,1)=2a(K,J)\\
&\quad+2[b(K,J)-a(K,J)]g_K/g_S+2c(K,J)g_p/g_S.\qquad(4)
\end{aligned}$$

The quadratic separations of a set of transitions of the type $\Delta M_J=\pm1$ of a state K, J may be conveniently expressed in terms of the mean frequency, $f(K,J)$, of the set:

$$\delta(K,J)=d(K,J)[f(K,J)]^2.\qquad(5)$$

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[14] S. L. Miller and C. H. Townes, Phys. Rev. 90, 537 (1953).

Here $\delta(K,J)$ is the separation between adjacent transitions of the type $\Delta M_J = \pm 1$ and the quantities $d(K,J)$ are calculated from (2c) and are tabulated in Table II. The total quadratic width of a set of $\Delta M_J = \pm 1$ transitions of a state K, J will be $(2J-1)\delta(K,J)$.

APPARATUS

The apparatus was a modification of one previously described.[15] For the present experiments it was necessary to change only the source, the radio-frequency components, and the C field.

The oxygen source was a small chamber attached to the bottom of a cold trap. The oxygen gas passed from a storage manifold at atmospheric pressure to the chamber through a needle valve and a 0.32-cm diameter nickel tube which was soldered to the cold trap for a considerable length to insure thermal equilibrium of the gas at the trap temperature. The chamber pressure ranged from 1 to 4 mm Hg, and the exit slit was 0.0033 cm wide and 0.325 cm high. In planning the experiment it had been thought that the source temperature should be kept low, in order to obtain as large a population as possible in the low-rotational states. The lowest temperature easily attainable was 77°K, by use of liquid nitrogen. In fact, tests at 77°K and at room temperature, 300°K, showed that the available beam intensity in the low-rotational states of interest was about the same at both temperatures. At the lower temperature the scattering of the beam was so severe that the total beam intensity was reduced to the point where the advantage gained from increased population of the low-rotational states was lost entirely. Even with no advantage in beam intensity, however, it was worthwhile to make observations at the lower temperature because of the reduced line-width and increased deflecting power of the magnets, and all observations on oxygen were made with the source at 77°K.

In the experiment to determine g_S in O_2, it was necessary to make a rapid interchange of beams of hydrogen atoms and oxygen molecules. The hydrogen atom source was a Wood's discharge tube which remained stationary in an appropriate position to supply the hydrogen beam, while the oxygen source chamber was in this case attached by a heavy copper bar to a cold trap which could be rotated under vacuum by means of a ground joint. A rotation of the trap interposed the oxygen source between the discharge tube and the fore slit to give an oxygen beam.

TABLE I. Numerical coefficients for the linear Zeeman frequencies of Eq. (3). The quantities $a(K,J)$, $b(K,J)$ and $c(K,J)$ are the bracket terms which appear as coefficients of g_S, g_K, and g_p in Eq. (2b), except for states of the type $J=K-1$, where the signs of $a(K,J)$ and $b(K,J)$ are reversed to give positive frequencies in Eq. (3).

K,J	$a(K,J)$	$b(K,J)$	$c(K,J)$
1,1	0.500000	0.500000	0
1,2	0.483996	0.516004	−0.407048
3,2	0.317328	−1.317328	−0.407048
3,4	0.247357	0.752643	−0.223409
5,4	0.197357	−1.197357	−0.223409
5,6	0.165797	0.834203	−0.154238
7,6	0.141987	−1.141987	−0.154238
7,8	0.124612	0.875388	−0.117822

TABLE II. Quadratic separations of oxygen states. The tabulated values of $\delta(K,J)$ refer to a magnetic field strength in which the $f(1,1)$ frequency is 164.1 Mc/sec.

State K,J	$d(K,J)$ (10^{-11} sec)	$\delta(K,J)$ calculated (kc/sec)	$\delta(K,J)$ observed (kc/sec)
1,1	5.6646	1525	1513±2
1,2	1.272	321	313±2
3,2	1.917	209	214
3,4	1.500	99	
5,4	1.854	78	
5,6	1.536	45	
7,6	1.820	40	
7,8	1.550	26	

The oscillating magnetic field necessary to induce the various transitions was supplied by radio-frequency currents in a copper loop with a length of 1 cm along the beam. Studies of the residual fields of the deflecting magnets indicated that a longer transition region would result in substantial line-broadening due to field inhomogeneity. In most of the measurements of the O_2 Zeeman spectrum at low fields, the copper loop was enclosed in a grounded shield. The rf current at frequencies below 50 Mc/sec was supplied by a General Radio Type 805 C oscillator, and at frequencies above 100 Mc/sec by a General Radio Type 757 oscillator. In both cases the frequency could be varied continuously and was stable over the time required to observe the transition maximum, and to measure the frequency at the maximum.

