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# THEORY OF THE FINE STRUCTURE OF THE MOLECULAR OXYGEN GROUND STATE AND THE MEASUREMENT OF ITS PARAMAGNETIC SPECTRUM

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# Theory of the Fine Structure of the Molecular Oxygen Ground State*

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A rather complete solution for the fine-structure problem in the oxygen molecule is given in the framework of the Born-Oppenheimer approximation. The reduction of the effect of the electronic state on the fine structure to an effective Hamiltonian, involving only the resultant electronic spin in addition to rotational and vibrational quantum numbers, is demonstrated. In this Hamiltonian the parameters $\lambda$ and $\mu$ measure the effective coupling of the spin to the figure axis and the rotational angular momentum, respectively. The contributions to these parameters which are diagonal in electronic quantum numbers, namely $\lambda'$ and $\mu'$, are evaluated by using an expression for the electronic wave function as a superposition of configurations. It turns out that $\lambda'$ gives almost all of $\lambda$, whereas $\mu'$ gives only 4 percent of $\mu$. The second-order contributions of spin-orbit coupling and rotation-induced electronic angular momentum to $\lambda$ and $\mu$, and the electronic contribution to the effective moment of inertia are related to each other and to certain magnetic effects to be given later. This interrelation enables them all to be essentially evaluated experimentally.

The effective Hamiltonian is diagonalized through terms in $(B/\hbar\omega)^2$ and the eigenvalues compared with the experimental spectra. The fitting establishes the constants: $\mu=252.67\pm0.05$ Mc/sec; $\lambda_e=59\,386\pm20$ Mc/sec; $\lambda_1=[Rd\lambda/dR]_e=16\,896\pm150$ Mc/sec; $\lambda_2=[(R^2/2)(d^2\lambda/dR^2)]_e=(5\pm2)\times10^4$ Mc/sec; $\lambda_{eff}(v=0)=19\,501.57\pm0.15$ Mc/sec. The transformation that diagonalizes the Hamiltonian is given with respect to both Hund case $(a)$ and case $(b)$ bases. These transformations are applied to matrix elements of $S_Z$. The results are tabulated and applied to calculate the exact intensity factors for spectral lines. This calculation shows slight deviations from the usual case $(b)$ results for allowed lines and predicts quite sizeable intensities for the "forbidden" $\Delta K=2$ lines.

## I. INTRODUCTION

ALTHOUGH the general principles are well established, there exist few cases in which the Born-Oppenheimer[1] approximation has been carried through to give a complete solution for the eigenfunctions and eigenvalues of a molecule. The recent publication of a reasonably good and analytically convenient solution for the $^3\Sigma$ electronic ground state of $O_2$ by Meckler[2] and the existence of precise microwave[3] and infrared[4] data on the energy levels make the oxygen molecule a particularly attractive one for study. Interest was increased by the presence of a spin-dependent fine structure which showed some discrepancies from earlier theoretical predictions. To develop certain internal theoretical relations between parameters, and because of the great diversity of existing treatments, we shall give a unified systematic treatment that incorporates the new results and indicates their connection with previous work. It is hoped that this treatment will serve as an example that shows the relation between the wave mechanical electronic theory and the traditionally matrix mechanical fine structure theory. It will also show how far the calculation can be carried in an actual case.

The over-all problem can be stated as that of determining the eigenvalues and eigenfunctions of the Hamiltonian operator

$$\mathcal{H}=\mathcal{H}_{el}+V_{nuc}+T_{nuc}+\mathcal{H}_{so}+\mathcal{H}_{ss}+\mathcal{H}_{hfs}. \qquad (1)$$

In this $\mathcal{H}_{el}$ is the electronic energy operator used by

† National Science Foundation Predoctoral Fellow.
[1] M. Born and J. R. Oppenheimer, Ann. Physik 84, 457 (1927).
[2] A. Meckler, J. Chem. Phys. 21, 1750 (1953).
[3] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. 79, 651 (1950).
[4] H. Babcock and L. Herzberg, Astrophys. J. 108, 167 (1948).

Meckler which includes the electronic kinetic energy, mutual repulsion energy, and the attraction to the nuclei; $V_{nuc}$ is the Coulomb repulsion of the nuclei, and $T_{nuc}$ is the kinetic energy of the nuclei that can be decomposed into vibration, rotation, and center-of-mass motion; $\mathcal{H}_{so}$ is the spin-orbit energy, and $\mathcal{H}_{ss}$ is the spin-spin energy resulting from the magnetic dipole interaction between the electronic spins; $\mathcal{H}_{hfs}$ is the interaction of nuclear magnetic dipole and electric quadrupole moments with their environment.

The eigenfunctions will be functions of space and spin coordinates of the electrons, separation and angles of orientation of the nuclei, and center-of-mass coordinates of the molecule. In general, we would also have nuclear spin coordinates entering, but since $O^{16}$ has no spin these terms do not concern us here. Those eigenfunctions must be antisymmetric on interchange of electrons and symmetric on interchange of the $O^{16}$ nuclei. The essence of the Born-Oppenheimer approximation is that we can express the total state function to a good approximation as

$$\Psi=\psi_{el}\psi_{vib}\psi_{rot}\psi_{nuc\ spin}\psi_{trans}, \qquad (2)$$

and that this approximation can be improved by use of perturbation theory between functions of this sort. In determining these functions, we can approximately compute each $\psi_i$ by considering the $\psi_j$ corresponding to other energy terms and coordinates to be fixed, or at least reduced to parameters. Thus Meckler solved for $\psi_{el}$ by considering the nuclei fixed and neglecting the terms $T_{nuc}$, $\mathcal{H}_{so}$, $\mathcal{H}_{ss}$, and $\mathcal{H}_{hfs}$. His result is an energy $E_{el}(R)$ and an electronic wave function $\psi_{el}(\mathbf{r}_j,\mathbf{s}_j|R)$, with the internuclear distance $R$ entering as a parameter and with no dependence at all on the other "lower-energy" coordinates.

In solving the rest of the problem, we should take this $E_{el}(R)$ as the effective potential for vibration and

use this $\psi_{el}$ to evaluate such things as the spin-spin coupling constants. In practice, we shall approximate $E_{el}(R)$ by a two-term power-series expansion about the minimum. This is justified, since we are only concerned with the two lowest vibrational levels. (For study of the higher vibrational levels, more terms would have to be taken or else recourse be made to a Morse curve or other analytic approximation.[5]) Thus our vibrational Hamiltonian is taken to be

$$\mathcal{K}_{vib} = P_R{}^2/2M + \tfrac{1}{2}M\omega_e{}^2R_e{}^2\xi^2 + b\xi^3, \qquad (3)$$

where $\xi = (R-R_e)/R_e$, $R_e$ is the equilibrium internuclear distance, and $M$ is the reduced mass. The rotational Hamiltonian is

$$\mathcal{K}_{rot} = \mathbf{N}^2/2MR^2 = B_e(1-2\xi+3\xi^2)\mathbf{N}^2, \qquad (4)$$

where $\mathbf{N}$ is the angular momentum of nuclear rotation and $B_e$ is the reciprocal moment of inertia of the nuclei at $R_e$. The expansion in $\xi$ allows for the change in moment of inertia with centrifugal stretching and vibration.

The effect of $\mathcal{K}_{so}+\mathcal{K}_{ss}$ in determining the fine structure can be reduced (see Sec. II) to an effective Hamiltonian,

$$\mathcal{K}_{spin} = \tfrac{2}{3}(\lambda_e+\lambda_1\xi+\lambda_2\xi^2)(3S_z{}^2-\mathbf{S}^2)+\mu\mathfrak{R}\cdot\mathbf{S}, \qquad (5)$$

where $\mathbf{S}$ is the resultant electronic spin vector, and $\lambda$ and $\mu$ are spin coupling constants to be determined from $\psi_{el}(\mathbf{r}_j,\mathbf{s}_j|R)$. The term in $\mu$ will be seen to come largely from the interaction of rotation-induced electronic angular momentum with the spin through the spin-orbit coupling. We shall also see that the principal part of the term in $\lambda$ comes from the diagonal spin-spin energy in the electronic ground state. It is noteworthy that if one tried to estimate $\lambda$ from the simple model of two interacting spins with one concentrated at each center the values obtained for $\lambda_e$ and $(\lambda_1/\lambda_e)$ would even have the wrong *sign*. Thus it is clear that our more accurate calculation is necessary to explain the observed behavior of $\lambda$. In this calculation, exchange effects, inclusion of ionic states, and the rapid change of configuration mixing coefficients with $R$ play the leading roles.

In $(O^{16})_2$ we have $I=0$, allowing only the one state, $\psi_{nuc\ spin}=1$. Thus there can be no hyperfine effects. The translational motion of the center-of-mass is of no interest to us here, but $\psi_{trans}$ would be simply a plane wave satisfying appropriate boundary conditions. This motion will be neglected throughout the rest of the paper.

Our solution of the fine structure problem,

$$(\mathcal{K}_{vib}+\mathcal{K}_{rot}+\mathcal{K}_{spin}-E)\psi_{vib}\psi_{rot}\psi_{spin}=0, \qquad (6)$$

is by purely matrix methods. (Here, $\psi_{spin}$ describes the state of the resultant electronic spin that enters into

$\mathcal{K}_{spin}$.) The matrix components of the Hamiltonian are readily obtained (see Sec. III) in a Hund case $(a)$ basis[6] characterized by the quantum numbers $v, J, M, S$, and $\Sigma$, where $J$ is the total angular momentum of all kinds, and $\Sigma=S_z$. This matrix is then diagonalized to high approximation, yielding $E(v,K,J)$ and the corresponding eigenvectors. These eigenvalues $E$ fit the microwave results satisfactorily to their limit of accuracy (approximately 1 in $10^5$), explaining the discrepancy mentioned above. This fitting establishes the constants $\lambda_e$, $\lambda_1$, and $\lambda_2$ for comparison with the calculated values found in II. The eigenvectors are listed with respect to Hund case $(a)$ eigenfunctions and also with respect to Hund case $(b)$ eigenfunctions, in which $\mathfrak{R}^2$ rather than $S_z$ is diagonal.

With these eigenvectors, the intensities of both allowed and "forbidden" transitions are calculated in Sec. IV. This reveals small corrections to the usual Hund case $(b)$ values for the allowed transitions, and quite appreciable intensities for $\Delta K=2$ transitions. The latter are made possible by the breakdown of the rotational quantum number $\mathfrak{R}$ in the presence of the spin-spin coupling energy.

## II. DEDUCTION OF THE EFFECTIVE HAMILTONIAN

The coupling of angular momenta in molecules and the general methods of establishing an effective fine structure Hamiltonian have recently been reviewed by Van Vleck.[7] The calculations of this section are an application of those general methods to a specific case which can be carried particularly far. Our choice of angular momentum notation generally follows that given by Van Vleck. One slight extension is the use of $\mathbf{N}$ for the true instantaneous nuclear orbital angular momentum. $\mathfrak{R}=\mathbf{N}+\mathbf{L}=\mathbf{J}-\mathbf{S}$ differs from $\mathbf{N}$ only by "high-frequency" off-diagonal elements of the electronic orbital angular momentum. We shall introduce $K$ in Sec. III as the conventional label for the final eigenfunctions; it has the magnitude of $\mathfrak{R}$ for the pure Hund $(b)$ state which is dominant in the eigenfunction.

The basis functions in terms of which we shall describe the state of the molecule are products of the form (2). In this form the $\psi_{el}(\mathbf{r}_j,\mathbf{s}_j|R)$ are solutions to $\mathcal{K}_{el}$ for the case in which the nuclei are not rotating and are "clamped" a distance $R$ apart. When the molecule rotates, the coordinates $\mathbf{r}_j$ are referred to the axes fixed in the molecule, but the wave function still describes the system with respect to a fixed frame. The $\psi_{vib}$ are harmonic oscillator eigenfunctions of the internuclear distance $R$ for the angular frequency of oscillation $\omega_e$; the $\psi_{rot}$ are symmetrical top eigenfunctions for a linear rotor with internal spin angular momentum.[8]

[5] For details, see G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Publishing Company, Inc., New York, 1950), Chap. III.

[6] F. Hund, Z. Physik **36**, 657 (1926). These coupling cases are also discussed in reference 5, Chap. V.

[7] J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

[8] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929); F. Reiche and H. Rademacher, Z. Physik **39**, 444 (1926); **41**, 453 (1927).

As stated above, $\psi_{\text{nuc spin}}$ is trivial for $I=0$, and $\psi_{\text{trans}}$ is suppressed.

In the lowest order Born-Oppenheimer approximation, one takes a single product of these eigenfunctions as the total eigenfunction and takes the diagonal value of the complete Hamiltonian over it as the energy eigenvalue. This would give the sum of the unperturbed electronic energy $E_n{}^0$, reasonable approximations to the vibrational and rotational energy, the diagonal spin-spin energy in $\lambda$, and the small diagonal contribution to $\mu$ coming from the magnetic coupling of the electronic spins in the field of the rotating nuclei. However, it fails to include any electronic spin-orbit effects because the $^3\Sigma$ ground electronic state has no net orbital angular momentum,[9] and it fails to account for the coupling between electronic, vibrational, and rotational motions such as centrifugal distortion. These latter effects are found by going to a second-order approximation.

## A. First-Order Contributions

These terms are to be evaluated by finding the diagonal values of the perturbative term over the electronic wave function. We start with the spin-spin contribution to the parameter $\lambda$, defined in (5), which measures the effective coupling of the spin to the $z$ (internuclear) axis.

### Spin-Spin Contribution to $\lambda$

Since Van Vleck gives no formulas for the coefficient $\lambda$ and since Kramers'[10] treatment is in terms of permutation group theory rather than in the framework of the usual determinantal method, we must develop our result from the basic Hamiltonian,[11]

$$\mathcal{H}_{ss}=g^2\beta^2\sum_{k>i}\left[(\mathbf{s}_j\cdot\mathbf{s}_k)r_{jk}{}^2-3(\mathbf{s}_j\cdot\mathbf{r}_{jk})(\mathbf{s}_k\cdot\mathbf{r}_{jk})\right]r_{jk}{}^{-5}, \quad (7)$$

where $\mathbf{r}_{jk}=\mathbf{r}_j-\mathbf{r}_k$. By simply expanding into components and regrouping, this can be written

$$\mathcal{H}_{ss}=-g^2\beta^2\sum_{k>i}\left[\frac{3x_{jk}y_{jk}}{r_{jk}{}^5}(s_{jx}s_{ky}+s_{jy}s_{kx})\right.$$

$$+\frac{3y_{jk}z_{jk}}{r_{jk}{}^5}(s_{jy}s_{kz}+s_{jz}s_{ky})+\frac{3z_{jk}x_{jk}}{r_{jk}{}^5}(s_{jz}s_{kx}+s_{jx}s_{kz})$$

$$+\frac{3}{2}\frac{x_{jk}{}^2-y_{jk}{}^2}{r_{jk}{}^5}(s_{jx}s_{kx}-s_{jy}s_{ky})+\frac{1}{2}\frac{3z_{jk}{}^2-r_{jk}{}^2}{r_{jk}{}^5}$$

$$\left.\times(3s_{jz}s_{kz}-\mathbf{s}_j\cdot\mathbf{s}_k)\right]. \quad (8)$$

The symmetry of the molecule causes all except the last term to vanish when integrated over the electronic state. All of these spin functions are of the forms which, as Van Vleck points out, have matrix components proportional to corresponding elements of $\mathbf{S}$. (This can be proved by direct multiplication of the matrix elements of a vector of the type $\mathbf{T}$.[12]) Thus all elements of $(3s_{jz}s_{kz}-\mathbf{s}_j\cdot\mathbf{s}_k)$ are proportional to those of $(3S_z{}^2-S^2)$, and the proper dependence of the interaction on $\mathbf{S}$ is shown. To evaluate $\lambda$, it is convenient to compute the diagonal element of $\mathcal{H}_{ss}$ for the state $S_z=\Sigma=1$, and to note that the diagonal part of $\lambda$ is given by

$$\lambda'(\xi)=\lambda_e'+\lambda_1'\xi+\lambda_2'\xi^2=\tfrac{3}{2}E_{ss}\,|\,_{\Sigma=1}. \quad (9)$$

The $\xi$ dependence enters because $\psi_{\text{el}}$ depends parametrically on $R$ (or $\xi$).

The electronic wave function given by Meckler[2] is expressed as a superposition of configurations,

$$\psi_{\text{el}}=\sum_\mu C_\mu\phi_\mu, \quad (10)$$

where each $\phi_\mu$ is a determinant or linear combination of determinants which is a spin eigenfunction with $S=1$ and $\Sigma=0$. The corresponding eigenfunctions for $\Sigma=1$, obtained by applying $S_+/\sqrt{2}$ to Meckler's eigenfunctions, have been given by Kleiner.[13] They are more convenient here because the dominant configuration is then a single determinant. The coefficients $C_\mu$ are given for several values of $R$. Near the equilibrium distance $R_e$, one configuration ($\mu=c$) is dominant, $|C_c|$ being of the order 0.97. The next largest has $C_\mu$ of the order 0.1. Since the $C$'s are real, the diagonal energy is simply

$$E_{ss}=\sum_{\mu\mu'}C_\mu C_{\mu'}H_{\mu\mu'}. \quad (11)$$

It is clear that we make an error of the order of only one percent if we neglect terms that do not involve the dominant configuration. Since other sources of error are larger, we shall make some simplifications of this kind. Our problem then is to compute the matrix components of

$$\mathcal{H}_{ss}=\frac{-g^2\beta^2}{2}\sum_{k>i}\frac{3z_{jk}{}^2-r_{jk}{}^2}{r_{jk}{}^5}\left[2s_{jz}s_{kz}-\frac{s_{j+}s_{k-}+s_{j-}s_{k+}}{2}\right] \quad (12)$$

(where $s_{j\pm}=s_{jx}\pm is_{jy}$) between these configurations.

These matrix components are reduced to sums of 2-electron integrals in terms of single electron orbitals by the usual methods developed by Slater.[14] The spin part of (12) gives a factor of $\pm\tfrac{1}{2}$ depending on whether the two spins involved are parallel or antiparallel. Thus, in summing to get the diagonal elements, all integrals involving paired spins cancel out. For the diagonal element over the dominant configuration, for

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[9] Of course, one could start with electronic eigenfunctions for the problem including spin-orbit interaction. These, however, could not have $\Lambda, \Sigma$ as good quantum numbers. As usual, all magnetic-spin-coupling effects are neglected in Meckler's solution.

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

[11] W. Heisenberg, Z. Physik **39**, 514 (1926).

[12] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951), p. 59 ff.

[13] W. H. Kleiner, Quarterly Progress Report No. 9, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1953 (unpublished).