A uniform magnetic field perpendicular to the beam was produced in the C region by a set of Helmholtz coils. The narrow width of the vacuum envelope in the C region made it possible to put the Helmholtz coils outside the apparatus, and to have them of sufficient size to give a uniform field over the 1-cm transition region. The coils had a mean diameter of 25 cm, and at a current of 75 amp drawn from storage cells produced a field of 120 gauss. The current in the Helmholtz coil was monitored continuously by a potentiometer connected across a standard resistance in series with the coils. A mercury rheostat was manually adjusted to maintain a constant current.

LINE WIDTHS AND INTENSITIES

The line widths are attributable to four effects: the natural width, rf power-broadening, quadratic splitting, and field inhomogeneity. The natural width arises from the uncertainty in the transition energy due to the finite time a particle spends in the transition region and is given by $\Delta f \Delta t \approx 1$. For oxygen molecules at

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[15] A. G. Prodell and P. Kusch, Phys. Rev. 88, 184 (1952).

77°K, $\Delta f = 20$ kc/sec, and for hydrogen atoms at 300°K, $\Delta f = 222$ kc/sec.

Power-broadening results from use of a stronger oscillating field than is necessary to obtain the maximum transition probability. A common technique in beams experiments to eliminate power-broadening is to observe transition intensity as a function of rf power, and to set the rf power at the lowest level for which a small increase in power gives no increase in transition intensity. This procedure was followed for the hydrogen line, which had a signal-to-noise ratio of about 45 (12-cm intensity against 2 to 3 mm of noise on the galvanometer scale). The oxygen lines were of smaller intensity, however, with signal-to-noise ratios of 2 to 4, and it was difficult to judge the proper level of the rf power. In these circumstances there was a strong tendency of the observer to adjust the rf power to a level higher than was necessary. Further, in some of the observations on unresolved lines at low field the rf power was set well above the optimum level for $\Delta M_J = \pm 1$ transitions in order to develop multiple transitions, $\Delta M_J = \pm 2, \pm 3$. The advantage of such a procedure was in the proportionately larger moment changes associated with the multiple transitions and in the improved deflecting power of the apparatus which resulted. It should be pointed out that for unresolved lines the transition statistics are not improved by developing the multiple transitions. At high magnetic fields, however, where all lines are resolved, the intensity of an individual $\Delta M_J = \pm 1$ transition may be increased by superposition of a multiple-quantum transition. A profile of a resolved line at 120 gauss, previously published,[16] shows the $\Delta M_J = \pm 1$ transitions with widths of about 50 kc/sec at a power level sufficient to develop the double- and triple-quantum transitions.

In the low-field measurements on oxygen, where unresolved envelopes of transitions were observed, the quadratic splitting of the component transitions caused a broadening of the envelope. To minimize the effect, observations were made at fields sufficiently low so that the quadratic splitting was considerably less than the natural line-width. The "high" and "low" fields referred to in this paper are defined by the quadratic splitting: a "high" field being one at which the component transitions of the $f(1,1)$ and $f(1,2)$ lines are resolved, and a "low" field being one for which the quadratic splitting contributes little to the width of the unresolved envelope. All of the "high"-field measurements refer to a field of 120 gauss, while typical "low" fields were 10 to 16 gauss.

The field-inhomogeneity broadening was reduced to a small part of the total line-width by use of a short (1-cm) transition region.

The intensity of a given transition depends upon the rf transition probability, the efficiency of detection of the apparatus, and the populations of the states involved in the transition. In general the rf transition probability increases with increasing rf power to a maximum of 0.72 and then falls to a constant value of 0.50 for a further increase in rf power.[17] For the hydrogen line, the rf power was set in such a way as to give a transition probability near the maximum. For the oxygen lines, the rf power was generally on the high side, for reasons discussed earlier, and the transition probability closer to 0.50.