[14] Reference 12, p. 171; J. C. Slater, Phys. Rev. **34**, 1293 (1929).

example, this leaves just

$$(\mathcal{K}_{ss})_{cc} \equiv H_{cc} = \frac{-g^2\beta^2}{4}\left(\int\int \chi_+^*(1)\chi_-^*(2)\frac{3z_{12}^2-r_{12}^2}{r_{12}^5}\right.$$

$$\times \chi_+(1)\chi_-(2)d\tau_1 d\tau_2 - \int\int \chi_+^*(1)\chi_-^*(2)$$

$$\left.\times\frac{3z_{12}^2-r_{12}^2}{r_{12}^5}\chi_-(1)\chi_+(2)d\tau_1 d\tau_2\right), \quad (13)$$

where $\chi_\pm$ is Meckler's notation for the $2p\pi_g^\pm$ symmetry orbitals. The subtracted term is, of course, the exchange integral. To evaluate the integrals, we insert Meckler's LCAO molecular orbital functions using Gaussian atomic orbitals. As we shall see, these Gaussians make it possible to evaluate the integral exactly. After some reduction, (13) becomes

$$H_{cc} = \frac{-64g^2\beta^2b^5K^4}{\pi^3}\int\int [r_1\sin\theta_1\exp(-br_1^2)\sinh bRz_1]^2$$

$$\times [r_2\sin\theta_2\exp(-br_2^2)\sinh bRz_2]^2$$

$$\times \sin^2(\varphi_2-\varphi_1)(3z_{12}^2-r_{12}^2)/r_{12}^5 d\tau_1 d\tau_2. \quad (14)$$

This resembles the classical average of the interaction between two identical electron clouds, each of which is concentrated in two toroids of charge encircling the axis of the molecule at the two nuclei. The axis is a nodal line and the perpendicularly bisecting plane is a nodal plane because of the $p\pi_g$ nature of these $\chi_\pm$ orbitals in which the unpaired spins are most apt to be found. However, the factor $\sin^2(\varphi_2-\varphi_1)$ gives a correlation in position tending to concentrate the two interacting electrons in perpendicular planes through the axis. This correlation is a direct result of the exchange integral and hence of the antisymmetry of the wave function. Also noteworthy is the fact that there is a large chance of both electrons being near the same center. This is the result of having ionic states given equal weight with nonionic states in a simple molecular orbital treatment. The principal contribution to the integral then comes when the two electrons are on the same center [because $(3z_{12}^2-r_{12}^2)/r_{12}^5$ is large then] and in perpendicular planes. Also, viewed in this way, the seemingly anomalous sign of $\lambda$ is explained. Thus the characteristic distance of separation for the interaction is the *atomic* radius, not the internuclear distance.

Evaluation of (14) is made possible by changing variables to

$$\begin{aligned}
\xi &= x_{12} = x_1 - x_2, & \xi' &= x_1 + x_2, \\
\eta &= y_{12} = y_1 - y_2, & \eta' &= y_1 + y_2, \\
\zeta &= z_{12} = z_1 - z_2, & \zeta' &= z_1 + z_2.
\end{aligned} \quad (15)$$

$$\rho^2 = \xi^2 + \eta^2 + \zeta^2 = r_{12}^2,$$

The integral then becomes

$$H_{cc} = \frac{-g^2\beta^2 K^4 b^5 \exp(-bR^2)}{2\pi^3}$$

$$\times \int\int \exp(-b\rho^2)\left(\frac{3\zeta^2-\rho^2}{\rho^5}\right)(\xi\eta'-\xi'\eta)^2$$

$$\times \exp(-b\rho'^2)[\cosh bR\zeta' - \cosh bR\zeta]^2 d\tau d\tau'. \quad (16)$$

If one replaces these Cartesian coordinates by cylindrical primed coordinates and spherical relative coordinates, the integration can be carried out analytically. Power-series expansion is required for the last integration. The result is[15]

$$H_{cc} = g^2\beta^2b^{\frac{3}{2}}2K^4\pi^{-\frac{1}{2}}\left\{\frac{1}{30}+\frac{\exp(-bR^2)}{15}+2\exp(-\tfrac{3}{4}bR^2)\right.$$

$$\left.\times S_1(bR^2) - \frac{\exp(-bR^2)}{2}S_1(4bR^2)\right\}, \quad (17)$$

where

$$S_1(x) = \sum_{n=0}^{\infty}\frac{2n-1}{1\cdot3\cdot5\cdots(2n+5)}\left(\frac{x}{2}\right)^n \quad (18)$$

and

$$K^2 = [1-\exp(-bR^2/2)]^{-1}.$$

We note that this is the product of a characteristic energy $g^2\beta^2b^{\frac{3}{2}}$ depending on the atomic scale factor $b$ times a dimensionless factor which is a function only of $bR^2$, that is, of the degree of overlap of the two atomic orbitals. The latter is true, since $\exp(-bR^2)$ is the amplitude of one Gaussian orbital at the center of the other. Computation shows that the dependence on $bR^2$ is very weak. The total range $R$ varying between zero and infinity, is only 30 percent; and since the region of interest is near a minimum, it is very nearly constant there. Thus the principal dependence of $H_{cc}$ on the molecular wave function is on the degree of concentration of the *atomic* orbitals as measured by $b^{\frac{3}{2}}\sim\langle 1/r^3\rangle$. This result should be independent of the detailed choice of wave function.

Kleiner[13] has noted that the Gaussians used by Meckler give a very poor value for $\langle 1/r^3\rangle$ because of their failure to rise rapidly near $r=0$. In view of these remarks, it seemed best to fit the $b$ in the Gaussian to give $\langle 1/r^3\rangle$ for the atomic orbital equal to that computed from the Hartree-Fock wave function of the oxygen atom.[16] This gave $b=1.696$, as opposed to the value $b=0.8$ (atomic units) chosen by Meckler from consideration of overlap. Numerical results are given

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[15] Following Meckler's notation we use $J$, $K$, $L$, and $M$ to denote normalization constants in electronic wave functions. No confusion with the usual angular momentum quantum numbers should result.

[16] Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) A238, 229 (1939). A very useful analytic fitting as the sum of three exponentials is given by P. O. Löwdin, Phys. Rev. 90, 120 (1953).

with this higher value of $b$ used in the $b^{\frac{3}{2}}$ factors, but in the overlap factors, $bR^2$ has Meckler's value.

Other matrix elements computed in a similar way are given in Appendix A. Using these results, the numerical values of the matrix components were evaluated for $R=2.236$ and $R=2.372$ atomic units, corresponding to $bR^2=4.0$ and 4.5. These values bracket the equilibrium distance $R_e=2.28$. The coefficients $C_\mu$ were determined for these same values of $R$ by interpolating between Meckler's given values. The nonvanishing results are given in Table I, with energies expressed in kMc/sec. From these energies, the spin-spin contribution to $\lambda$ was computed, and the results are compared with the experimental values (obtained in Sec. III) in Table II.

In view of the crudeness of the Gaussian approximation, these calculated results must be considered unreliable despite the adjustment made in $b$. This is illustrated by the fact that even for the Hartree-Fock function $\langle 1/r^3 \rangle$ is 29 percent less than the "experimental value" obtained from the magnetic hyperfine structure in $O^{16}O^{17}$ by Miller, Townes, and Kotani.[17] Although the uncertainty of interpretation of the latter makes it unwise to make a further adjustment of $b$, it does indicate that our calculation is apt to *underestimate* the true magnitude.

We thus conclude that the spin-spin interaction provides the major part of the coupling constant $\lambda$. This conclusion is supported by the estimation of the contribution of second-order spin-orbit effects given later in the paper.

Inspection of Table I reveals that the $R$ dependence of $\lambda$, which determines $\lambda_1$, comes almost entirely from the change in the configuration mixing coefficients $C_\mu$, the values of the matrix components being relatively constant. Presumably this behavior would also hold if a wave function constructed from better atomic orbitals were used. This presumption is strengthened by the fact that Ishiguro has obtained similar configuration mixing coefficients in a treatment now in progress using better orbitals.[18] This mechanism for the change in $\lambda$ again shows that a rather detailed examination of the electronic wave function is necessary for explaining the observed values of $\lambda$.

TABLE I. Contributions to the spin-spin energy as given in Eq. (11).

| $bR^2$ | $H_{\mu\mu'}$ 4.0 | 4.5 | Combined coefficient 4.0 | 4.5 | Contribution to energy kMc/sec 4.0 | 4.5 |
|---|---|---|---|---|---|---|
| $H_{ee}=H_{ee}$ | 27.656 | 27.286 | 0.9620 | 0.9526 | 26.606 | 25.992 |
| $H_{dd}=H_{ff}$ | 20.370 | 20.148 | 0.0165 | 0.0210 | 0.335 | 0.423 |
| $H_{cd}=H_{ef}$ | 39.434 | 38.998 | −0.2494 | −0.2788 | −9.820 | −10.866 |
| $H_{cg}=-H_{ch}=-H_{ci}$ | 186.22 | 191.10 | 0.0321 | 0.0436 | 5.974 | 8.324 |
| | | | | | 23.095 | 23.873 |

[17] Miller, Townes. and Kotani, Phys. Rev. **90**, 542 (1953).
[18] E. Ishiguro (unpublished).

TABLE II. Comparison of calculated and experimental values of $\lambda$ (kMc/sec).

| | Calc. | Exp. |
|---|---|---|
| $\lambda_e$ | 35.0 | 59.386 |
| $\lambda_1=(d\lambda/d\xi)_e$ | 19.6 | 16.90 |

*Nuclear Contribution to $\mu$*

Van Vleck's[7] Eq. (37) gives the magnetic interaction energy of an assembly of electron spins with each other and with the electronic and nuclear orbital motions. The only terms giving diagonal contributions in a $\Sigma$ state are the spin-spin energy evaluated above and the terms having nuclear rather than electronic velocities as factors. Separating out the latter, we have[19]

$$\mathcal{H}_1=\frac{-g\beta}{c}\sum_{K,j}\frac{Z_Ke}{r_{jK}^3}[\mathbf{r}_{jK}\times\mathbf{v}_K]\cdot\mathbf{s}_j. \qquad (19)$$

The velocities and coordinates are measured in a fixed frame but referred to gyrating axes. As Van Vleck points out, it is permissible to replace $\mathbf{v}_K$ by $\omega\times\mathbf{r}_K$ or $(\mathfrak{R}/MR^2)\times\mathbf{r}_K$, since the difference between the true nuclear angular momentum $\mathbf{N}$ and $\mathfrak{R}$ is only the oscillatory electronic orbital angular momentum which averages to zero in this sort of an interaction. We assume a rigid nuclear frame, so the $\mathbf{r}_K$ are constant vectors of $\pm\frac{1}{2}R\mathbf{k}$, where $k$ is a unit vector in the $z$-direction. Also $\mathfrak{R}_z=0$, since we have a diatomic molecule. Finally, symmetry causes terms which are odd in $x_j$ or $y_j$ to vanish. By using these facts, expansion of $H_1$ in components reduces to

$$\mathcal{H}_1=\frac{-4Z}{A}\frac{g\beta\beta_N}{R}\left[\sum_j\frac{z_j-R/2}{r_{jK}^3}\mathbf{s}_j\right]\cdot\mathfrak{R}. \qquad (20)$$

Here, $Z$ is the atomic number, $A$ is the atomic weight, $\beta_N$ is the nuclear magneton, and $r_{jK}$ is $|\mathbf{r}_j-\frac{1}{2}R\mathbf{k}|$.

Matrix components of the bracketed operator are reduced to single electron integrals by the method of Slater.[20] Since $\mathfrak{R}_z=0$, we have only terms in $s_x$ and $s_y$, which are both nondiagonal in $\Sigma$. Thus we seek elements that are diagonal in orbital quantum numbers but off-diagonal in $\Sigma$. Using Meckler's[2] dominant configuration $c$, namely, $(I+I_a)/\sqrt{2}$, for $\Sigma=0$, and Kleiner's[13] derived configuration $\phi_c$ for $\Sigma=1$, application of the general methods yields

$$(c\Sigma=0|\mathcal{H}_1|c\Sigma=1)$$
$$=\frac{1}{\sqrt{2}}[(\chi_-\beta|\mathcal{H}_1|\chi_-\alpha)+(\chi_+\beta|\mathcal{H}_1|\chi_+\alpha)].$$

The single electron spin operators $s_{jx}$ and $s_{jy}$ in $\mathcal{H}_1$ yield contributions which are just $1/\sqrt{2}$ times the matrix

[19] Correcting the trivial omission of $r_{jK}^{-3}$ in his more general Eq. (39).
[20] Reference 12, p. 169.

elements of $S_x$ and $S_y$. Also, $|\chi_-|^2 = |\chi_+|^2$, so that the two orbital integrals can be combined. This reduces the element to

$$(c\Sigma = 0 |\mathfrak{IC}_1| c\Sigma = 1)$$

$$= \frac{-4Z}{A} \frac{g\beta\beta_N}{R} \left( \chi_+ \left| \frac{z - R/2}{r_{jK}^3} \right| \chi_+ \right) \mathfrak{R} \cdot \mathbf{S} \equiv \mu' \mathfrak{R} \cdot \mathbf{S}. \quad (21)$$

This effective Hamiltonian form shows that this term gives a cosine-like coupling of the spin in the magnetic field of the rotating nuclei.

The final problem is to actually evaluate the co-efficient $\mu'$ by integration over the electronic $\chi_+$ orbitals. To carry this out, we transform to spherical coordinates about the nucleus at $z = R/2$. The integration then proceeds just as in the evaluation of the spin-spin energy and leads to

$$\mu' = \frac{-4Z}{A} \frac{g\beta\beta_N}{R^3} K^2 \left( \frac{2}{\pi b R^2} \right)^{\frac{1}{2}} \exp(-bR^2)$$

$$\times [S_5(2bR^2) - \tfrac{1}{8} \exp(-bR^2) S_5(8bR^2)], \quad (22)$$

where

$$S_5(x) = \sum_{n=1}^{\infty} \frac{(8n+1)}{1 \cdot 3 \cdot 5 \cdots (2n+1)} \left( \frac{x}{2} \right)^n. \quad (23)$$

Noting that this depends on $b$ only through the overlap parameter $bR^2$ and not on the atomic scale factor $b$ separately, this should be evaluated by using Meckler's $b = 0.8$ atomic unit, not the value obtained above by fitting $\langle 1/r^3 \rangle$. If this is done, the result is $\mu' = +10.0$ Mc/sec, compared to a total experimental value of $\mu = -252.7$ Mc/sec. This shows that the magnitude of the first-order contribution is only 4 percent of the total value, the rest being from the second-order effects of spin-orbit coupling discussed in the next section.

To make the physical nature of this first-order term clear, we note that simply calculating the energy of the electron spin in the magnetic field at one nucleus due to the rotation of the other about it would give a coupling constant of $2(Z/A)(g\beta\beta_N/R^3)$ or about $+8$ Mc/sec. The increase in magnitude from 8 to 10 Mc/sec is the result of distributing the electron over a region of radius $\sim R/2$, giving an increase in $\langle (z - R/2)/r_{jK}^3 \rangle$. From this picture, we see that the dependence of $\mu'$ on the detailed electronic wave function is of secondary importance. Further, $\mu'$ makes only a small contribution to $\mu$. Finally, there are no off-diagonal elements of $\mathfrak{IC}_1$ between the dominant $\phi_c$ configuration and the others in Meckler's wave function. Thus any contributions from the other configurations would be second-order effects of the order of one percent of $\mu'$ or 0.1 percent of $\mu$. In view of the other more serious sources of error, it was not considered worth carrying this calculation further in order to evaluate these corrections.

## B. Second-Order Contributions

### Perturbation of the Electronic State

As our first step in improving the zeroth-order eigen-function and first-order energy, we find the modification of the $^3\Sigma$ ground state by spin-orbit and rotational effects. We assume the conventional approximate form $A\mathbf{L} \cdot \mathbf{S}$ for the spin-orbit coupling energy rather than try to handle the rigorous microscopic Hamiltonian in terms of coordinates, velocities, and spins of the individual electrons.[21] The rotation-electronic coupling is through the term $-2B\mathbf{L} \cdot \mathfrak{R}$ in the rotational energy:[22]

$$\mathfrak{IC}_{\text{rot}} = B\mathbf{N}^2 = B(\mathfrak{R} - \mathbf{L})^2$$

$$= B\mathfrak{R}^2 - 2B\mathfrak{R} \cdot \mathbf{L} + B(L_x^2 + L_y^2). \quad (24)$$

This cross term is precisely the effective perturbing term that appears in the electronic problem if the time-dependent problem of motion with respect to a classically rotating set of force centers is reduced to finding a wave function that is stationary with respect to the rotating frame.[23] If we assume that electronic excited states lie reasonably high, we can take account of these effects by first-order perturbation theory with the result that

$$\psi_0 = \psi_0^0 - \sum_n \frac{(n | A\mathbf{L} \cdot \mathbf{S} - 2B\mathbf{L} \cdot \mathfrak{R} | 0)}{E_n - E_0} \psi_n^0. \quad (25)$$

The indicated matrix elements are quadratures over orbital functions. Since the operators $\mathbf{S}$ and $\mathfrak{R}$ are independent of the orbital wave functions, they may be simply taken out and treated as numbers at this stage. We note that elements of $L_z$ are diagonal in $\Lambda$ and proportional to $\Lambda$ and thus vanish for the $\Sigma$ state with which we are dealing. Further, in a field of axial symmetry, we have the relation[24]

$$(\Lambda | L_y | \Lambda \pm 1) = \pm i(\Lambda | L_x | \Lambda \pm 1), \quad (26)$$

all other elements vanishing. Thus the perturbed $^3\Sigma$ wave function has only $\pi$ states mixed in, and the mixing is proportional to the matrix elements of elec-

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[21] This rather phenomenological replacement is supported by the considerable success it has had in application to molecular spectra by Van Vleck [Phys. Rev. 33, 467 (1929)] and others. It is theoretically insecure in that even for the one electron case the form $\mathbf{l} \cdot \mathbf{s}$ is rigorous only in a central field. For the case of many electrons, it is necessary to consider a form at least as general as $\sum_i a_i \mathbf{l}_i \cdot \mathbf{s}_i$ to get the possibility of matrix elements between states of different multiplicity [R. Schlapp, Phys. Rev. 39, 806 (1932)]. Despite these objections, we adopt the assumption as the most reasonable one-parameter form, since more rigorous calculation with the exact interaction is precluded by computational difficulty and the lack of reliable wave functions for excited states.

[22] The $B$ in this expression is the half reciprocal moment $B_N$ of the bare nuclei, the electronic contribution to the rotational energy being given explicitly by the cross terms. To simplify notation, we simply write $B$ here. It is included in the quadrature because it is still an operator. We would only neglect the higher order effects of vibration on the electronic motion through the rotation by replacing $B$ by the constant $B_e$ without any $\xi$ dependence.

[23] G. C. Wick. Z. Physik 85, 25 (1933); Phys. Rev. 73, 51 (1948).