The Pirani gauge detector depends on the thermal conductivity of a gas at low pressure for its action. The detection efficiency of the gauge is therefore proportional to (molecular mass)$^{-\frac{1}{2}}$. A hydrogen beam is detected readily, and an oxygen beam less so by a factor of four, for the same number of particles reaching the gauge per second. The magnitudes of the refocused beams were, for hydrogen, 40 to 45 cm, and for oxygen 16 to 20 cm of galvanometer-scale deflection. The hydrogen beam could have been increased by increasing the source pressure. For the 77°K oxygen beams, on the other hand, scattering immediately in front of the source slits limited the pressure in the source to a value which gave about 20 cm of refocused beam.

The fractional population of an oxygen state K, J of rotational and fine-structure energy $W^0(K,J)$ is given by the Boltzmann expression

$$P(K,J) = \frac{(2J+1)\exp[-W^0(K,J)/kT]}{\sum_{K,J}(2J+1)\exp[-W^0(K,J)/kT]}. \qquad (6)$$

Table III gives the populations of oxygen rotational states at 77°K and 300°K. The fraction of the refocused beam appearing in a given transition is equal to the sum of the fractional populations of the two states involved multiplied by the transition probability. For a refocused oxygen beam of 20 cm, the individual ΔM_J transitions in $f(1,1)$ and $f(1,2)$ had an intensity of 4.8 mm at maximum transition probability. Because of the reduced populations in the rotational states above $K, J = 3, 2$, the individual ΔM_J transitions disappeared into the noise and were not observable. At low fields,

Table III. Populations of oxygen rotational states at 77°K and 300°K.

	77°K		300°K	
State K,J	% in J	% in M_J	% in J	% in M_J
1,0	1.76	1.76	0.46	0.46
1,1	4.91	1.64	1.34	0.45
1,2	8.47	1.69	2.26	0.45
3,2	6.50	1.30	2.11	0.42
3,4	11.68	1.30	3.79	0.42
3,3	8.75	1.25	2.93	0.42
5,4	7.20	0.80	3.35	0.37
5,6	10.42	0.80	4.85	0.37
5,5	8.49	0.77	4.06	0.37
7,6	5.20	0.40	4.05	0.31
7,8	6.82	0.40	5.31	0.31
7,7	5.77	0.38	4.63	0.31

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[16] P. Kusch, Phys. Rev. **93**, 1022 (1954) and **101**, 627 (1956).

[17] H. C. Torrey, Phys. Rev. **59**, 293 (1941).

however, the superposition of all of the single and multiple transitions available in a state K, J into an unresolved envelope made possible observation of states up to $K, J=7, 8$.

The intensity of the hydrogen line as observed on the galvanometer scale was about 25 times the maximum intensity observed for any resolved oxygen line. The center of the line could, therefore, be determined to high precision.

PROCEDURE

Since the apparatus was arranged to focus at the detector molecules which had the same moment throughout the trajectory, a transition was observed as a decrease in signal at the galvanometer. Two methods were used to determine the center of a line. The first was to approach the line alternately from higher and lower frequencies, each time noting the frequency which seemed to correspond to a maximum in line intensity. The average of 10 to 20 such observations was than taken as a single determination of the line frequency. The second method was to measure the frequencies of two equal-intensity points on the line, one each side of the center. The average of 4 to 6 such pairs of points then formed a determination of the line frequency. In either method a second line was similarly measured, or perhaps several other lines, and then the whole sesequence was repeated several times. During such a run the C-field current was continuously monitored by a second observer who also recorded the data. Since the deflecting magnet currents were not monitored, the deflecting fields drifted somewhat in the course of a run, and contributed a time-variable component to the C field. This field drift was generally monotonic, and always of small magnitude, so that the procedure of observing two lines alternately several times permitted the effect to be removed from the data by appropriate interpolation.

In observing some of the weaker lines where the signal-to-noise ratio was poor, it became clear that there was considerable danger of introducing a prejudiced repetitive error. To avoid such errors the C field was changed between each set of observations. The observer was told that the field had been changed, but not the direction or magnitude of the change, and he then had to make a fresh and unbiased determination of the line frequencies. This technique gave a large number of independent values of a frequency ratio, each of low precision but with random errors. Field drift was compensated in these measurements by alternating the order of the two lines in successive ratios.

TABLE IV. The ratios of line frequencies observed in the Zeeman spectrum.