[24] See reference 7, p. 219.

tronic orbital angular momentum perpendicular to the axis.

$$\psi_\Sigma = \psi_\Sigma^0 - \sum_{n=\pi} \sum_{g=x,y} \frac{(n|AL_g|0)S_g - (n|2BL_g|0)\Re_g}{E_n - E_0} \psi_n^0. \tag{27}$$

### Effect on Energy

Next we find the contribution of these perturbation terms to the energy. This is

$$E'' = -\sum_n \sum_{gg'} \frac{[(n|AL_g|0)S_g - (n|2BL_g|0)\Re_g][(n|AL_{g'}|0)^*S_{g'}^* - (n|2BL_{g'}|0)^*\Re_{g'}^*]}{E_n - E_0}. \tag{28}$$

Using the property (26) of the matrix elements of $L$, we see that $xy$ terms drop out, and this reduces to the form

$$E'' = \tfrac{2}{3}\lambda''[3S_z^2 - S(S+1)]$$
$$+ \mu''\Re \cdot S - B''\Re^2 + \text{const}, \tag{29}$$

where

$$\lambda'' = \tfrac{1}{2}\sum_n \frac{|(n|AL_x|0)|^2}{E_n - E_0}, \quad B'' = 4\sum_n \frac{|(n|BL_x|0)|^2}{E_n - E_0},$$

$$\mu'' = 4\,\mathrm{Re}\sum_n \frac{(0|AL_x|n)(n|BL_x|0)}{E_n - E_0}. \tag{30}$$

These results are the same as those found by Hebb[25] except for a factor of two stemming from the fact that he counts each $\pi$ state once whereas each appears twice (as $\Lambda = \pm 1$) in our expression. The term in $\lambda''$ is the second-order effect of the spin-orbit energy and turns out to be small. The term in $\mu''$ gives the spin-orbit coupling energy to the electronic angular momentum of the $\pi$ states admixed by the rotation. $B''$ lowers the effective reciprocal moment of inertia from the nuclear value, $B_N$, essentially by the addition of electronic mass to the rotating frame.[26]

Since the actual matrix elements required cannot be calculated in the absence of wave functions for the $\pi$ states, these sums cannot be evaluated from first principles. However, to a reasonably good approximation these may be simplified by treating $A$ and $B$ as constants rather than as functions of the configuration. In particular, $B$ can be considered to have the value observed in the electronic ground state and the order of magnitude of $A$ can be estimated from the multiplet separation of the $\pi$ states. With $A$ and $B$ removed, all the sums become the same, namely,

$$\sum_n \frac{(n|L_x|0)^2}{E_n - E_0} = \frac{L(L+1)}{h\nu}. \tag{31}$$

The right member is merely symbolic, but if we use Van Vleck's "hypothesis of pure precession"[27] it could be used to infer the characteristic energy separation $h\nu$. This sum then becomes a single disposable parameter, and theoretical relations between the various quantities become possible. This feature is greatly enhanced by the fact that the theory of the interaction of the molecule with a magnetic field (to be given in a subsequent paper) reveals two other experimentally accessible quantities of this same form. By combining all of these, a remarkably complete separation of effects, with some internal checks, becomes possible.

### C. Analysis of Results

If we now collect the terms that depend on other than electronic coordinates, we have the effective Hamiltonian for vibration, rotation, and spin orientation. It is

$$\mathcal{H}_{\mathrm{eff}} = P_R^2/2M + \tfrac{1}{2}M\omega_e^2 R_e^2\xi^2 + b\xi^3$$
$$+ B\Re^2 + \tfrac{2}{3}\lambda(3S_z^2 - S^2) + \mu\Re \cdot S, \tag{32}$$

where

$$B = B_N - B'', \quad \lambda = \lambda' + \lambda'', \quad \mu = \mu' + \mu''. \tag{33}$$

Because they enter in exactly the same form, $\lambda'$, $\lambda''$; $\mu'$, $\mu''$; and $B$, $B''$ will be indistinguishable in the eigenvalues of this operator. They can be separated, however, if one uses the results of the theoretical calculations and of the Zeeman-effect experiments.

With the known experimental value of $\mu = \mu' + \mu''$ (see Sec. III), and the value of $\mu'$ calculated in the previous section, we can determine $\mu''$ to be $-262.7$ Mc/sec. Taking $B = 43.1$ kMc/sec, this implies that $AL(L+1)/h\nu$ is $-1.52 \times 10^{-3}$ which is consistent with reasonable values of $A$, $L(L+1)$, and $h\nu$. In particular, the minus sign checks with the plus sign for $A$ in the $\pi$ states of $O_2^+$ according to Van Vleck's general theory.[28] Using the value $A = -21$ cm$^{-1}$ indicated by the Zeeman-effect studies, we find $\lambda''$ to be $465$ Mc/sec, leaving $58\,920$ Mc/sec of the experimental value to the first-order spin-spin mechanism. This establishes the previous statement that the spin-spin contribution dominates. In fact, the second-order contribution is so small that errors in its estimation will not introduce much

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

[26] It is interesting to note that the diagonal value of $H_{\mathrm{el}}$ itself is *raised* by precisely $B''\Re^2$ due to the increased momentum of the electrons with respect to the fixed frame. The nuclear energy is lowered by $2B''\Re^2$ because the added mass reduces its share of the quantized total angular momentum. The net effect is the lowering of energy quoted above.

[27] See reference 8, p. 488.

[28] See reference 8, p. 499.

uncertainty in the correct value for the spin-spin part. Therefore $\lambda$ serves as a reliable check on the quanity of the wave function. The facts are that the calculated value was 40 percent low even after adjusting $b$ to give a better approximation to the Hartree-Fock atomic orbital near the nucleus, and it was 80 percent low with Meckler's choice of $b$. We must conclude that wave functions chosen to minimize the electronic energy cannot be expected to give good results for a quantity which has a dependence on coordinates that differs from that of the electronic energy. On the other hand, if a wave function did give a good result for $\lambda$ as well as for the electronic energy, there would be grounds for believing that it is a superior approximation to the true eigenfunction.

Using the same values for $B$ and $L(L+1)/h\nu$, we compute $B'' = 17.3$ Mc/sec, which is a correction of 400 ppm (parts per million). The usual procedure of using atomic rather than nuclear masses reduces this correction by 270 ppm, leaving 130 ppm. Since the experimentally quoted values for $B$ from infrared data are presumed to be accurate to 10 ppm (being quoted to 1 ppm[4]), it is clear that this rather sizable correction should be applied in inferring the internuclear distance from $B_{\text{eff}}$ and the atomic masses. This correction decreases the computed $R$ by 65 ppm. Recalculation,[29] using Herzberg's value for $(B_{\text{eff}})_e$ and the newly adjusted atomic constants, yields $R_e = 1.20741_5$ A.

## III. SOLUTION OF THE FINE-STRUCTURE PROBLEM

### A. Energy Levels and Spectrum

As outlined in Sec. I, our problem is to find eigenvalues and eigenvectors for the Hamiltonian operator $\mathcal{JC} = \mathcal{JC}_{\text{vib}} + \mathcal{JC}_{\text{rot}} + \mathcal{JC}_{\text{spin}}$. Since we will solve this in a Hund case $(a)$ representation with $v$, $J$, $M$, $S$, and $\Sigma$ diagonal, we eliminate $\mathfrak{N}$ from (32) by noting that $\mathfrak{N} = \mathbf{J} - \mathbf{S}$. This leads to

$$\mathcal{JC} = P_R^2/2M + \tfrac{1}{2}M\omega_e^2 R_e^2 \xi^2 + b\xi^3 + B\mathbf{J}^2 + 2\lambda S_z^2$$
$$+ (\mu - 2B)\mathbf{J}\cdot\mathbf{S} + (B - \mu - \tfrac{2}{3}\lambda)\mathbf{S}^2, \quad (34)$$

where

$$B = B_e(1 - 2\xi + 3\xi^2),$$
$$\lambda = \lambda_e + \lambda_1\xi + \lambda_2\xi^2. \quad (35)$$

The expansion of $B$ to allow for the nonrigidity of the molecule is well known. The first two coefficients in the expansion of $\lambda$ have been estimated theoretically in Sec. II but all three are treated as parameters to be evaluated by fitting the experimental data. No $\xi$ de-

pendence has been given $\mu$ because the same value sufficed for both $v=0$ and $v=1$ states as observed in the infrared spectra[30] whereas a change in $\lambda$ was required.

The required matrix components are (suppressing quantum numbers in which the element is diagonal and which have no effect on its value, and suppressing $h$):

$$(J|\mathbf{J}^2|J) = J(J+1),$$

$$(S\Sigma|S_z|S\Sigma) = \Sigma,$$

$$(JS\Sigma|\mathbf{J}\cdot\mathbf{S}|JS\Sigma') = \tfrac{1}{2}[J(J+1) - \Sigma(\Sigma\pm1)]^{\frac{1}{2}}$$
$$\times[S(S+1) - \Sigma(\Sigma\pm1)]^{\frac{1}{2}}\delta_{\Sigma',\Sigma\pm1} + \Sigma^2\delta_{\Sigma',\Sigma},$$

$$(v|\xi|v') = \epsilon^{\frac{1}{2}}[(v+1)^{\frac{1}{2}}\delta_{v',v+1} + v^{\frac{1}{2}}\delta_{v',v-1}],$$

$$(v|\xi^2|v') = \epsilon[(v+1)^{\frac{1}{2}}(v+2)^{\frac{1}{2}}\delta_{v',v+2} + (2v+1)\delta_{v',v}$$
$$+ v^{\frac{1}{2}}(v-1)^{\frac{1}{2}}\delta_{v',v-2}], \quad (36)$$

$$(v|\xi^3|v') = \epsilon^{\frac{3}{2}}[(v+1)^{\frac{1}{2}}(v+2)^{\frac{1}{2}}(v+3)^{\frac{1}{2}}\delta_{v',v+3}$$
$$+ 3(v+1)^{\frac{3}{2}}\delta_{v',v+1} + 3v^{\frac{3}{2}}\delta_{v',v-1}$$
$$+ v^{\frac{1}{2}}(v-1)^{\frac{1}{2}}(v-2)^{\frac{1}{2}}\delta_{v',v-3}],$$

where $\epsilon = B_e/h\omega_e = h/2MR_e^2\omega_e$ and $\delta_{v',v}$ is the Kronecker symbol. The elements of $\mathbf{J}\cdot\mathbf{S}$ are obtained by noting that $J$ satisfies the "reversed" commutation relation[7] in the gyrating frame and that $J_z = \Sigma$ since $N_z = 0$. Since $\mathbf{S}$ obeys ordinary commutation relations, we have the result given above. The elements of $\xi^2$ and $\xi^3$ are obtained by matrix multiplication of the familiar matrix elements of $\xi$ for the harmonic oscillator.

Using these elements, the Hamiltonian matrix is readily written explicitly. Since all elements are diagonal in $J$, $M$, and $S$, we can write the elements simply as $(v\Sigma|\mathcal{JC}|v'\Sigma')$. Since the vibrational level separation is so large, compared to rotational and spin energies, we can apply the Van Vleck transformation to reduce this matrix to an effective Hamiltonian matrix for the structure within each vibrational level.[31] Using

$$(v\Sigma|H_{\text{eff}}|v\Sigma') = -\sum_{\Sigma''v'}\frac{(v\Sigma|\mathcal{JC}|v'\Sigma'')(v'\Sigma''|\mathcal{JC}|v\Sigma')}{E_{v'} - E_v}, \quad (37)$$

we obtain a $3\times3$ matrix between the $\Sigma = \pm1, 0$ states for a given vibrational (and total angular momentum) state. Including terms of order $\epsilon^2$,[32] these reduced ele-

[29] It is significant to note that the recommended lease-squares fitted value of $(Nh/c)^{\frac{1}{2}}$, which enters in the conversion, has increased by 76 ppm between 1947 and 1952 [J. W. M. Dumond and E. R. Cohen, Revs. Modern Phys. 20, 82 (1948) and 25, 691 (1953)]. By chance, this almost exactly cancels this new theoretical correction for the electrons. Thus it is clear that the last decimal places of quoted values for $R_e$ are significant only when a precise allowance can be made for the electronic contribution and even then only to the limit of our knowledge of the fundamental constants.

[30] In some excited states, such as the $^3\Sigma_u^-$ state, $\mu$ is an order of magnitude larger than it is in the ground state, and its $\xi$ dependence can no longer be overlooked [P. Brix and G. Herzberg, Can. J. Phys. 32, 110 (1954)]. Inclusion of this $\xi$ dependence would involve no difficulty. However, for the high vibrational states observed in the $^3\Sigma_u^-$ state our simple approximation to the vibrational potential would have to be greatly extended. We avoid these accumulating complications by confining our treatment to the ground state.

[31] E. C. Kemble, The Fundamental Principles of Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1937).

[32] Detailed consideration shows that a somewhat more accurate treatment in this case of the anharmonic oscillator is obtained by replacing $\epsilon = B_e/h\omega_e$ by $\epsilon' = B_{(0)}/h\omega_{01}$, where $h\omega_{01} = E_0(v=1) - E_0(v=0)$. This has been done in the numerical evaluations.

ments are

$$w = (vJ1|H_{eff}|vJ1) = B_v J(J+1)$$
$$- \epsilon^2[(8B-8\lambda_1)J(J+1)+4BJ^2(J+1)]$$

$$x = (vJ0|H_{eff}|vJ0) = -(2\lambda_v+\mu)+B_v(J^2+J+2)$$
$$- \epsilon^2[4B(J^2+J+2)^2+16BJ(J+1) \quad (38)$$
$$+16\lambda_1(J^2+J+2)/3+4\lambda_1^2/3B],$$

$$y = (vJ0|H_{eff}|vJ1) = [J(J+1)/2]^{\frac{1}{2}}$$
$$\times\{\mu-2B_v+\epsilon^2[16B(J^2+J+1)+8\lambda_1/3]\},$$

$$z = (vJ1|H_{eff}|vJ-1) = -\epsilon^2 8BJ(J+1),$$

where

$$B_v = B_e[1+(2v+1)(3\epsilon+12b\epsilon^3 B^{-1})],$$
$$\quad (39)$$
$$\lambda_v = \lambda_e + (2v+1)(\epsilon\lambda_2 - 6b\epsilon^3 B^{-1}\lambda_1).$$

We note that large vibration-dependent terms can be taken out by defining $v$-dependent constants $\lambda_v$ and $B_v$. This is the first-order Born-Oppenheimer approximation. However, there are higher-order centrifugal distortion terms that cannot be eliminated in this way. In these terms the distinction between $B_e$ and $B_v$ is unnecessary and the subscripts are dropped. (Numerical evaluation was actually made with the use of $B_v$.) The diagonal elements given here are such that the zero of energy is

$$E_0(v) = (v+\tfrac{1}{2})\hbar\omega_e$$
$$-30b^2\epsilon^3(\hbar\omega_e)^{-1}(v^2+v+11/30)+\tfrac{2}{3}\lambda_v-\mu. \quad (40)$$

Application of the Wang[33] symmetrizing transformation to the Hamiltonian matrix with the elements (38) yields a factored secular equation by separating symmetric and antisymmetric states. This allows an exact solution, the eigenvalues being

$$E - E_v(v) = w - z,$$
$$\tfrac{1}{2}(w+x+z)\pm\{[(w-x+z)/2]^2+2y^2\}. \quad (41)$$

The results can be stated concisely as

$$E(J=K) - E_0(v) = w - z$$
$$= (B_v+8\epsilon^2\lambda_1/3)K(K+1)-4B\epsilon^2 K^2(K+1)^2, \quad (42)$$

$$\nu_-(K) = E(J=K) - E(J=K-1) = \lambda_v+\mu/2+B_v(2K-1)$$
$$+4\epsilon^2[B(-4K^3+6K^2-6K+2)$$
$$+(\lambda_1/3)(3K^2+K+4+\lambda_1/2B)]$$
$$-[\sum_{n=0}^{3} A_n K^n(K-1)^n]^{\frac{1}{2}}, \quad (43)$$

$$\nu_+(K) = E(J=K) - E(J=K+1) = \lambda_v+\mu/2-B_v(2K+3)$$
$$+4\epsilon^2[B(4K^3+18K^2+30K+18)$$
$$+(\lambda_1/3)(3K^2+5K+6+\lambda_1/2B)]$$
$$+[\sum_{n=0}^{3} A_n(K+1)^n(K+2)^n]^{\frac{1}{2}}, \quad (44)$$

[33] S. C. Wang, Phys. Rev. 34, 249 (1929); King, Hainer, and Cross, J. Chem. Phys. 11, 27 (1943).
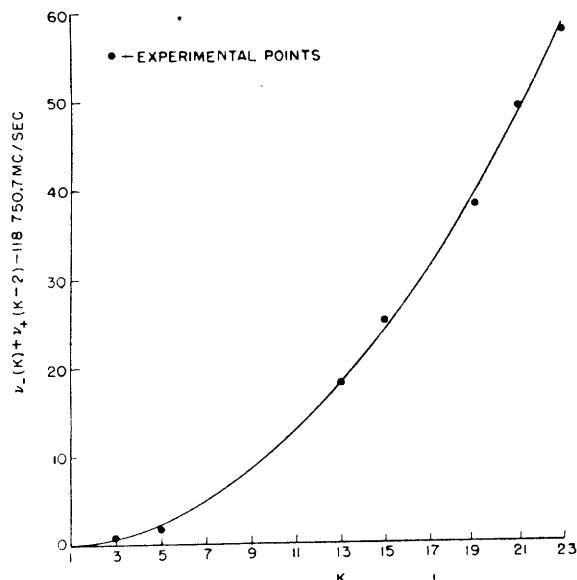


FIG. 1. Comparison of theoretical and experimental dependence of the sum $\nu_-(K)+\nu_+(K-2)$ on the rotational quantum number $K$.

where

$$A_0 = [(\lambda_v+\mu/2-B_v)+\epsilon^2(8B+16\lambda_1/3+2\lambda_1^2/3B)]^2,$$

$$A_1 = [\mu-2B_v+\epsilon^2(16B+8\lambda_1/3)]^2+\epsilon^2(16B+8\lambda_1)$$
$$\times[\lambda+\mu/2-B+\epsilon^2(8B+16\lambda_1/3+2\lambda_1^2/3B)],$$

$$A_2 = \epsilon^2\{32B[(\mu-2B)+\epsilon^2(16B+2\lambda_1/3)]$$
$$+\epsilon^2(8B+4\lambda_1)^2\}, \quad (45)$$

$$A_3 = \epsilon^4 256B^2.$$

$J=0$ is a special case in which the secular equation reduces to a linear one. The results are

$$E(J=0, K=1) - E_0(v) = -(2\lambda_v+\mu)$$
$$+2B_v-4\epsilon^2(4B+8\lambda_1/3+\lambda_1^2/3B)$$

and

$$\nu_-(1) = 2\lambda_v+\mu+16\epsilon^2[\lambda_1+\lambda_1^2/12B]. \quad (43')$$

These results are labeled using $K$ as the rotational quantum number to conform to the usual practice. Because of the spin coupling, $\mathfrak{K}^2$ is not a rigorous constant of the motion, but $K$ describes the dominant value of $\mathfrak{K}$ when the eigenfunctions are expanded in a Hund case (b) representation. The fact that the state function of $(O^{16})_2$ must be totally symmetric on interchange of nuclei requires that only states with odd $K$ exist. This restriction does not exist with $O^{16}O^{17}$ or $O^{16}O^{18}$.