K,J	$[f(K,J)/f(1,1)]_{\text{obs}}$	$a(K,J)/a(1,1)$	$[f(K,J)/f(1,1)]_{\text{calc}}$
1,2	0.969334±0.000043	0.967992	0.969309
3,2	0.635727±0.000050	0.634656	0.635770
3,4	0.495512±0.000046	0.494714	0.495496
5,4	0.395262±0.000031	0.394714	0.395265
5,6	0.332145±0.000023	0.331594	0.332171
7,6	0.284374±0.000044	0.283974	0.284316
7,8	0.249706±0.000034	0.249224	0.249695

The frequency measurement of the rf field was made with a General Radio 620–A wave meter. With this instrument, frequencies were measured in terms of an internal crystal oscillator which was found to be stable to several parts per million over long periods of time.

RESULTS

A. Oxygen Zeeman Spectrum

Experimental results on the frequency ratios $f(K,J)/f(1,1)$ are given in Table IV. These are the mean frequencies of the sets of transitions within the states K, J, and are given in the theory by just the terms linear in the field. The quadratic terms contribute only a symmetric splitting of the lines about the linear frequency, and cubic and higher power terms are negligible at the fields used in these experiments. The experimental frequency ratios may be used with Eqs. (4) in a least squares solution for g_K/g_S and g_p/g_S. The result of this calculation is

$$g_K/g_S=+(6.08\pm0.74)\times10^{-5},$$
$$g_p/g_S=-(1.613\pm0.028)\times10^{-3},$$

where the errors are standard deviations. The accuracy is poor because the quantities g_K and g_p give small effects in the spectrum compared to the g_S terms. It will be noted that the g_S coefficient ratios, $a(K,J)/a(1,1)$, given in Table IV, fail by a substantial margin to give the observed frequency ratios. If the frequency ratios are calculated from (4) with the g_K/g_S and g_p/g_S values determined above, the results fall well within experimental error, as shown in Table IV.

In terms of the customary definition of the gyromagnetic ratio, where the moment is measured in terms of the Bohr magneton,

$$g_K=+(1.22\pm0.15)\times10^{-4},$$
$$g_p=-(3.226\pm0.056)\times10^{-3}.$$

The part of g_K which refers to rotation of the two oxygen nuclei about one another, $g_K{}^n$, is just $-\frac{1}{2}(m/M)=-2.72\times10^{-4}$, where m and M are the electron and proton masses, respectively. The electronic part of g_K, $g_K{}^e$, is then

$$g_K{}^e=8\ \mathrm{Re}\Sigma_{\Pi}[(\Sigma|BL_y|\Pi)(\Pi|L_y|\Sigma)/(E_\Pi-E_\Sigma)]$$
$$=+(3.94\pm0.15)\times10^{-4}.$$

These values may be compared with those of Tinkham and Strandberg,[3] who quote $g_K=-(1.35\pm0.30)\times10^{-4}$ and $g_p=-(2.94\pm0.05)\times10^{-3}$. The g_K values are in excellent agreement, while those for g_p differ by substantially

Table V. Total g-values of the oxygen rotational states.

State K,J	$g_J(K,J)$	State K,J	$g_J(K,J)$
1,1	1.001017±0.000013	5,4	0.394584±0.000020
1,2	0.968323±0.000018	5,6	0.331764±0.000014
3,2	0.634446±0.000028	7,6	0.283857±0.000018
3,4	0.494918±0.000014	7,8	0.249379±0.000014

more than the stated errors.[18] It should be noted that Tinkham and Strandberg obtain g_K and g_p from a least-squares fit of microwave spectra under the assumption that $g_S(O_2)$ has the free-electron value, 2.00229, to a precision of $\pm 60\times 10^{-6}$. As is discussed in the next section, the present experiment shows that $g_S(O_2)$ deviates from the free-electron value by -190×10^{-6}. Although the deviation is not large, it is amplified by the fact that the g_S terms dominate the Zeeman energy expressions, and this may in part account for the lack of agreement in the g_p values.

The total g-values of the oxygen rotational states are given in Table V.

The quadratic splittings at 120 gauss of the three states for which observation of the resolved transitions was possible are given in Table II.

In both of the states in which a statistically significant body of data was obtained for the splitting, $K, J=1, 1$ and 1, 2, the observed and calculated splittings differ by substantially more than the estimated experimental errors. The source of the difference is unknown.