In fitting the spectrum it is useful to note that

$$\nu_-(K)+\nu_+(K-2)$$
$$= 2\lambda_v+\mu+8\epsilon^2\lambda_1(K^2-K+2+\lambda_1/6B). \quad (46)$$

The precision with which this parabolic form fits the experimental data is shown in Fig. 1. By considering sums of this sort, one readily determines $(2\lambda_v+\mu)$ and

TABLE III. Experimental spin coupling constants (Mc/sec).

| | |
|---|---|
| $\lambda_e = 59\,386 \pm 20$ | $\lambda_{(0)} = 59\,501.57 \pm 0.15$ |
| $\lambda_1 = 16\,896 \pm 150$ | $\lambda_{(1)} = 59\,730.00 \pm 40$ |
| $\lambda_2 = (5 \pm 2) \times 10^4$ | $\mu = \quad 252.67 \pm 0.05$ |

$\lambda_1$. With these constraints, $\mu$ and $\lambda_v$ are separately fixed by considering individual frequencies, using (43) and (44). Because the results are so insensitive to $B$, $b$, and $\omega_e$, the precise infrared values were used rather than attempting a fitting from the microwave data. In making the conversions, the velocity of light was taken to be $2.99790 \times 10^{10}$ cm/sec. Some of the derived constants are $B_{(0)} = 43.1029$ kMc/sec, $b = -32.012$ kMc/sec, and $\epsilon = B_{(0)}/\hbar\omega_{01} = 0.92384 \times 10^{-3}$.

To determine $\lambda_2$ it is necessary to use data from an excited vibrational state. For this purpose, the infrared data of Babcock and Herzberg[4] for the $v = 1$ state of $(O^{16})_2$ were fitted with (46) to determine $\lambda_{(v=1)}$. This fitting gave a result agreeing within its precision with the value obtained by Babcock and Herzberg by fitting the less accurate Schlapp[34] formula.

The results of all the fittings are tabulated in Table III. The indicated errors in $\lambda$ are the statistically expected standard errors in the quoted mean values.

Table IV lists all of the microwave experimental data[3,35–37] and the theoretical frequencies computed by the use of these constants and formulas (43) and (44). The quoted fitting was made using the data of Burkhalter et al.[3] and of Gokhale and Strandberg,[35] neglecting the apparently erroneous $\nu_-(25)$ and the wave-meter measurements. Since then the data of Mizushima and Hill[36] has become available. It improves the previous values of $\nu_-(1)$ and $\nu_-(25)$ and fills in some gaps in the spectrum previously known only to wave-meter accuracy. If $\lambda_{(0)}$ and $\lambda_1$ are determined by fitting this new data with (46), the means agree with the above results well within the standard error, but the standard errors in the new data are twice as large as the old (which are quoted above).

At this point, let us relate this solution with previous ones. In the works of Kramers,[10] of Hebb,[25] and of Schlapp[34] the nonrigidity of the nuclear framework is neglected. Thus $\epsilon = B/\hbar\omega = 0$. Further, all their results are in error in that $B$ must be replaced by $(B - \frac{1}{2}\mu)$. Kramers and Hebb both quote their results only to first order in $\lambda/B$, but Hebb indicates the manner in which the more exact solution using the radical is obtained from the work of Hill and Van Vleck.[38] Schlapp gives the form with the radical. His solution gave satisfactory agreement with the infrared data, provided that different values of $B$ and $\lambda$ were chosen for excited vibrational states.

The precise microwave measurements of Burkhalter et al.[3] revealed substantial deviations from the Schlapp formulas. In particular, the sum $\nu_-(K) + \nu_+(K-2)$ was not constant as predicted by the Schlapp formula (our (46) with $\epsilon = 0$), but increased with $K$. Burkhalter obtained a reasonable fit by empirically adding $\delta K + \alpha K(K+1)^{-\frac{1}{2}}$ to Schlapp's $\nu_-(K)$, leaving $\nu_+(K)$ unchanged. Gokhale[39] considered the effect of centrifugal distortion on $B$, but assumed $\lambda$ and $\mu$ independent of $R$. Thus he failed to obtain a theoretical explanation for the deviations. He did, however, correct the confusion between $B$ and $B - \frac{1}{2}\mu$, as did all succeeding workers.

Miller and Townes[40] reviewed the problem, and fitted the spectrum satisfactorily by making both $B$ and $\lambda$ in their formulas depend on $K$ through centrifugal distortion correction terms proportional to $K(K+1)$. Their formulas are

$$\nu_-(K) = \lambda + \mu K + (2K-1)(B - \tfrac{1}{2}\mu)$$
$$- [\lambda^2 - 2\lambda(B - \tfrac{1}{2}\mu) + (2K-1)^2(B - \tfrac{1}{2}\mu)^2]^{\frac{1}{2}},$$
$$\nu_+(K) = \lambda - \mu(K+1) - (2K+3)(B - \tfrac{1}{2}\mu) \quad (47)$$
$$+ [\lambda^2 - 2\lambda(B - \tfrac{1}{2}\mu) + (2K+3)^2(B - \tfrac{1}{2}\mu)^2]^{\frac{1}{2}}.$$

TABLE IV. Comparison of experimental and calculated frequencies in Mc/sec for $(O^{16})_2$ fine-structure transitions.

| K | Burkhalter et al.[a] | Experimental Gokhale and Strandberg[b] | Mizushima and Hill[c] | Calculated |
|---|---|---|---|---|
| | | $\nu_+(K)$ | | |
| 1 | 56 265.1 | 56 265.2±0.5 | 56 265.6±0.6 | 56 264.7 |
| 3 | 58 446.2 | 58 446.3±0.4 | 58 446.2±0.2 | 56 446.9 |
| 5 | 59 610[d] | | 59 591.4±0.2 | 59 591.5 |
| 7 | 60 436[d] | | 60 433.4±0.2 | 60 435.5 |
| 9 | 61 120[d] | | 61 149.6±0.2 | 61 151.3 |
| 11 | 61 800.2 | | 61 799.8±0.4 | 61 800.9 |
| 13 | 6? 411.7 | 62 412.9±0.8 | 62 413.8±0.4 | 62 411.9 |
| 15 | 62 970[d] | | 62 996.6±0.2 | 62 998.5 |
| 17 | 63 568.3 | | 63 567.2±0.2 | 63 568.7 |
| 19 | 64 127.6 | | 64 128.0±0.8 | 64 127.6 |
| 21 | 64 678.9 | | 64 678.2±0.2 | 64 678.2 |
| 23 | 65 220[d] | | 65 224.2±0.8 | 65 222.7 |
| 25 | 65 770[d] | | | 65 762.6 |
| | | $\nu_-(K)$ | | |
| 1 | 118 745.5[e] | | 118 750.5±0.5 | 118 750.7 |
| 3 | 62 486.1 | 62 486.2±0.4 | 62 487.2±0.4 | 62 486.7 |
| 5 | 60 306.4 | | 60 308.0±0.2 | 60 306.1 |
| 7 | 59 163.4 | 59 164.2±0.2 | 59 163.4±0.2 | 59 164.0 |
| 9 | 58 324.0 | 58 324.9±0.3 | 58 323.2±0.1 | 58 323.6 |
| 11 | 57 612.0 | 57 612.3±0.4 | 57 611.4±0.2 | 57 612.1 |
| 13 | 56 968.7 | | 56 970.8±0.4 | 56 967.8 |
| 15 | 56 362.8 | 56 364.2±0.5 | 56 364.0±0.4 | 56 363.1 |
| 17 | 55 784.1 | | 55 784.6±0.4 | 55 783.6 |
| 19 | 55 220.8 | | 55 221.6±0.4 | 55 221.5 |
| 21 | 54 672.5 | | | 54 671.6 |
| 23 | 54 130.0 | | 54 129.4±0.4 | 54 130.9 |
| 25 | 53 592.2 | | 53 599.4±0.8 | 53 597.3 |

[a] See reference 3.
[b] See reference 35.
[c] See reference 36.
[d] Wave-meter reading.
[e] See reference 37.

[34] R. Schlapp, Phys. Rev. 51, 342 (1937).
[35] B. V. Gokhale and M. W. P. Strandberg, Phys. Rev. 84, 844 (1951).
[36] M. Mizushima and R. M. Hill, Phys. Rev. 93, 745 (1954).
[37] Anderson, Johnson, and Gordy, Phys. Rev. 83, 1061 (1951).
[38] E. L. Hill and J. H. Van Vleck, Phys. Rev. 32, 250 (1928).

[39] B. V. Gokhale, Ph.D. thesis, Massachusetts Institute of Technology, 1951 (unpublished).
[40] S. L. Miller and C. H. Townes, Phys. Rev. 90, 537 (1953).

Since these formulas are derived from a secular equation connecting several $K$ states, the values of $B$ and $\lambda$ are not well defined and this procedure is not rigorous. Further, it fails to give a value for $d\lambda/dR$, and it fails to provide the single Hamiltonian (for all $K$) needed in deriving diagonalizing transformations preparatory to introducing other perturbations. Finally, while this work was being completed, Mizushima and Hill[36] have published a treatment that takes account of centrifugal distortion under the adiabatic approximation but assumes a harmonic vibrational potential. This treatment fails to provide a value for $\lambda_e$ or $\lambda_2$,[41] and does not give the diagonalizing transformation. Thus the present treatment verifies Mizushima and Hill's general results and gives somewhat more information about the molecule. The closeness of fit to the experimental data is about equal to that of the methods of Miller and Townes and of Mizushima and Hill.

## B. State Functions

We now obtain the $3\times3$ diagonalizing matrix which expresses the eigenvectors of the matrix (38) in the Hund case $(a)$ representation. Our eigenvalues as given by (41) are inserted into the matrix equation

$$\{H_{\text{eff}}-[E+E_0(v)]\}\psi=0,$$

where

$$H_{\text{eff}}=\begin{bmatrix} w & y & z \\ y & x & y \\ z & y & w \end{bmatrix}. \qquad (48)$$

The quantities $w$, $x$, $y$, and $z$ are matrix elements defined in (38). The result of solving this equation is the transformation matrix:

$$T_J=(\psi_{K=J-1},\psi_{K=J},\psi_{K=J+1})$$

$$=\begin{matrix} \Sigma=-1 \\ 0 \\ 1 \end{matrix}\begin{bmatrix} a_J & -1/\sqrt{2} & c_J \\ \sqrt{2}c_J & 0 & -\sqrt{2}a_J \\ a_J & 1/\sqrt{2} & c_J \end{bmatrix}, \qquad (49)$$

where

$$c_J=2^{-\frac{1}{2}}ra_J=2^{-\frac{1}{2}}r(2+r^2)^{-\frac{1}{2}},$$
$$r=[E-E_v(v)-w-z]x^{-1}|_{J=K+1}. \qquad (50)$$

These coefficients are listed in Table V for the states occurring in $(O^{16})_2$.

For comparison, we note that if oxygen were a rigorous example of Hund's case $(b)$, in which $K=\mathfrak{K}$ is a good quantum number, the transformation could be obtained by simply diagonalizing the operator $\mathfrak{K}^2=J^2+S^2-2\mathbf{J}\cdot\mathbf{S}$. If this is done, the result is of the same form but with

$$a_{J'}=\frac{1}{2}\left(\frac{J+1}{J+\frac{1}{2}}\right)^{\frac{1}{2}}, \quad c_{J'}=\frac{1}{2}\left(\frac{J}{J+\frac{1}{2}}\right)^{\frac{1}{2}}. \qquad (51)$$

---

[41] Note that his $\lambda_1$ is related to ours by $(\lambda_1)_M=4\epsilon^2(\lambda_1)_T$. Also note that he has apparently omitted a numerical factor of $2\pi$ in going from his Eq. (17b) to (18). As a result, his value for $(d\lambda/dR)_e$ is inconsistent with ours.

TABLE V. Transformation coefficients of eigenvectors. $a_J$ and $c_J$ give O₂ eigenvectors with respect to Hund $(a)$ basis, and $a_J{'}$ and $c_J{'}$ give Hund $(b)$ eigenvectors with respect to Hund $(a)$ basis, by use of Eq. (49). $b_J$ and $d_J$ express O₂ eigenfunctions with respect to Hund $(b)$ basis by Eq. (54).

| $J$ | $a_J$ | $c_J$ | $a_J{'}$ | $c_J{'}$ | $b_J$ | $d_J$ |
|---|---|---|---|---|---|---|
| 2 | 0.480462 | 0.518803 | 0.547723 | 0.447214 | 0.990351 | 0.138582 |
| 4 | 0.489369 | 0.510410 | 0.527046 | 0.471404 | 0.997059 | 0.076638 |
| 6 | 0.492680 | 0.507214 | 0.518874 | 0.480384 | 0.998594 | 0.053009 |
| 8 | 0.494413 | 0.505525 | 0.514496 | 0.485071 | 0.999178 | 0.040530 |
| 10 | 0.495480 | 0.504480 | 0.511766 | 0.487950 | 0.999462 | 0.032813 |
| 12 | 0.496202 | 0.503769 | 0.509902 | 0.489898 | 0.999620 | 0.027569 |
| 14 | 0.496723 | 0.503256 | 0.508548 | 0.491304 | 0.999717 | 0.023776 |
| 16 | 0.497117 | 0.502867 | 0.507519 | 0.492366 | 0.999782 | 0.020902 |
| 18 | 0.497424 | 0.502562 | 0.506712 | 0.493197 | 0.999825 | 0.018652 |
| 20 | 0.497671 | 0.502318 | 0.506061 | 0.493865 | 0.999858 | 0.016842 |
| 22 | 0.497873 | 0.502117 | 0.505525 | 0.494413 | 0.999881 | 0.015355 |
| 24 | 0.498042 | 0.501950 | 0.505076 | 0.494872 | 0.999900 | 0.014112 |
| 26 | 0.498185 | 0.501808 | 0.504695 | 0.495261 | 0.999914 | 0.013057 |

Using this latter transformation, we may transform (48) to a Hund case $(b)$ basis. The result is

$$H_{\text{eff}}=\begin{matrix} \mathfrak{K}=J-1 \\ J \\ J+1 \end{matrix}\begin{bmatrix} \alpha & 0 & \delta \\ 0 & \beta & 0 \\ \delta & 0 & \gamma \end{bmatrix}, \qquad (52)$$

where

$$\alpha=B_vJ(J-1)-2\lambda_v\frac{J}{2J+1}+\mu J-\epsilon^2\left[4BJ^2(J-1)^2\right.$$
$$+\frac{8}{3}\lambda_1\frac{J(J-1)^2}{2J+1}+\frac{4}{3}\frac{\lambda_1^2}{B}\frac{J}{2J+1}\right],$$

$$\beta=B_vJ(J+1)-\epsilon^2J(J+1)[4BJ(J+1)-(8/3)\lambda_1],$$

$$\gamma=B_v(J+1)(J+2)-2\lambda_v\frac{J+1}{2J+1}-\mu(J+1)$$
$$-\epsilon^2\left[4B(J+1)^2(J+2)^2+\frac{8}{3}\lambda_1\frac{(J+1)(J+2)^2}{2J+1}\right.$$
$$\left.+\frac{4}{3}\frac{\lambda_1^2}{B}\frac{(J+1)}{(2J+1)}\right],$$

$$\delta=\frac{[J(J+1)]^{\frac{1}{2}}}{2J+1}\{2\lambda_v+\epsilon^28\lambda_1[(J^2+J+1)+\lambda_1/6B]\}. \qquad (53)$$

This matrix is of course identical to that which would have been obtained if the entire problem had been set up in terms of Hund's case $(b)$ instead of $(a)$.[42]

The transformation which gives the oxygen eigenvector, characterized by $K$, with respect to the Hund $(b)$ basis, characterized by $\mathfrak{K}$, is found to be

$$T_J{}^{(b)}=(T_J{'})^{-1}T_J=\begin{matrix} \mathfrak{K}=J-1 \\ J \\ J+1 \end{matrix}\begin{bmatrix} b_J & 0 & d_J \\ 0 & 1 & 0 \\ -d_J & 0 & b_J \end{bmatrix}, \qquad (54)$$

---

[42] This has been verified with the use of the case $(b)$ matrix elements given by J. H. Van Vleck [Revs. Modern Phys. 23, 213 (1951), p. 222]. The effective Hamiltonian matrix in Mizushima and Hill's manuscript (reference 36) gives somewhat different coefficients for $\lambda_1$. His error seems to have arisen in subtracting a $\frac{2}{3}\lambda$, treated as independent of $\mathfrak{K}$, from the diagonal elements.

TABLE VI. Matrix elements of the direction cosines.[a]

| $J' =$ | $J-1$ | $J$ | $J+1$ |
|---|---|---|---|
| $(J|\Phi|J')$ | $[J(4J^2-1)^{\frac{1}{2}}]^{-1}$ | $[J(J+1)]^{-1}$ | $\{(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}\}^{-1}$ |
| $(J\Omega|\Phi_{Fz}|J'\Omega)$ | $[J^2-\Omega^2]^{\frac{1}{2}}$ | $\Omega$ | $[(J+1)^2-\Omega^2]^{\frac{1}{2}}$ |
| $(J\Omega|\Phi_{Fx}|J'\Omega\pm1)=\pm i(J\Omega|\Phi_{Fy}|J'\Omega\pm1)$ | $\pm\frac{1}{2}[(J\mp\Omega)(J\mp\Omega-1)]^{\frac{1}{2}}$ | $\frac{1}{2}[J(J+1)-\Omega(\Omega\pm1)]^{\frac{1}{2}}$ | $\mp\frac{1}{2}[(J\pm\Omega+1)(J\pm\Omega+2)]^{\frac{1}{2}}$ |
| $(JM|\Phi_{Zz}|J'M)$ | $[J^2-M^2]^{\frac{1}{2}}$ | $M$ | $[(J+1)^2-M^2]^{\frac{1}{2}}$ |
| $(JM|\Phi_{Xz}|J'M\pm1)=\mp i(JM|\Phi_{Yz}|J'M\pm1)$ | $\pm\frac{1}{2}[(J\mp M)(J\mp M-1)]^{\frac{1}{2}}$ | $\frac{1}{2}[J(J+1)-M(M\pm1)]^{\frac{1}{2}}$ | $\mp\frac{1}{2}[(J\pm M+1)(J\pm M+2)]^{\frac{1}{2}}$ |

[a] In wave mechanical language, these elements are simply integrals of the cosine of the angle between the space-fixed $F$ axis and the gyrating $g$ axis, over the symmetric top eigenfunctions specified by $(J\Omega M|J'\Omega'M')$. Since these angular eigenfunctions are completely determined by the angular momenta, these rather obscure integrals can be replaced by a matrix algebraic deduction from the commutation relations. In this deduction one finds that the elements of $\Phi_{Fg}$ may be factored in the form

$$(J\Omega M|\Phi_{F'g'}|J'\Omega'M') = (J|\Phi|J')(J\Omega|\phi_{Fg'}|J'\Omega')(JM|\phi_{F'g}|J'M').$$

where $\Omega$ is $J_z$ and $M$ is $J_Z$. With our phase choice [which follows that of Condon and Shortley rather than that of Cross, Hainer, and King, J. Chem. Phys. 12, 210 (1944), for example], the factors are as tabulated.

where

$$b_J = 2(a_J a_J' + c_J c_J') \approx 1,$$
$$d_J = 2(c_J a_J' - a_J c_J') \approx [3(J+\tfrac{1}{2})]^{-1}. \tag{55}$$

These coefficients are also given in Table V. From these, it is clear that oxygen eigenvectors approach Hund case $(b)$ eigenvectors as $J$ becomes very large. This was to be expected since the rotational splittings increase as $J$, whereas the spin-spin energy which breaks down the case $(b)$ coupling is constant.

## IV. LINE INTENSITIES

Because of its homonuclear symmetry, no electric dipole transitions are possible in oxygen. The existence of a magnetic dipole moment of two Bohr magnetons makes magnetic dipole transitions allowed, and in fact quite intense. The perturbative Hamiltonian inducing transitions in an absorption experiment is

$$H' = -g_s{}^e\beta\mathbf{S}\cdot\mathbf{H}_{rf} = -\mathbf{\mu}\cdot\mathbf{H}_{rf}.$$

A well-known analysis[43] shows that for well-separated lines the absorption coefficient $\alpha$ is given by

$$\alpha_{ij} = \frac{4\pi\omega^2 N}{ckT}\sum_M |(\mu_{ij})_M|^2\frac{\tau^{-1}}{(\omega-\omega_{ij})^2+\tau^{-2}}\frac{e^{-E_j/kT}}{\sum_n e^{-E_n/kT}}, \tag{56}$$

where $N$ is the number of molecules per unit volume,

$\mu_{ij}$ is the matrix element of the magnetic dipole moment, $\tau^{-1}=2\pi\Delta\nu$, $E_j$ is the energy of the $j$th state, and the sum over $n$ is the usual partition sum. Since $\alpha$ is proportional to $|\mu_{ij}|^2$, it is proportional to $|(S_Z)_{ij}|^2$ if the magnetic vector of the incident rf radiation is polarized along $Z$. By the isotropy of field-free space we know that when summed over the orientational degeneracy quantum number $M$,

$$\sum_M |(S_X)_{ij}|^2 = \sum_M |(S_Y)_{ij}|^2 = \sum_M |(S_Z)_{ij}|^2.$$

Thus all of the necessary information for the general case is obtained by evaluating the simplest of these, namely,

$$\sum_M |(S_Z)_{ij}|^2.$$

In this, of course, $i, j$ indicate the final and initial states, each characterized by quantum numbers $J, K$.

To compute the matrix elements of $S_Z$ (where $Z$ is a space-fixed coordinate) from the known elements of $S$ in the gyrating $(g)$ axes we use the known direction cosine matrix elements in the equation

$$S_Z = \sum_g \Phi_{Zg}S_g. \tag{57}$$

These direction cosine matrix elements are given in Table VI with the phase conventions we have used. Noting that $\Omega=\Sigma$ for our $\Lambda=0$ state, we find the following elements for $S_Z$ in a Hund case $(a)$ representation.

$$(JMS\Sigma|S_Z|JMS\Sigma) = \frac{\Sigma^2 M}{J(J+1)},$$

$$(JMS\Sigma|S_Z|JMS\Sigma\pm1) = \frac{M[J(J+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}}[S(S+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}}}{2J(J+1)},$$

$$(JMS\Sigma|S_Z|J-1, MS\Sigma) = \frac{\Sigma(J^2-\Sigma^2)^{\frac{1}{2}}(J^2-M^2)^{\frac{1}{2}}}{J(4J^2-1)^{\frac{1}{2}}},$$

$$(JMS\Sigma|S_Z|J-1, MS\Sigma\pm1) = \frac{\pm[(J^2-M^2)(J\mp\Sigma)(J\mp\Sigma-1)]^{\frac{1}{2}}[S(S+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}}}{2J(4J^2-1)^{\frac{1}{2}}}.$$

$$\tag{58}$$

[43] J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. 17, 227 (1945).

The $(J|J+1)$ elements of $S_Z$ are found by using the Hermiticity of the matrix. These elements must now be transformed to the basis which diagonalizes the unperturbed (field-free) Hamiltonian. Then the off-diagonal elements will give the transition probabilities between the actual eigenfunctions. Since these matrix elements are not diagonal in $J$, our transformation $T_J$ must be extended as follows:

$$T^{-1}S_ZT = \begin{pmatrix} T_0^{-1} & & & 0 \\ & T_1^{-1} & & \\ & & T_2^{-1} & \\ 0 & & & \cdot \\ & & & \cdot \end{pmatrix}\begin{pmatrix} S_{00} & S_{01} & 0 & 0 & \cdot \\ S_{10} & S_{11} & S_{12} & 0 & \cdot \\ 0 & S_{21} & S_{22} & S_{23} & \cdot \\ 0 & 0 & S_{32} & S_{33} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}\begin{pmatrix} T_0 & & & 0 \\ & T_1 & & \\ & & T_2 & \\ 0 & & & T_3 \\ & & & \cdot \end{pmatrix}$$

$$= \begin{pmatrix} T_0^{-1}S_{00}T_0 & T_0^{-1}S_{01}T_1 & 0 & 0 & \cdot \\ T_1^{-1}S_{10}T_0 & T_1^{-1}S_{11}T_1 & T_1^{-1}S_{12}T_2 & 0 & \cdot \\ 0 & T_2^{-1}S_{21}T_1 & T_2^{-1}S_{22}T_2 & \cdot & \cdot \\ 0 & 0 & T_3^{-1}S_{32}T_2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}. \quad (59)$$

In these expressions, $T_J$ and $S_{JJ'}$ are $3\times3$ matrices.

Carrying out the indicated matrix multiplication, we find the following matrix elements of the form $(K,J,M|S_Z|K',J',M)$:

$$(K,K,M|S_Z|K,K,M) = \frac{M}{J(J+1)} = \frac{g(K,J=K)}{g_s{}^e}M,$$

$$(K,K+1,M|S_Z|K,K+1,M) = \frac{2a_JM}{[J(J+1)]^{\frac{1}{2}}}$$

$$\times\left[2c_J + \frac{a_J}{[J(J+1)]^{\frac{1}{2}}}\right] = \frac{g(K,J=K+1)}{g_s{}^e}M,$$

$$(K,K-1,M|S_Z|K,K-1,M) = \frac{-2c_JM}{[J(J+1)]^{\frac{1}{2}}}$$

$$\times\left[2a_J - \frac{c_J}{[J(J+1)]^{\frac{1}{2}}}\right] = \frac{g(K,J=K-1)}{g_s{}^e}M,$$

$$(J-1,J,M|S_Z|J+1,J,M)$$

$$= 2M\left[\frac{a_Jc_J}{J(J+1)} + \frac{c_J{}^2-a_J{}^2}{[J(J+1)]^{\frac{1}{2}}}\right] = h_JM, \quad (60)$$

$$(J-2,J-1,M|S_Z|J,J,M)$$

$$= f(J,M)\left[\frac{a_{J-1}}{(J)^{\frac{1}{2}}} - \frac{c_{J-1}}{(J-1)^{\frac{1}{2}}}\right] = A_{J-1}(J^2-M^2)^{\frac{1}{2}},$$

$$(J-1,J-1,M|S_Z|J-1,J,M)$$

$$= f(J,M)\left[\frac{a_J}{(J)^{\frac{1}{2}}} + \frac{c_J}{(J+1)^{\frac{1}{2}}}\right] = B_J(J^2-M^2)^{\frac{1}{2}},$$

$$(J,J-1,M|S_Z|J,J,M)$$

$$= f(J,M)\left[\frac{c_{J-1}}{(J)^{\frac{1}{2}}} + \frac{a_{J-1}}{(J-1)^{\frac{1}{2}}}\right] = C_{J-1}(J^2-M^2)^{\frac{1}{2}},$$

$$(J-1,J-1,M|S_Z|J+1,J,M)$$

$$= f(J,M)\left[\frac{c_J}{(J)^{\frac{1}{2}}} - \frac{a_J}{(J+1)^{\frac{1}{2}}}\right] = D_J(J^2-M^2)^{\frac{1}{2}},$$

where

$$f(J,M) = \left[\frac{2(J^2-1)(J^2-M^2)}{J(4J^2-1)}\right]^{\frac{1}{2}},$$

with the special case

$$(1,0,0|S_Z|1,1,0) = -\left[\tfrac{2}{3}(1-M^2)\right]^{\frac{1}{2}} = C_0(1-M^2)^{\frac{1}{2}}. \quad (60')$$

If we insert the tabulated values of $a_J$ and $c_J$, we obtain the proper transformed matrix elements, whereas if we insert $a_J'$ and $c_J'$ we get the matrix elements for $S_Z$ in a pure Hund case $(b)$ system. In the latter case, inspection of $a'$ and $c'$ shows that all $(K|K')$ elements of $S_Z$ vanish if $K' \neq K$. This is not true using $a$ and $c$. Thus our precise calculation has revealed the possibility of $\Delta K=2$ transitions. Also, the formulas for $\Delta K=0$ transitions differ from Hund $(b)$, especially for

TABLE VII. Line intensities: $I(K',J'|K'',J'')=3 \Sigma_M |(K'J'M|S_Z|K''J''M)|^2$.

| K | $I(K, K+1|K, K)$ Exact | Case (b) | $I(K, K-1|K, K)$ Exact | Case (b) | $I(K, K|K+2, K+1)$ Exact | $I(K, K+1|K+2, K+1)$ Exact | $I(K, K+1|K+2, K+2)$ Exact |
|---|---|---|---|---|---|---|---|
| 1 | 2.452 | 2.500 | 2.000 | 2.000 | 0.006110 | 0.3924 | 0.1280 |
| 3 | 6.710 | 6.750 | 6.539 | 6.667 | 0.005045 | 0.2128 | 0.06343 |
| 5 | 10.80 | 10.833 | 10.736 | 10.800 | 0.003874 | 0.1466 | 0.04175 |
| 7 | 14.85 | 14.875 | 14.82 | 14.86 | 0.003109 | 0.1119 | 0.03103 |
| 9 | 18.88 | 18.90 | 18.86 | 18.89 | 0.002589 | 0.09043 | 0.02466 |
| 11 | 22.90 | 22.92 | 22.88 | 22.91 | 0.002216 | 0.07607 | 0.02046 |
| 13 | 26.91 | 26.93 | 26.90 | 26.92 | 0.001937 | 0.06561 | 0.01749 |
| 15 | 30.92 | 30.94 | 30.92 | 30.93 | 0.001720 | 0.05770 | 0.01527 |

low $J$. For precise work, as in inferring line breadths from calculated intensity and observed signal strength. these corrections should be made.

The diagonal elements give the weak field $g$ factors for the Zeeman effect. These also differ appreciably from the vector model results calculated with the assumption of pure case (b) coupling.[44] The numerical values are given in Table VII, but further discussion will be deferred to a subsequent paper giving a complete treatment of the interaction with a magnetic field.

To calculate the total intensity, we sum the squared matrix elements over the degenerate $M$ states and multiply by 3 to include the 3 equivalent spacial directions. This results in an intensity factor $I$ defined by

$$I(K''J''|K'J')=3 \sum_M |(K''J''M|S_Z|K'J'M)|^2. \quad (61)$$

The sum is readily evaluated explicitly using the fact that

$$\sum_{M=-J}^{J} M^2 = \frac{J(J+1)(2J+1)}{3}.$$

The results have been tabulated in Table VIII for $J \leq 16$, and the Hund (b) result[45] has been given for comparison when it is not zero. Evidently the differ-

ences are at most a few percent for the transitions allowed in Hund case (b). However, the predicted intensities for the "forbidden" $\Delta K = 2$ lines is a completely new result, which can be checked when radiation of sufficiently high frequency is available. The skirts of these lines will give some effects at lower frequencies if the transmission is through oxygen (or air) at atmosphere pressure.

We can write the frequency of a $K_1 \to K_1 + 2$ transition in terms of the frequency difference

$$\nu(K_1, K_1+2) = E(J=K=K_1+2) - E(J=K=K_1)$$

and the frequencies of the 5-mm lines as follows:

$$\nu_{J, J+1; J=K} = \nu_{K, K+2} - \nu_{-}(K+2).$$

$$\nu_{J, J; J=K+1} = \nu_{K, K+2} - \nu_{-}(K+2) + \nu_{+}(K). \quad (62)$$

$$\nu_{J, J+1; J=K+1} = \nu_{K, K+2} + \nu_{+}(K).$$

Making an analytic approximation to the $I(K''J''|K'J')$ and using Eq. (56), one finds the following approximate results at 300°K, assuming the same line breadth parameter as in the millimeter spectrum:

$$\alpha_{J, J+1; J=K} = 0.046(J+1)^{-\frac{1}{2}} \nu^2 10^{-10} e^{-0.0069 K(K+1)},$$

$$\alpha_{J, J; J=K+1} = 4.2 J^{-1} \nu^2 10^{-10} e^{-0.0069 K(K+1)}, \quad (63)$$

$$\alpha_{J, J+1; J=K+1} = 1.4 J^{-1} \nu^2 10^{-10} e^{-0.0069 K(K+1)}.$$

In these, $\alpha$ is the value when $\nu = \nu_{ij}$ and $\nu$ is expressed in kMc/sec. As particular examples, the three lowest frequency lines are $K=1 \to 3$ lines predicted to lie at 368 522 Mc/sec, 424 787 Mc/sec, and 487 274 Mc/sec. The absorption coefficients are calculated to be 0.44 $\times 10^{-6}$, $38 \times 10^{-6}$, and $17 \times 10^{-6}$ cm$^{-1}$, respectively.

TABLE VIII. Matrix elements of $S_Z$ with respect to the basis in which the field-free problem is diagonal.[a]

| K | $g(K, K-1)/g_e$ | $g(K,K)/g_e$ | $g(K, K+1)/g_e$ |
|---|---|---|---|
| 1 | | 0.5000000 | 0.483997 |
| 3 | −0.317330 | 0.0833333 | 0.247357 |
| 5 | −0.197357 | 0.0333333 | 0.165797 |
| 7 | −0.141987 | 0.0178571 | 0.124612 |
| 9 | −0.110723 | 0.0111111 | 0.0997945 |
| 11 | −0.0907038 | 0.00757576 | 0.0832115 |
| 13 | −0.0768013 | 0.00549451 | 0.0713505 |
| 15 | −0.0665888 | 0.00416666 | 0.0624471 |
| 17 | −0.0587707 | | |

| J | $h_J$ | $A_J$ | $B_J$ | $C_J$ | $D_J$ |
|---|---|---|---|---|---|
| 2 | 0.114371 | −0.0349195 | 0.285889 | 0.249546 | 0.04000515 |
| 4 | 0.0343857 | −0.0113202 | 0.163182 | 0.147276 | 0.01254283 |
| 6 | 0.0163845 | −0.00553032 | 0.112209 | 0.1041814 | 0.00595644 |
| 8 | 0.0095616 | −0.00326702 | 0.0853207 | 0.0805423 | 0.00346085 |
| 10 | 0.0062568 | −0.00215461 | 0.0687875 | 0.0656293 | 0.00225829 |
| 12 | 0.0044164 | −0.00152705 | 0.0576082 | 0.0553697 | 0.00158879 |
| 14 | 0.0032823 | −0.00113872 | 0.0495493 | 0.0478813 | 0.00117839 |
| 16 | 0.0025354 | −0.00088177 | 0.0434660 | 0.0421754 | 0.00090875 |

[a] These elements are given in Eq. (60) as the product of a $J$-dependent factor and a simple factor depending on both $J$ and $M$. The $J$-dependent factors are tabulated here. In these, $g_e$ is the algebraic electronic spin $g$ factor, −2.00229, and $g(K,J)$ is the algebraic $g$ factor of the $K,J$ energy level.

[44] R. M. Hill and W. Gordy, Phys. Rev. 93, 1019 (1954).
[45] J. H. Van Vleck, Phys. Rev. 71, 413 (1947).

## APPENDIX A. MATRIX ELEMENTS OF SPIN-SPIN HAMILTONIAN

By the same methods used in Sec. II, the following matrix elements between configurations may be computed. We let $bR^2 = \Delta$, for simplicity.

$$H_{ee} = H_{cc} = g^2 \beta^2 b^{\frac{3}{2}} 2K^4 \pi^{-\frac{1}{2}}$$
$$\times \{1/30 + e^{-\Delta}/15 + 2e^{-3\Delta/4} S_1(\Delta) - \tfrac{1}{2} e^{-\Delta} S_1(4\Delta)\},$$

$$H_{dd} = H_{ff} = g^2 \beta^2 b^{\frac{3}{2}} 2L^4 \pi^{-\frac{1}{2}}$$
$$\times \{1/30 + e^{-\Delta}/15 - 2e^{-3\Delta/4} S_1(\Delta) - \tfrac{1}{2} e^{-\Delta} S_1(4\Delta)\},$$

$$H_{cd} = H_{ef} = g^2\beta^2 b^{\frac{3}{2}} L^2 K^2 \pi^{-\frac{3}{2}} \{1/15 + e^{-\Delta} S_1(4\Delta)\},$$

$$H_{ca} = H_{cb} = H_{ce} = H_{cf} = 0,$$

$$H_{ad} = H_{bd} = H_{ae} = H_{be} = H_{af} = H_{bf} = H_{de} = H_{df} = 0,$$

$$H_{cg} = -H_{ch} = -H_{ci} = 2^{-\frac{1}{2}} Re H_{cE} = g^2\beta^2 b^{\frac{3}{2}} JKLM(2\pi)^{-\frac{3}{2}} e^{-\Delta}$$
$$\times \{ (e^{\Delta}/15)[\Delta + B\Delta^{\frac{1}{2}} - BE + \tfrac{1}{2} - 5e^{-\Delta}/14]$$
$$- (B + \Delta^{\frac{1}{2}})(E + \Delta^{\frac{1}{2}}) S_1(4\Delta)$$
$$- 4[\Delta + \Delta^{\frac{1}{2}}(2B - E)] e^{\Delta/4} S_1(\Delta) - \tfrac{1}{2} S_2(4\Delta)$$
$$+ \tfrac{1}{4}\Delta^{-\frac{1}{2}}(3\Delta^{\frac{1}{2}} + 2B + E) S_3(4\Delta)$$
$$+ 4\Delta^{-\frac{1}{2}}(\Delta^{\frac{1}{2}} + 2B - E) e^{\Delta/4} S_3(\Delta) + \tfrac{1}{8}\Delta^{-2} S_4(4\Delta)\}.$$

In these,

$$S_2(x) = \sum_{n=1}^{\infty} \frac{1}{1 \cdot 3 \cdot 5 \cdots (2n+3)} \left(\frac{x}{2}\right)^n,$$

$$S_3(x) = \left(\frac{x}{2}\right) \sum_{n=1}^{\infty} \frac{(2n)(2n-1)}{1 \cdot 3 \cdot 5 \cdots (2n+5)} \left(\frac{x}{2}\right)^n,$$

$$S_4(x) = \left(\frac{x}{2}\right) \sum_{n=1}^{\infty} \frac{2n(2n-1)^2}{1 \cdot 3 \cdot 5 \cdots (2n+5)} \left(\frac{x}{2}\right)^n,$$

and the constants $B$, $E$, $J$, $L$, and $M$ are as defined by Meckler.[2] In evaluating $H_{cg}$, the terms in $\phi_0$ and $\chi_0$ giving orthogonality to the $1s$ orbitals have been dropped as negligible to allow integration by our artifice (which requires a common Gaussian factor for all orbitals). We note that all of the elements have the same sort of dependence on $b^{\frac{1}{2}}$ and $bR^2 = \Delta$, the $\Delta$ dependence turning out to be rather slight.