B. g_S of Oxygen

In a series of runs at high fields, sixteen independent sets of measurements of the two frequencies $f(1,1)$ of oxygen and f_H of the line $[F, M_F=1,0\leftrightarrow 1, -1]$ of the hydrogen hyperfine structure were obtained. The frequency of the hydrogen line is given by[19]

$$f_H=\tfrac{1}{2}\Delta\nu_H[(1+y^2)^{\frac{1}{2}}-(1-y)]+g_I\mu_0 H/h, \qquad (7)$$

where $y=[g_J(H)-g_I]\mu_0 H/h\Delta\nu_H$, g_I is the proton g-value, and $\Delta\nu_H$ is the hyperfine splitting. All of the parameters in (7) are known to high precision from other experiments:

$$\begin{aligned}\Delta\nu_H&=1420.40573\pm 0.00005\text{ Mc/sec},^{20}\\ g_J(H)/g_I&=-658.2171\pm 0.0006,^{21}\\ 2g_L/g_I&=-657.475\pm 0.008,^{22}\end{aligned}\qquad (8)$$

where $g_L=1$, the electron orbital g-value. From the observed hydrogen frequencies we determine the corresponding values of y. The ratio of $f(1,1)$ of oxygen to y does not contain $\mu_0 H/h$:

$$f(1,1)/y=\tfrac{1}{2}g_S(O_2)/g_J(H)[1+g_K/g_S(O_2)]\\ \times\{\Delta\nu_H/[1-g_I/g_J(H)]\}. \qquad (9)$$

The experimental value of the ratio $f(1,1)/y$ is

$$f(1,1)/y=709.0466\pm 0.0071\text{ Mc/sec}, \qquad (10)$$

where the error is the standard deviation of the data. To a sufficient accuracy for our purpose the hydrogen g-value, $g_J(H)$, is equal to $g_S(H)$, the spin g-value of the electron bound in the hydrogen atom.[21] The $g_S(H)$, in turn, differs from the spin g-value of the free electron by a well known relativistic correction[23]:

$$g_J(H)/g_s(\text{free})=g_S(H)/g_s(\text{free})\\ =\tfrac{1}{3}[1+2(1-\alpha^2)^{\frac{1}{2}}]=1-(17.8\times 10^{-6}). \qquad (11)$$

The combination of (9), (10), and (11) yields the ratio of the spin g-value of the unpaired electrons in O_2 to that of a single free electron:

$$g_S(O_2)/g_s(\text{free})=1-(190\pm 13)\times 10^{-6}.$$

Since $g_s(\text{free})/g_L=2.002292$,[21] we also have

$$g_S(O_2)/g_L=2.001910\pm 0.000026.$$

Rigorously, this value of $g_S(O_2)$ should also carry the notation $K, J=1, 1$ since only the $f(1,1)$ transition entered into its determination. Since, however, the calculated ratios $f(K,J)/f(1,1)$ agree within experimental error with the observed ratios after a suitable choice of the constants g_K and g_p, there is no evidence of a deviation of the value of $g_S(O_2)$ in states of K, J other than 1, 1 from the value given above.

As noted above, the observed high-field quadratic splitting of the $f(1,1)$ transition fails to agree with the calculated value by 12 kc/sec. If this difference is the result of an undetected systematic error in the measurement of $f(1,1)$, then an additional uncertainty of 6 parts in 160 000 must be assigned to the ratio $f(1,1)/y$. The quantity $g_S(O_2)/g_s(\text{free})$ then becomes $1-(190\pm 40)\times 10^{-6}$.

The deviation of -190×10^{-6} between $g_S(O_2)$ and $g_s(\text{free})$ may be compared to a similar deviation in atomic oxygen. Rawson and Beringer[24] have measured the atomic g_J values of the $^3P_1$ and $^3P_2$ states and find

$$g_J(^3P_1)_{\text{obs}}/g_J(^3P_1)_{\text{calc}}=1-\tfrac{2}{3}(174\times 10^{-6}),$$
$$g_J(^3P_2)_{\text{obs}}/g_J(^3P_2)_{\text{calc}}=1-\tfrac{2}{3}(240\times 10^{-6}).$$

where the calculated g_J values are both given by $\frac{1}{2}[g_L+g_s(\text{free})]$, with g_L equal to unity and $g_s(\text{free})$

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[18] Differences in sign between the papers of Tinkham and Strandberg and the present work are due to the different g-value conventions used. Thus, our g-values $g_S, g_K, g_K{}^n$, and $g_K{}^e$ are of different sign than those of Tinkham and Strandberg, while g_p is of the same sign. A factor of 2 difference appears in the numerical coefficients of the sums over Π states because of the method of summing used by Tinkham and Strandberg: see p. 943 of reference 3.

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$=2.002292$. Kambe and Van Vleck[25] have examined corrections to $g_J(^3P_1)_{\text{calc}}$ and $g_J(^3P_2)_{\text{calc}}$ arising from departures from Russell-Saunders coupling in atomic oxygen, motion of the nucleus, relativistic corrections, and interference of the external magnetic field with the various magnetic interactions within the atom. Their results are that corrections of -171×10^{-6} and -232×10^{-6} must be applied to $g_J(^3P_1)_{\text{calc}}$ and $g_J(^3P_2)_{\text{calc}}$, respectively, in excellent agreement with the experiments. Presumably effects similar to those discussed by Kambe and Van Vleck occur in O_2, and account for the deviation between $g_S(O_2)$ and g_s(free) observed in the present experiment.

We gratefully acknowledge the generous assistance of Professor Henry Foley in the clarification of theoretical questions.

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PHYSICAL REVIEW VOLUME 107, NUMBER 3 AUGUST 1, 1957

Hyperfine-Structure Separations and Magnetic Moments of Rb^{81}, Rb^{82}, Rb^{83}, and Rb^{84}†

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(Received April 25, 1957)

Measured by an atomic-beam magnetic resonance method, the hyperfine-structure separations and magnetic moments of four neutron-deficient isotopes are found to be

Rb^{81}, $\Delta\nu=5097\pm13$ Mc/sec, $\mu_I=+2.05\pm0.02$ nm;
Rb^{82}, $\Delta\nu=3094.1\pm2.4$ Mc/sec, $\mu_I=+1.50\pm0.02$ nm;
Rb^{83}, $\Delta\nu=3183.3\pm5.8$ Mc/sec, $\mu_I=+1.42\pm0.02$ nm;
Rb^{84}, $\Delta\nu=3077.5\pm5.1$ Mc/sec, $\mu_I=-1.32\pm0.02$ nm.

I. INTRODUCTION

IN several previous papers,[1–3] accounts have been given of the measurements of the spins of four neutron-deficient isotopes of rubidium and a metastable state of one of these isotopes. Also, the hyperfine structure and magnetic moment of Rb^{81} have been measured by the zero-moment atomic-beam method.[1] In this paper, report is made of the measurement of the atomic hyperfine structures (hfs) of Rb^{81}, Rb^{82}, Rb^{83}, and Rb^{84} by use of the atomic-beam magnetic resonance method and radioactive detection. A different method of preparing the radioisotope Rb^{84} for atomic-beam purposes is discussed in some detail, because the low intensities used in the previous work had to be augmented to obtain sufficient sensitivity to determine the sign as well as the absolute value of the hfs. Because of the small numbers of atoms produced in the Berkeley 60-inch cyclotron, special procedures were employed in the search for resonance lines to minimize the amount of material required. No attempt was made to determine the hfs any more accurately than was necessary to determine the sign of the moment.

II. ISOTOPE PREPARATION

For most of these experiments, the radioisotopes were produced by alpha particles on natural Br^{79} and Br^{81}. The chemical extraction and beam preparation have been described in reference 2. However, in order to increase the signal-to-noise ratio, absorber foils were used to select the particular (α,kn) reaction desired. In a general way this procedure improved matters except for Rb^{84}, for which the (α,n) reaction yield is very poor. Although several curves were run using this reaction, it was decided to use (p,n) reactions on Kr in an attempt to increase the Rb^{84} yield. Fortunately Kr^{84} is 57% abundant, compared with 12% for Kr^{83}, so that production of Rb^{84} is favored over that of Rb^{83}. The improvement in signal-to-noise ratio over the Br bombardments was about 4 to 1. In addition, runs using the $Kr^{84}(p,n)Rb^{84}$ reaction provided an independent assignment of spin 2 for Rb^{84}.

In practice approximately 2 liters of krypton at atmospheric pressure is contained in a water-cooled, rectangular tube of cast aluminum with a 1-mil aluminum window at one end for the 12-Mev proton beam. Following suitable exposure to a proton beam of approximately 25 microamperes, the assembly is allowed to stand for several days to permit the short-lived activities to decay. After the krypton is frozen out and replaced with air, the entire assembly is washed with several hundred ml of water containing controlled amounts (~20 mg) of RbBr carrier. This is boiled away to a few drops of RbBr solution, and the concen-

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† This work was done under the auspices of the U. S. Atomic Energy Commission and the Office of Naval Research.

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