# Interaction of Molecular Oxygen with a Magnetic Field*

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The dominant interaction of O₂ with a magnetic field is through the electronic spin magnetic moment. However, a precise comparison with experiment of the results of calculating the microwave paramagnetic spectrum, assuming only this interaction, shows a systematic discrepancy. This discrepancy is removed by introducing two corrections. The larger (approximately 0.1 percent, or 7 gauss) is a correction for the second-order electronic orbital moment coupled in by the spin-orbit energy. Its magnitude is proportional to the second-order term $\mu''$ in the spin-rotation coupling constant. The smaller (approximately 1 gauss) is a correction for the rotation-induced magnetic moment of the molecule. Since the dependence of this contribution on quantum numbers is quite unique, this coefficient can also be determined by fitting the magnetic spectrum. A total of 120 X-band and 78 S-band lines were observed. The complete corrections have been made on 26 lines with a mean residual error of roughly 0.5 Mc/sec. This excellent agreement confirms the anomalous electronic moment to 60 parts per million (ppm) and also confirms the validity of the Zeeman-effect theory.

A new result is the rotational magnetic moment of $-0.25 \pm 0.05$ nuclear magnetons per quantum of rotation. Knowledge of this moment allows the electronic contribution to the effective moment of inertia to be determined. Making this correction of 65 ppm, and using the latest fitting of the universal atomic constants, the equilibrium internuclear distance is recomputed to be $R_e = 1.20741 \pm 0.00002$ A. We can also deduce that the magnitude of $\lambda''$, the second-order spin-orbit contribution to the coupling of the spin to the figure axis, is $465 \pm 50$ Mc/sec, or less than one percent of the total coupling constant $\lambda$.

Theoretical intensities of a number of the microwave transitions are calculated and successfully compared with experiment over a range of 100 to 1 in magnitude. It turns out that $\Delta M = 0$ transitions are over a hundred times weaker than the $\Delta M = \pm 1$ transitions and thus are too weak to observe. Also, $J$ breaks down as a quantum number in the presence of a magnetic field. This allows $\Delta J = \pm 2$ transitions to comprise roughly half of all lines observed.

IN a previous paper[1] (referred to as TSI), we gave a rather complete and precise treatment of the eigenvalues, eigenvectors, and transition intensities of the oxygen molecule in field-free space. Using this work as a foundation, we now give a similarly complete and precise treatment of the perturbations produced by a magnetic field. The dominant interaction will, of course, be that between the electronic spin magnetic moment and the external field; namely,

$$\mathcal{H}_{ms} = -g_s e \beta \mathbf{S} \cdot \mathbf{H}. \tag{1}$$

Accordingly, the effects of this perturbation on the eigenvalues and eigenvectors is first determined to high accuracy. It is then found necessary to introduce the small effects of spin-orbit coupling and rotation-induced moments as additional perturbations to fit the precise experimental data. The fitting evaluates certain sums of matrix elements which are important in interpreting the field-free parameters $\lambda$ and $\mu$. Incidentally, the fit may also be considered to confirm the theoretical anomalous moment of the electron to $\pm 60$ parts per million (ppm). Selection rules and intensities will also be discussed and compared with experiment. It turns out that $\Delta M = \pm 1$, 0 transitions are allowed, but the $\Delta M = 0$ lines are at least 100 times weaker than the $\Delta M = \pm 1$.

[1] M. Tinkham and M. W. P. Strandberg, preceding paper [Phys. Rev. **97**, 937 (1955)].

## I. INTERACTION OF ELECTRONIC SPIN WITH EXTERNAL FIELD

### A. Eigenvalues

If we define the direction of the external field to be the $Z$ direction, then the matrix of our perturbed Hamiltonian is that of[2]

$$\mathcal{3C}=\mathcal{3C}_0+\mathcal{3C}_{ms}=\mathcal{3C}_0-g_s{}^e\beta HS_Z, \qquad (2)$$

where $g_s{}^e=-2.00229$, $\beta$ is the Bohr magneton, $H$ is the magnitude of the applied field, and $\mathcal{3C}_0$ is the field-free Hamiltonian treated in TSI. Matrix elements of $S_Z$ in the basis which diagonalizes the field-free problem have been given previously [TSI Eq. (60) and Table VIII]. Noting that there are $\Delta K=\pm2$, 0 as well as $\Delta J=\pm1$, 0 elements, we find that $\mathcal{3C}_{ms}$ does not factor into smaller submatrices which can be diagonalized exactly. If $O_2$ were a rigorous example of Hund's case (b) in which $K$ is a good quantum number, there would be no $\Delta K=\pm2$ elements and the problem would be factored into $3\times3$ submatrices, one for each value of $K$. This factored form is the starting point taken for further approximations in the treatment of Schmid, Budó, and Zemplén,[3] but is completely inadequate for our purposes. Although it is a better approximation, Henry's method[4] is also too inaccurate.

The matrix of the complete Hamiltonian has the form:

$$ \qquad (3) $$

Since the energy separation between rotational levels is large compared to the magnetic perturbation, the dominant effect will come from the elements diagonal in $K$. The effects of elements which are off-diagonal in $K$ may be reduced to the diagonal (in $K$) by the Van Vleck transformation.[5,6] The resulting $(J|\mathcal{3C}|J')$ elements for the effective $3\times3$ Hamiltonian matrix for the $K$th rotational level are:

$$H_{11}=(K-1|\mathcal{3C}|K-1)=-\nu_-(K)-g(K,K-1)M\beta H$$

$$+\left\{\frac{D_{K-1}{}^2[(K-1)^2-M^2]}{(4K-2)B-\nu_-(K)}+\frac{h_{K-1}{}^2M^2}{(4K-2)B+[g(K-2,K-1)-g(K,K-1)]\beta HM}\right\}(g_s{}^e)^2\beta^2H^2,$$

$$H_{22}=(K|\mathcal{3C}|K)=-g(K,K)M\beta H+\frac{A_{K-1}{}^2(K^2-M^2)(g_s{}^e)^2\beta^2H^2}{(4K-2)B}-\frac{D_{K+1}{}^2[(K+1)^2-M^2](g_s{}^e)^2\beta^2H^2}{(4K+6)B},$$

$$H_{33}=(K+1|\mathcal{3C}|K+1)=-\nu_+(K)-g(K,K+1)M\beta H$$

$$-\left\{\frac{h_{K+1}{}^2M^2}{(4K+6)B-[g(K+2,K+1)-g(K,K+1)]M\beta H}+\frac{A_{K+1}{}^2[(K+2)^2-M^2]}{(4K+6)B+\nu_+(K)}\right\}(g_s{}^e)^2\beta^2H^2, \qquad (4)$$

$$H_{12}=(K|\mathcal{3C}|K-1)=-C_{K-1}(K^2-M^2)^{\frac{1}{2}}g_s{}^e\beta H+\frac{h_{K-1}A_{K-1}M(K^2-M^2)^{\frac{1}{2}}(g_s{}^e)^2\beta^2H^2}{(4K-2)B},$$

$$H_{23}=(K|\mathcal{3C}|K+1)=-B_{K+1}[(K+1)^2-M^2]^{\frac{1}{2}}g_s{}^e\beta H-\frac{h_{K+1}D_{K+1}M[(K+1)^2-M^2]^{\frac{1}{2}}(g_s{}^e)^2\beta^2H^2}{(4K+6)B},$$

$$H_{13}=(K-1|\mathcal{3C}|K+1)=0.$$

[2] Our systematic notation is to use superscripts $e$ and $n$ to distinguish electronic and nuclear contributions, and we use subscripts $s$, $l$, $r$ to distinguish spin, spin-orbit, and rotation. All $g$-factors have the appropriate sign so that $\mu=g\beta J$; for example, that of the electron is a negative number. To conform to conventional usage we denote the magnetic field by $H$ but give numerical values in gauss, the units of magnetic induction.

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

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

[5] E. C. Kemble, Fundamental Principles of Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1939).

[6] To get sufficient accuracy here, we use some energy denominators corrected to first order. This procedure is readily justified if the elements are derived by the method of continued fraction reduction. The error remaining from the reduction is then definitely less than 1 Mc/sec for all cases of interest.

In the diagonal elements we have suppressed the common term $BK(K+1)$. The secular equation is

$$\begin{vmatrix} H_{11}-E & H_{12} & 0 \\ H_{12} & H_{22}-E & H_{23} \\ 0 & H_{23} & H_{33}-E \end{vmatrix} = 0. \qquad (5)$$

The complex dependence of the elements on parameters makes a straight numerical solution the most attractive procedure. For this purpose, the continued fraction forms are most useful. They are

$$E_1 = H_{11} - \frac{H_{12}^2}{H_{22}-E_1-H_{23}^2/(H_{33}-E_1)}$$

and $\qquad (6)$

$$E_2 = H_{22} + \frac{H_{23}^2}{E_2-H_{33}} + \frac{H_{12}^2}{E_2-H_{11}}.$$
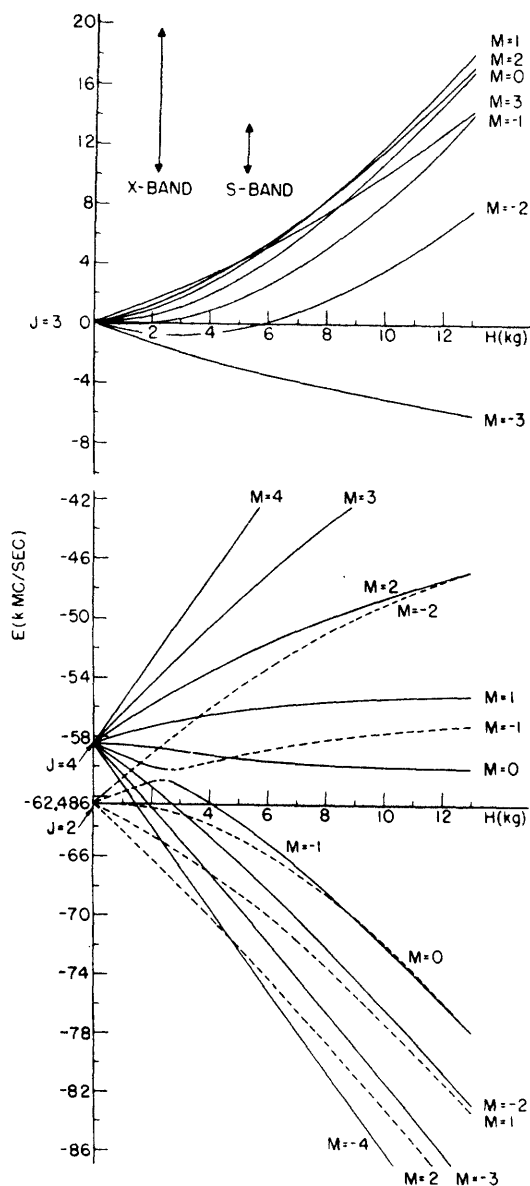


FIG. 1. Magnetic splitting of the $K=3$ energy levels.
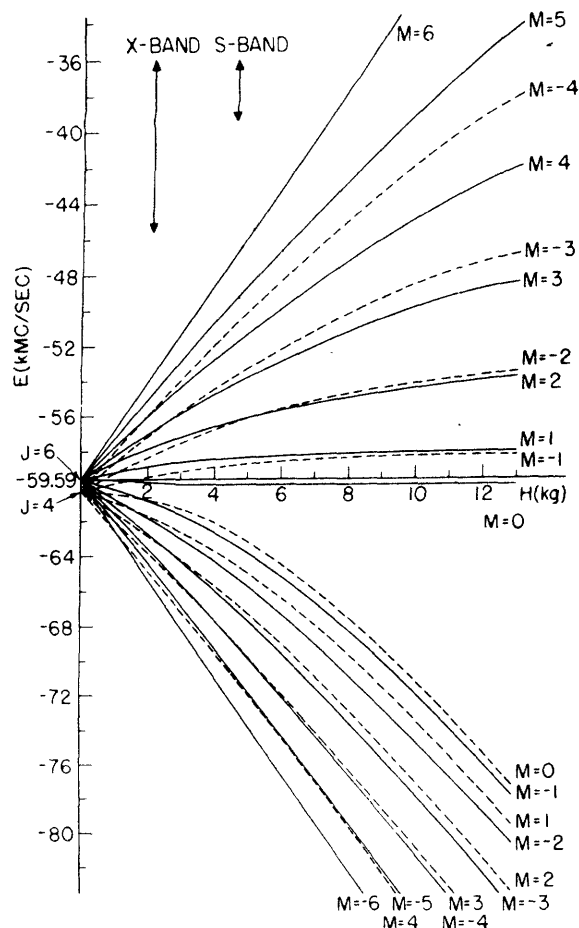


Fig. 2. Magnetic splitting of the $K=5$; $J=4,6$ energy levels.

The expression for $E_3$ is obtained from that for $E_1$ by interchanging the subscripts 1 and 3. These equations are exact equivalents of (5) and not a perturbation approximation. If the roots are well separated, convergence to the desired root on iteration is rapid. If two roots are close together, convergence is slow.

The roots $E_1$, $E_2$, and $E_3$ have been evaluated to $\pm10$ Mc/sec at $H=4$, 8, and 12 kilogauss for most $M$ states for $K \leqslant 13$. The results have been plotted against $H$ by graphical interpolation.[7] Some examples are shown in Figs. 1 and 2. The small $g$-factors for $J=K$ states [roughly $-2/K(K+1)$] make their splittings very small, only three cases being as wide as 9400 Mc/sec for fields under 12 kilogauss. Thus most attention can be concentrated on the $J=K\pm1$ levels. For $K \geqslant 3$, the families of curves are all quite similar. (The $K=1$ curves are simpler, since the $J=0$ and $J=2$ levels are widely separated.) For $H$ less than a few hundred gauss, the splittings closely resemble the linear Zeeman splitting predicted by the field-free $g$-factors (TSI, Table VIII). At very high fields the Paschen-Back effect

[7] The numerical results and more graphs are given in the Ph.D. thesis of M. Tinkham, Massachusetts Institute of Technology, 1954 (unpublished).
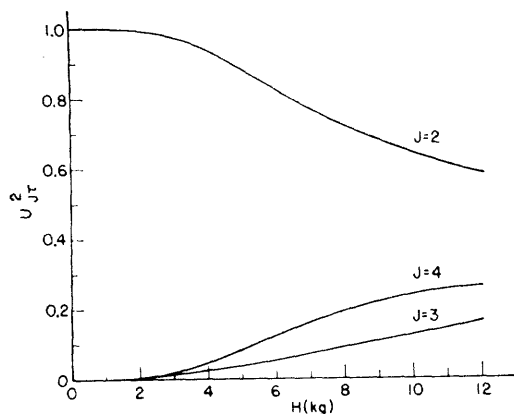
FIG. 3. Mixing coefficients of the $J$ components in the $K=3$, $M=0$ state of lowest energy.

sets in and we approach the limiting case of a completely decoupled spin. Then there must be $(2K+1)$ levels corresponding to each of $M_S=\pm 1$, 0. That this tendency is observed becomes clear if we note by inspection of the graphs that all the $(2K+1)$ levels from $J=K$ are asymptotically going to $M_S=1$ except the $M=-K$ level, which goes to $M_S=0$. Similarly the $(4K+2)$ sublevels from $J=K\pm 1$ provide $(2K+1)$ of $M_S=-1$, $2K$ of $M_S=0$, and the single $M=K+1$ sublevel of $M_S=1$. These numbers check the proper limiting behavior. Even at fields as low as 8 kilogauss there is a marked tendency for the set of $M_S=-1$ levels to split off into a bundle of nearly parallel lines of slope equal to $g_s{}^e\beta$. In the intermediate region, which is of most interest, we find the characteristic repulsion of levels of the same $M$ and the accompanying strong curvature.

From these curves the approximate values of $H$ for a given resonant frequency $\nu$ (energy level separation) may be found to an accuracy of about $\pm 100$ gauss. This is close enough to identify many lines of the spectrum if full use is made of experimental information on $K$ and $\Delta M$. However, to give a secure identification and to check the theory in detail, each line must be calculated individually.

This calculation was made by computing the position (to $\pm 0.5$ Mc/sec) of both levels involved in the transition for two values of $H$ separated by 200 gauss and centered about the approximately correct field, determined graphically. If the transition frequency is then expressed as

$$\nu(H)=\nu(H_0)+(d\nu/dH)(H-H_0), \qquad (7)$$

the two calculated points fix $\nu(H_0)$ and $d\nu/dH$. This formula allows the calculated resonant field for any given experimental frequency to be determined to approximately $\pm 0.5$ gauss, since the curvature can be shown to be small over a region of a hundred gauss. The value of $d\nu/dH$ is also necessary to interpret linewidth measurements at constant frequency and to make corrections for various perturbations to be con-

sidered later. The values of $H$ for the experimental $\nu$, and the value of $d\nu/dH$ at that $H$, are given for many lines of the spectrum in Tables I and III.

## B. Eigenvectors

From the form of (3) it is evident that only $M$ is a good quantum number in the presence of a magnetic field, since, in principle, all $J$'s and $K$'s are mixed. However, the principal mixing is between the three $J$ values corresponding to one $K$. The admixture of other $K$ states is small and could be treated by perturbation theory. In the worst case this amounts to only about a one percent mixing amplitude even at 10 kilogauss. Since this is too small to have any serious effect on any of our subsequent calculations, we neglect these effects and only compute the transformation between the field-free and final eigenfunctions within a given $K$ rotational triplet.

This transformation matrix is made up of the eigenvectors of the matrix equation corresponding to (5), and it is written

$$U_K=\begin{array}{c} \\ J=K-1 \\ J=K \\ J=K+1 \end{array}\begin{array}{ccc} \tau=1 & \tau=2 & \tau=3 \\ \left[\begin{array}{ccc} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{23} \\ U_{31} & U_{32} & U_{33} \end{array}\right]. \end{array} \qquad (8)$$

In this, $\tau$ denotes the new eigenfunctions but signifies no constant of the motion except the energy. The elements $U_{J\tau}$ are defined by

$$\frac{U_{2\tau}}{U_{1\tau}}=\frac{E_\tau-H_{11}}{H_{12}} \qquad \frac{U_{3\tau}}{U_{2\tau}}=\frac{H_{23}}{E_\tau-H_{33}} \qquad (9)$$

and normalization.

Examples plotted in Figs. 3 and 4 show two typical cases. In Fig. 3 we see the distortion of the $K=3$, $M=0$ state which starts as $J=2$ at zero field. At a field of 6 kilogauss the amplitude of $J=4$ has risen to 0.35, and that of $J=3$ has risen to 0.24. These figures show the substantial breakdown of $J$ as a quantum number
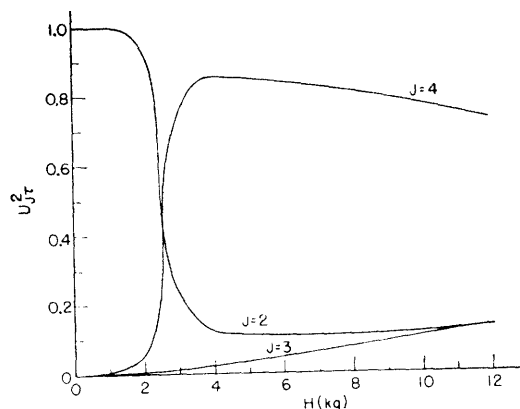


FIG. 4. Mixing coefficients of the $J$ components in the $K=3$, $M=-1$ state of lowest energy.

under a magnetic field. This makes all $\Delta M = \pm 1, 0$ transitions "allowed," regardless of the principal or original value of $J$, provided the field is moderately strong. We will later see that the majority of the observed $X$-band transitions are of this field-allowed type. Figure 4 shows the more unusual case of two levels which attempt to cross each other but, instead, repel. At the point of closest approach the $J$'s are completely mixed, and as the levels move apart again, the dominant $J$'s are found to have interchanged. Since the strong mixing dies out rapidly, there is seldom any doubt as to which $J$ is dominant in an eigenstate for a given field. We will use $J$ in this sense throughout the paper rather than use the less suggestive $\tau$ notation introduced for the purpose of setting up the transformations $U$. The correct sense of $J$ will always be clear from the context.

Numerical values for the transformation coefficients for a number of cases required in later parts of the calculation are given in Table VII. Inspection of this table shows how universal is the large degree of mixing.

## II. CORRECTIONS FOR ROTATIONAL MAGNETIC MOMENT AND ELECTRONIC ORBITAL MAGNETISM

When the results of the calculations of Sec. I are compared with experiment (Tables I and III), a systematic discrepancy of the order 0.1 percent is obvious. Since this was far beyond the expected error of either theory or experiment, it was assumed to be caused by neglect of these corrections. When the corrections treated in this section are made, the agreement is within the accuracy of the experiment and calculations, namely of the order $\pm 50$ ppm.

The straightforward and universally sound method of handling perturbative terms of this sort is simply to write down all matrix components of the energy in a convenient basis and then to eliminate the elements which are off-diagonal in electronic quantum numbers by the Van Vleck transformation.[5] For a case as simple as the diatomic molecule which we treat, however, the same results can be obtained without complication by using a shortcut method which gives a much clearer picture of the physical nature of the interactions. This second approach is followed here. Either method yields an effective Hamiltonian matrix involving fine structure quantum numbers only. The lowest-order contributions to the energy are then found by application of the transformation (within the fine structure levels) which diagonalizes the Hamiltonian $\mathcal{3C}_0 + \mathcal{3C}_{ms}$.

In TSI we noted that the spin-orbit coupling and the rotation-electronic interaction mixed $\pi$ states into the $\Sigma$ electronic orbital state as follows:

$$\psi_\Sigma = \psi_\Sigma{}^0 - \sum_{n=\pi} \sum_{g'=x,y} \frac{(n|AL_{g'}|0)S_{g'} - (n|2BL_{g'}|0)\mathfrak{K}_{g'}}{E_n - E_0}\psi_n{}^0.$$

(10)

The first-order electronic orbital angular momentum along the $g$th gyrating axis is then seen to be

$$L_g = -\sum_{n,g'} \frac{(0|L_g|n)(n|AL_{g'}|0)S_{g'} + \text{comp. conj.}}{E_n - E_0}$$

$$+ \sum_{n,g'} \frac{(0|L_g|n)(n|2BL_{g'}|0)\mathfrak{K}_{g'} + \text{comp. conj.}}{E_n - E_0}$$

$$= -(g_l{}^e S_g + g_r{}^e \mathfrak{K}_g)(1 - \delta_{g,z}),$$

(11)

where

$$g_l{}^e = 2\,\text{Re}\sum_n \frac{(0|L_x|n)(n|AL_x|0)}{E_n - E_0}$$

and

(12)

$$g_r{}^e = -4\,\text{Re}\sum_n \frac{(0|L_x|n)(n|BL_x|0)}{E_n - E_0}.$$

In making this reduction we have used the facts that with axial symmetry the elements of $L_x$ and $L_y$ differ only by a phase of $\pm i$ [TSI, Eq. (26)] and that elements of $L_z$ vanish for a $\Sigma$ state. In the general case of lower symmetry the $g$'s are not just diagonal tensors, but have the structure $(g_r{}^e)_{gg'}$, for example. Then $L_g$ would be a sum of terms over $g'$. The general case of rotation-induced moments has been treated in detail by Eshbach and Strandberg.[8]

To obtain the interaction of this electronic orbital angular momentum with the external field, we project it onto the space-fixed $Z$-axis by using the direction cosine[9] matrix elements $\Phi_{Zg}$:

$$L_Z = \sum_g \Phi_{Zg} L_g.$$

(13)

For our case, the matrix elements of this product operator which are diagonal in electronic quantum numbers between total state functions whose electronic part is (10) may be shown to be the same as those obtained by simply taking the product of the diagonal elements of $L_g$ given in (11) and the elements of $\Phi_{Zg}$ for the case $\Lambda = 0$. These $\Phi_{Zg}$ elements are the same as those used[9] in TSI to project $S_g$ onto $Z$. Combining (11) and (13),

$$L_Z = -g_l{}^e \sum_{g=x,y} \Phi_{Zg} S_g - g_r{}^e \sum_{g=x,y,z} \Phi_{Zg} \mathfrak{K}_g$$

$$= -g_l{}^e \sum_{g=x,y} \Phi_{Zg} S_g - g_r{}^e \mathfrak{K}_Z.$$

(14)

The second sum may be extended to include $g = z$ because $\mathfrak{K}_z$ is zero. This is more convenient, since it gives rise to the simple expression $\mathfrak{K}_Z$. Noting that $S_x$ and $S_y$ are purely off-diagonal in $\Sigma$, whereas $S_z$ is

[8] J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. **85**, 24 (1952).
[9] See TSI, Table VI.

purely diagonal, we can write (14) as[10]

$$(JM\Sigma|L_Z|J'M\Sigma') = -g_r{}^e(JM\Sigma|\Re_Z|J'M\Sigma')$$
$$- (1-\delta_{\Sigma\ \Sigma'})g_l{}^e(JM\Sigma|S_Z|J'M\Sigma'). \quad (15)$$

Before computing the effect of this electronic orbital angular momentum on the magnetic energy, let us note that elementary considerations show that the magnetic moment of the rotating nuclei in a homonuclear diatomic molecule is simply

$$\mu_r{}^n = \frac{Z}{A}\frac{m}{M}\Re \equiv g_r{}^n\beta\Re. \quad (16)$$

Again, the general asymmetric top has been treated by Eshbach and Strandberg.[8] If we combine this with the electronic rotation-induced moment $-\beta L_r = g_r{}^e\beta\Re$, we have a total rotational moment

$$\mu_r = \mu_r{}^n + \mu_r{}^e = (g_r{}^n + g_r{}^e)\beta\Re = g_r\beta\Re. \quad (17)$$

We now compute the energy contributed by the interaction of this total rotational moment with the external field. It is

$$\mathcal{3C}_{mr} = -g_r\beta H\Re_Z$$
$$= -g_r\beta H(M - S_Z). \quad (18)$$

$M$ is, of course, a known good quantum number. For this small correction term we need only to use the diagonal value of $S_Z$, $\langle S_Z\rangle$, in the representation in which the sum of $\mathcal{3C}_0$ and the interaction of the spin moment with the external field is diagonal. We note that the eigenenergy is given by the diagonal elements of $\mathcal{3C}_0$ and $S_Z$ in this representation as

$$E_M = \langle\mathcal{3C}_0\rangle - g_s{}^e\beta H\langle S_Z\rangle_M.$$

Thus, to first order,

$$\langle S_Z\rangle_M = -(1/g_s{}^e\beta)(\partial E/\partial H)_M. \quad (19)$$

The total first-order energy shift caused by the rotational moment is then

$$\langle\mathcal{3C}_{mr}\rangle_M = -g_r\beta H[M + (1/g_s{}^e\beta)(\partial E/\partial H)_M]. \quad (20)$$

Accordingly, the change in frequency for a transition from $M\rightarrow M+\Delta M$ is

$$\Delta\nu_r = \langle\mathcal{3C}_{mr}\rangle_{M+\Delta M} - \langle\mathcal{3C}_{mr}\rangle_M$$
$$= -g_r\beta H[\Delta M + (1/g_s{}^e\beta)(d\nu/dh)], \quad (21)$$

where $d\nu/dH = d(E_{M+\Delta M} - E_M)/dH$ is known from previous calculations (Eq. 7). The corresponding change in $H$ required to maintain the fixed experimental

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[10] It might appear anomalous that this argument does not also apply to eliminate $(\Sigma|\Sigma)$ elements of $\Re_Z$. The reason is that $\Phi$ and $\Re$ both operate in the relative coordinate domain, making $\Phi_{Z_g}\Re_g$ a true matrix produce in which $(\Sigma|\Sigma)$ elements are generated from the $(\Sigma|\Sigma\pm1)(\Sigma\pm1|\Sigma)$ elements. Since $S_g$ operates only on internal coordinates, in the case of $S$ we have a simple product and no such elements can be generated.

resonance frequency is

$$\frac{\Delta H_r}{H} = \frac{g_r}{g_s{}^e}\left[\frac{g_s{}^e\beta\Delta M}{(d\nu/dH)}+1\right]. \quad (22)$$

Let us now take account of the energy of the spin-orbit induced orbital angular momentum in (15). From that equation

$$(JM\Sigma|\mathcal{3C}_{ml}|J'M\Sigma\pm1)$$
$$= -g_l{}^e\beta H(JM\Sigma|S_Z|J'M\Sigma\pm1). \quad (23)$$

All other elements vanish. This clearly has a different form from the rotational interaction (18) or from the principal spin interaction $\mathcal{3C}_{ms}$. Thus all three will be experimentally separable. The first step in evaluating the contribution of (23) to the energy is to find the transformed elements in the basis which diagonalizes the field-free Hamiltonian $\mathcal{3C}_0$. This is done by using the transformation matrices $T_J$ in the method of TSI Eq. (59). However, the results differ somewhat from TSI Eq. (60) since the $(\Sigma|\mathcal{3C}_{ml}|\Sigma)$ elements vanish. This transformed matrix $(KJM|\mathcal{3C}_{ml}|K'J'M)$ has elements $K'=K$, $K\pm2$ and $J'=J$, $J\pm1$. For the reasons given in section I-B, we may neglect all except $K'=K$ elements. These are written as $(J|\mathcal{3C}_{ml}|J')$ in the following:

$$\mathcal{3C}_{11} = (K-1|\mathcal{3C}_{ml}|K-1)$$
$$= -g_l{}^e\beta H(-4a_{K-1}c_{K-1}M)[K(K-1)]^{-\frac{1}{2}},$$

$$\mathcal{3C}_{22} = (K|\mathcal{3C}_{ml}|K) = 0 = \mathcal{3C}_{13} = (K-1|\mathcal{3C}_{ml}|K+1),$$

$$\mathcal{3C}_{33} = (K+1|\mathcal{3C}_{ml}|K+1)$$
$$= -g_l{}^e\beta H(4a_{K+1}c_{K+1}M)/[(K+1)(K+2)]^{\frac{1}{2}},$$

$$\mathcal{3C}_{12} = (K-1|\mathcal{3C}_{ml}|K) \quad (24)$$
$$= -g_l{}^e\beta H\left[\frac{2(K+1)(K^2-M^2)}{K(4K^2-1)}\right]^{\frac{1}{2}}a_{K-1},$$

$$\mathcal{3C}_{23} = (K|\mathcal{3C}_{ml}|K+1)$$
$$= -g_l{}^e\beta H\left\{\frac{2K[(K+1)^2-M^2]}{(K+1)[4(K+1)^2-1]}\right\}^{\frac{1}{2}}c_{K+1},$$

with the special case

$$(1,0,0|\mathcal{3C}_{ml}|1,1,0) = +g_l{}^e\beta H[\tfrac{2}{3}(1-M^2)]^{\frac{1}{2}}.$$

In these, $a_J$ and $c_J$ are the transformation elements of $T_J$ given in Table V of TSI. They are both approximately $\frac{1}{2}$ for all $J$.

From these elements we may note that the magnitude of the total $g$-factors (diagonal matrix elements) of the $J=K\pm1$ levels are increased by (roughly) the fraction $g_l{}^e/g_s{}^e$, whereas those of the $J=K$ levels are unchanged. The off-diagonal elements are also increased, but in a different ratio. From these observations it is clear that if $g_l{}^e/g_s{}^e$ is positive (as it turns out to be), this inter-

action will tend to shift the resonance to lower fields. However, to investigate the effect rigorously we must transform $(J|\mathfrak{K}_{ml}|J')$ to the basis which diagonalizes $\mathfrak{K}_{ms}+\mathfrak{K}_0$. This is done with the transformation $U$ given in II-B. The result is

$$(\tau|\mathfrak{K}_{ml}|\tau) = (U^{-1}\mathfrak{K}_{ml}U)_{\tau\tau}$$
$$= U_{1\tau}{}^2\mathfrak{K}_{11} + 2U_{1\tau}U_{2\tau}\mathfrak{K}_{12}$$
$$+ 2U_{2\tau}U_{3\tau}\mathfrak{K}_{23} + U_{3\tau}{}^2\mathfrak{K}_{33}. \quad (25)$$

The shift in the calculated magnetic field to maintain the same resonant frequency is then

$$\Delta H_l = -(d\nu/dH)^{-1}[(\tau'|\mathfrak{K}_{ml}|\tau') - (\tau|\mathfrak{K}_{ml}|\tau)]. \quad (26)$$

In view of the difficulty of making these corrections, they have only been computed for 27 examples. These results are tabulated in Tables I and III. Clearly the agreement with experiment is satisfactory.

## III. COMPARISON WITH EXPERIMENT

### A. Experimental Method

Since the apparatus used will be described more fully elsewhere, only a brief sketch is given here. The microwave arrangement uses a Pound-Zaffarano[11] feedback circuit to stabilize the klystron frequency to the resonant frequency of the cavity containing the oxygen gas sample. This cavity is situated between the poles of a magnet the field of which is monitored by a flip coil. This flip-coil voltage is compared with a controllable fraction of the output of a small reference generator driven by the same shaft. The error signal is used in a feedback circuit to stabilize the field. The field is then slowly swept by using a geared down synchronous motor to vary the helipot which controls the comparison voltage. The stability is within a fraction of a gauss.

Upon this slowly sweeping field is superposed a 50-cps modulation, adjustable from 0 gauss to 80 gauss, peak to peak. It is also feedback-stabilized to eliminate phase and amplitude shifts with changing dc fields and hence changing properties of the iron core. Provided the modulation amplitude is small compared to the linewidth, this will produce a 50-cps component proportional to $d\chi''/dH$ (the derivative of the imaginary part of the sysceptibility) in the power absorbed in the gas, and hence in the reflection or transmission coefficient of the cavity. This modulated microwave power is detected with a crystal (or bolometer). The resulting 50-cps signal is amplified in a low-noise amplifier and converted to dc in a phase-sensitive detector which uses a Brown converter as the synchronous device. The output is recorded on a strip chart recorder. A block diagram of the apparatus is given in Fig. 5. (The bolometer bridge is, of course, absent when a crystal detector is used. This was the case for all measurements except those of absolute intensity.)
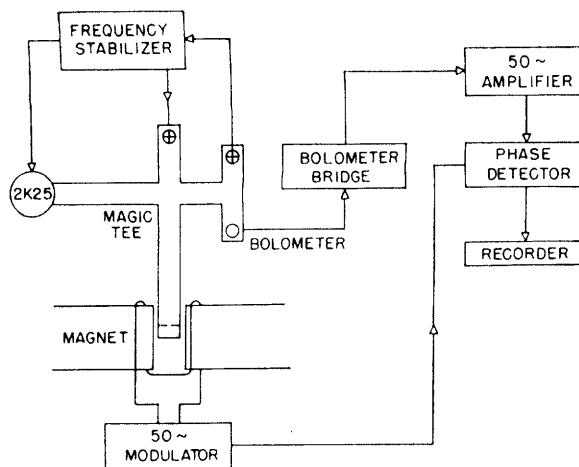


FIG. 5. Block diagram of the apparatus.

All precise measurements of the magnetic field are made by using proton resonance, the frequencies being measured with a BC-221 frequency meter accurate to ±40 ppm by comparison with the M.I.T. frequency standard. The flip-coil arrangement gives readings accurate to a few gauss under normal operating conditions. Precise frequency measurements were made by beating the klystron frequency with harmonics of the M.I.T. frequency standard. Other frequency measurements were made with a calibrated wave meter.

The X-band measurements were made with the use of three different cavities. A $TE_{011}$ cylindrical cavity with $Q_0$ of the order 35 000 was used for the highest sensitivity exploration. A much smaller $TE_{011}$ rectangular cavity was used for the precise measurements to minimize errors caused by field inhomogeneity by allowing smaller pole separations. Finally, a $TE_{111}$ cylindrical cavity was used in conjunction with special microwave plumbing to produce a circularly polarized radiation field in the cavity. This field is set up by exciting the two degenerate orthogonal modes 90° out of phase. This field configuration gives pure circularly polarized radiation only along the axis.[12] Averaging $H^2$ over the cavity, 52 percent is circular in one sense, 4 percent is circular in the other, and 44 percent is axial. Comparison of the spectra observed with the two senses of rotation relative to the static magnetic field unambiguously separates $\Delta M = \pm 1, 0$ transitions.

The rotational quantum number $K$ of the states involved in a transition can be determined by a comparison of the relative signal strengths of various lines at room temperature and at 78°K if we note that the Boltzmann factor is given by $\exp[-BK(K+1)/kT]$ and if we assume that all line widths change in the same proportion. The well-known difficulty of making reproducible intensity measurements limits the accuracy of this determination to a mean deviation in $K$

[11] R. V. Pound, Rev. Sci. Instr. 17, 490 (1946); F. P. Zaffarano and W. C. Galloway, Technical Report No. 31, Research Laboratory of Electronics, Massachusetts Institute of Technology, 1947 (unpublished).

[12] The fact that div$\mathbf{H} = 0$ makes this true for any configuration. With $TM$ modes the energy would be *equally* divided between the two circular senses when averaged over the entire cavity.

TABLE I. Results on precisely measured X-band lines. The first column gives the observed magnetic field for resonance at the experimental frequency 9476.75 Mc/sec. The second column gives the resonance field calculated on the assumption that only the electronic spin moment is present. The spin-orbit correction $\Delta H_l$ was made by using the value $g_l^e = -0.00294$ determined by a least-squares fit. The correction for rotation-induced magnetic moment $\Delta H_r$ was made with $g_r = -0.25m/M$. The values of $d\nu/dH$ give the rate of change of the resonance frequency with field in the vicinity of the observed values $H$, $\nu$. The calculated intensity factors listed in column 8 are the values of $4|(KJM|S_x|KJ'M')|^2 \exp(-BK(K+1)/kT)$ at $T=300°K$. The experimental results are signal strengths at optimum modulation expressed in arbitrary units. Provided the frequency widths of all lines are essentially equal, the latter should be proportional to the calculated (integrated) intensities.

| Experimental H (gauss) | Spin only, calculated H (gauss) | Corrections (gauss) $\Delta H_l$ | $\Delta H_r$ | Residual error (gauss) | (Mc/sec) | K | Transition J | M | $d\nu/dH$ (Mc/gauss) | Calculated intensity | Experimental signal strength |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1402.1 | 1404.2 | | | | | 3 | 2→4 | 2→3 | 3.88 | | 0.003 |
| 2342.4 | 2345.1 | | | | | 3 | 2→4 | 1→2 | 2.36 | | 0.031 |
| 3552.8 | 3558.5 | | | | | 3 | 4→2 | −3→−2 | 3.73 | | 0.041 |
| 4155.0 | | | | | | 5 | 6→4 | −3→−2 | | 0.135 | 0.12 |
| 4502.0 | | | | | | 7 | 8→6 | −3→−2 | | | 0.14 |
| 5158.0 | 5165.0 | | | | | 3 | 4→2 | −1→−2 | 2.70 | | 0.043 |
| 5264.4 | 5271.2 | −8.1 | 1.1 | −0.2 | −0.3 | 3 | 2→4 | 1→0 | 1.33 | 0.034 | 0.024 |
| 5353.2 | 5360.4 | | | | | 5 | 4→6 | 1→2 | 1.84 | | 0.37 |
| 5583.8 | 5586.4 | −2.2 | −0.1 | 0.3 | 0.5 | 1 | 1 | −1→0 | 1.96 | 0.741 | 0.78 |
| 5768.5 | 5777.3 | −8.5 | −0.4 | −0.1 | −0.1 | 3 | 2→4 | 0→1 | 1.33 | 0.404 | 0.48 |
| 5977.8 | 5986.0 | −8.3 | −0.1 | −0.2 | −0.5 | 3 | 4→2 | −2→−1 | 2.30 | 0.425 | 0.48 |
| 5999.3 | 6006.8 | −8.0 | 1.0 | 0.5 | 0.9 | 5 | 6→4 | −1→−2 | 1.88 | 0.060 | 0.034 |
| 6087.5 | 6094.7 | −7.0 | −0.2 | 0.0 | 0.0 | 1 | 2 | 1→2 | 1.74 | 1.21 | 1.34 |
| 6509.3 | 6517.7 | −8.2 | −0.4 | −0.2 | −0.4 | 5 | 6→4 | −2→−1 | 1.74 | 0.545 | 0.57 |
| 6684.1 | 6692.4 | | | | | 7 | 8→6 | −2→−1 | 1.52 | | 0.55 |
| 6710.2 | 6718.6 | −7.7 | −0.6 | 0.1 | 0.1 | 1 | 2 | 0→1 | 1.42 | 1.50 | 1.45 |
| 7019.6 | 7029.2 | | | | | 11 | 10→12 | 3→4 | 2.14 | | 0.21 |
| 7063.8 | 7072.9 | | | | | 9 | 8→10 | 2→3 | 2.01 | | 0.26 |
| 7254.3 | 7262.9 | −8.8 | −0.5 | −0.7 | −0.9 | 1 | 2 | −1→0 | 1.33 | 1.24 | 1.15 |
| 7354.9 | | | | | | 7 | 6→8 | 1→2 | | | 0.78 |
| 7513.3 | 7502.9 | −9.0 | 1.3 | −0.1 | −0.1 | 3 | 2 | 0→−1 | 1.77 | 0.351 | 0.31 |
| 7885.9 | 7892.9 | | | | | 5 | 4→6 | 1→0 | 1.72 | | 0.26 |
| 8026.9 | 8036.8 | | | | | 13 | 12→14 | 3→4 | 2.10 | | 0.36 |
| 8097.0 | 8106.1 | | | | | 5 | 4→6 | 0→1 | 1.72 | | 1.15 |
| 8266.0 | 8271.9 | −7.7 | 1.5 | −0.3 | −0.5 | 5 | 4 | 0→−1 | 1.76 | 0.285 | 0.43 |
| 8575.2 | 8582.6 | −7.3 | −0.4 | −0 3 | −0.6 | 3 | 4 | −1→0 | 1.68 | 1.39 | 1.36 |
| 8639.3 | | | | | | 7 | 8→6 | −1→0 | | | 1.03 |
| 8704.8 | 8711.3 | | | | | 7 | 6 | 1→0 | 1.80 | | 0.20 |
| 8729.4 | 8737.4 | −7.0 | −0.4 | 0.6 | 1.0 | 5 | 6 | −1→0 | 1.73 | 1.26 | 1.24 |
| 8813.8 | 8821.7 | | | | | 7 | 8 | 0→1 | 1.82 | | 1.11 |
| 8965.9 | 8972.6 | | | | | 9 | 8 | 1→0 | 1.80 | | 0.092 |
| 9001.6 | 9009.8 | | | | | 11 | 12 | 0→1 | 1.72 | | 0.61 |
| 9030.6 | 9038.2 | | | | | 9 | 10 | 0→1 | 1.81 | | 0.84 |
| 9604.2 | 9618.0 | −13.2 | −0.7 | −0.1 | −0.1 | 3 | 4 | 3→4 | 1.30 | 0.859 | 0.84 |
| 10450±3 | | | | | | 3 | 3 | −3→−2 | | 0.542 | 0.43 |
| 10749±3 | 10739.5 | 15.8 | −3.5 | 2.8 | 1.3 | 1 | 1 | 0→1 | 0.483 | 0.241 | 0.20 |

from the true value of roughly 0.8. Since only odd integral values of $K$ are allowed, this still gives a very useful restriction.

The S-band measurements were made with a $TM_{010}$ cylindrical transmission cavity fed through $\frac{7}{8}$-inch coaxial line. In the Pound-Zaffarano[11] circuit a hybrid ring ("rat race") was used in place of the magic Tee used with the X-band wave-guide arrangement.

## B. Results

Table I shows the results of the precise measurements and calculations for 36 X-band lines. The experimental field values should be accurate within roughly ±60 ppm. (The last two readings at highest fields had to be made with the flip coil since the field exceeded the range of our proton probe.) In the second column are given the values of $H$ for resonance if only $\mathfrak{IC}_{ms}$ were effective. The next two columns give the corrections $\Delta H_l$ and $\Delta H_r$ calculated with (22) and (26). In making

the corrections there are two parameters, $g_r$ and $g_l^e$. These were fitted by least squares (omitting the inaccurate high field line) with the results that $g_r = -(1.42 \pm0.22)\times10^{-4}$ and $g_l^e = -(2.94\pm0.05)\times10^{-3}$. The residual errors are tabulated both in field and frequency units. These are of course related by the $d\nu/dH$ factor tabulated in a later column. The agreement is well within the accuracy of the calculation and measurement of $H$.

Since the accurate calculation of even the uncorrected $H$ is very tedious, it was desirable to try to identify as many of the other observed lines as possible by other means. In Table II we list the positions of 84 additional lines (at X band, but at 9430 Mc/sec rather than the 9476.75 Mc/sec of Table I). For each of them we list the $K$ determined from the temperature dependence of the relative intensity and the $\Delta M$ determined by use of circular polarization. When these data in conjunction with the graphical plots of $E(H)$ mentioned in Sec. 1 permitted a reasonably secure identification, the com-

TABLE II. Survey of other X-band lines at 9430 Mc/sec. The accuracy of H is roughly ±0.05 percent unless stated to the contrary. K was determined from the temperature dependence of the intensity. $\Delta M$ was determined by use of circular polarization. Then an attempt was made to identify lines completely by using a graphical plot of $E(H)$. If this failed, $\Delta M$ was recorded as (+) or (−) according to whether $\Delta M = +1$ or $-1$. The signal strength has the same scale factor as in the table of precisely measured lines.

| Experimental H (gauss) | K | Transition J | M | Signal strength | Experimental H (gauss) | K | Transition J | M | Signal strength |
|---|---|---|---|---|---|---|---|---|---|
| 1914 | 5 | 4→6 | 4→5 | 0.006 | 7560 | 13 | 14→12 | 0→−1 | 0.031 |
| 2005 | 7 | 8→6 | −6→−5 | 0.006 | 7588 | ≥15 | | (+) | 0.055 |
| 2059 | 9 | 10→8 | −6→−5 | 0.012 | 7649 | 13 | 14→12 | −1→0 | 0.27 |
| 2210 | 3 | 2→4 | 2→1 | 0.004 | 7871 | | | (+) | 0.10 |
| 2215 | 5 | 6→4 | −5→−4 | 0.010 | 7969 | 11 | 12→10 | 0→−1 | 0.072 |
| 2465 | 5 | 4→6 | 3→4 | 0.019 | 7999 | | | (+) | <0.06 |
| 2917 | 5 | 6→4 | −4→−3 | 0.032 | 8089 | 11 | 10→12 | 2→3 | 0.40 |
| 3141 | 11 | | (+) | 0.034 | 8120 | 11 | 12→10 | −1→0 | 0.47 |
| 3177 | 7 | 8→6 | −4→−3 | 0.021 | 8163 | 15 | | (+) | 0.030 |
| 3194 | 7 | 6→8 | 4→5 | 0.065 | 8178 | 11 | 10→12 | 3→2 | 0.109 |
| 3269 | 9 | 10→8 | −4→−3 | 0.059 | 8303 | 15 | | (+) | 0.036 |
| 3418 | 5 | 4→6 | 2→3 | 0.069 | 8359 | 7−9 | | (−) | 0.19 |
| 3687 | ≤9 | | (−) | ≤0.01 | 8371 | | | (+) | <0.03 |
| 3715 | 11−13 | | (+) | 0.031 | 8391 | 9 | 8→10? | 1→2? | 0.63 |
| 3759 | 9 | | (+) | 0.051 | 8403 | 9 | 10→8? | −1→0? | 0.76 |
| 4048 | 7 | 6→8 | 3→4 | 0.082 | 8424 | | | (+) | 0.18 |
| 4192 | 13 | | (+) | 0.030 | 8652 | ≥15 | | (+) | 0.11 |
| 4264 | 9−11 | | (+) | 0.050 | 8663 | | | (+) | 0.02 |
| 4347 | 11 | 12→10 | −3→−2 | 0.072 | 8671 | ≥13 | | (+) | 0.16 |
| 4541 | 9 | 10→8 | −3→−2 | 0.11 | 8739 | 13 | 12 | 1→0 | <0.04 |
| 4645 | ≥13 | | (+) | 0.029 | 8753 | 13 | 12→14 | 2→3 | 0.21 |
| 4725 | 13 | | (+) | 0.052 | 8777 | 13 | 14 | 0→1 | 0.24 |
| 4901 | ≥13 | | (+) | 0.052 | 8813 | | | (+) | 0.22 |
| 4978 | 11 | | (+) | 0.099 | 8833 | 11 | 10→12 | 2→1 | 0.011 |
| 5063 | ≥13 | | (+) | 0.035 | 8841 | 13 | 12→14 | 2→3 | 0.011 |
| 5370 | ≥11 | | (+) | 0.075 | 8900 | 11 | 10→12 | 1→2 | 0.67 |
| 5427 | 7 | 6→8 | 2→3 | 0.315 | 8919 | 11 | | (−) | 0.070 |
| 5638 | 9 | 8→10 | 3→4 | 0.34 | 8934 | 11 | 10 | 1→0 | 0.042 |
| 5746 | | | (+) | 0.038 | 9017 | | | (+) | 0.11 |
| 5891 | 11 | 10→12 | 4→5 | 0.16 | 9044 | 15 | | (+) | 0.19 |
| 6100 | 11 | 12→10 | −2→−1 | 0.025 | 9052 | ≥15 | | (+) | 0.14 |
| 6165 | 13 | | (+) | 0.13 | 9074 | 15 | | (+) | 0.18 |
| 6255 | 11 | | (+) | 0.28 | 9087 | 13 | 12→14 | 1→2 | 0.43 |
| 6328 | 7 | 8→6 | −1→−2 | 0.080 | 9103 | 13−15 | | (−) | 0.06 |
| 6445 | 15 | | (+) | 0.113 | 9135 | ≥15 | | (+) | 0.06 |
| 6558 | 9 | 10→8 | −2→−1 | 0.39 | 9150 | ≥15 | | (+) | 0.16 |
| 6724 | ≥13 | | (+) | 0.050 | 9200 | ≥15 | | (+) | 0.08 |
| 7018 | ≥13 | | (−) | 0.126 | 9238 | ≥15 | | (+) | 0.06 |
| 7076 | ≤11 | | (+) | <0.06 | 11390±50 | | | | |
| 7093 | 9 | 8→10 | 3→2 | 0.06 | 11990±50 | | | | |
| 7395 | ≥15 | | (+) | 0.097 | 12090±50 | | | | |
| 7541 | ≥15 | | (+) | 0.031 | 12870±50 | | | | |

plete specification of the transition is given. In this manner, an additional 37 lines were identified.

We note that a majority of the transitions are ones in which J changes by ±2. These are allowed in the presence of the magnetic field, and theoretical intensities will be calculated in a subsequent section. Henry's[4] failure to consider the possibility of transitions of this sort accounts for his ability to identify only 6 lines of the total of 41 observed by Beringer and Castle.[13] The superior sensitivity of our sweep technique to the point-by-point technique of Beringer and Castle is demonstrated by our ability to measure 120 lines in the spectrum. The weakest observable lines are over a hundredfold weaker than the strongest lines of the spectrum at room temperature, and the range is 1000:1 at 78°K.

In Table III are listed the results of exact calculations for 34 S-band (2987 Mc/sec) lines and the corresponding

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

experimental values. This table corresponds to the X-band results in Table I. Because of the uncertainty in the magnetic field over the large S-band cavity, these results are not as reliable as the X-band data. However, the magnitudes of the $\Delta H_r$ corrections are enough larger to provide some additional check on the choice of $g_r$. To give somewhat better agreement here, the value chosen was shifted from $-(1.42\pm0.22)\times10^{-4}$ to $-(1.35\pm0.30)\times10^{-4}$. This of course leaves the X-band agreement essentially unchanged.

Table IV lists the positions and signal amplitudes of 43 more S-band lines. Since neither K nor $\Delta M$ was determined experimentally, it was impossible to identify any of these from the $E(H)$ curves.

## IV. DISCUSSION OF RESULTS

In Table V we collect parameters of the oxygen molecule which have become known or have been made more precise as a result of the work described in this

TABLE III. Identified lines of the $S$-band spectrum. The first column gives the observed magnetic field for resonance at the experimental frequency of 2987.0 Mc/sec. Limits of error are estimated to be ±0.06 percent. The other columns have the same significance as in the $X$-band table. The "signal amplitudes" are simply proportional to the deflections in a sweep made with constant amplitude magnetic field modulation.

| Experimental $H$ (gauss) | Spin only calculated $H$ (gauss) | Corrections (gauss) | | Residual error | | $K$ | Transition | | $dv/dH$ (Mc/gauss) | Relative signal amplitude |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $\Delta H_l$ | $\Delta H_r$ | (gauss) | (Mc/sec) | | $J$ | $M$ | | |
| 1977.6 | 1977.9 | −0.4 | −0.1 | −0.2 | −0.3 | 1 | 1 | −1→0 | 1.62 | 0.4 |
| 2091.0 | 2093.5 | −2.4 | −0.1 | 0.0 | 0.0 | 1 | 2 | 1→2 | 1.50 | 0.8 |
| 2162.3 | 2165.3 | −2.6 | −0.1 | 0.3 | 0.4 | 1 | 2 | 0→1 | 1.40 | 1.0 |
| 2239.1 | 2241.7 | −2.8 | −0.2 | −0.4 | −0.5 | 1 | 2 | −1→0 | 1.31 | 1.0 |
| 2333.3 | 2336.8 | −3.1 | −0.2 | 0.2 | 0.2 | 1 | 2 | −2→−1 | 1.20 | 0.3 |
| 2343 | 2348.5 | | | | | 1 | 1 | 0→1 | 1.14 | 0.3 |
| 2652 | 2651.8 | | | | | 3 | 4→2 | −1→−2 | 2.20 | 0.2 |
| 2887 | 2889.7 | | | | | 3 | 2 | 0→−1 | 0.92 | 0.2 |
| 3039 | 3040.5 | | | | | 3 | 4→2 | −2→−1 | 2.06 | 0.3 |
| 3372 | 3376.0 | | | | | 3 | 2 | −1→−2 | 1.01 | 0.3 |
| 3633 | 3638.7 | −8.1 | 1.2 | −1.2 | −0.8 | 3 | 2 | 1→0 | 0.68 | 0.2 |
| 3701 | 3703.6 | −3.4 | −0.5 | −1.3 | −1.2 | 3 | 4 | −1→0 | 0.90 | 0.6 |
| 3751 | 3755.6 | | | | | 3 | 4 | 3→4 | 0.90 | 0.4 |
| 3854 | 3857.6 | −4.4 | 0.9 | 0.1 | 0.1 | 5 | 4 | 0→−1 | 1.14 | 0.3 |
| 3945 | 3950.9 | −4.9 | −0.6 | 0.4 | 0.3 | 3 | 4 | 2→3 | 0.81 | 0.5 |
| 4167 | 4173.8 | | | | | 3 | 4 | 1→2 | 0.71 | 0.2 |
| 4218 | 4222.9 | | | | | 5 | 6 | −1→0 | 1.06 | 0.3 |
| 4379 | 4383.9 | | | | | 7 | 6 | 1→0 | 1.15 | 0.1 |
| 4613 | 4620.0 | | | | | 3 | 4 | 0→1 | 0.52 | 0.3 |
| 4681 | 4683.9 | | | | | 5 | 4 | −3→−4 | 0.71 | 0.3 |
| 5030 | 5043.8 | | | | | 3 | 4 | −3→−2 | 0.49 | 0.4 |
| 5066 | 5075.1 | | | | | 5 | 4 | −2→−3 | 0.58 | 0.3 |
| 5146 | 5155.3 | | | | | 3 | 4 | −4→−3 | 0.48 | 0.2 |
| 5177 | 5183.8 | | | | | 5 | 6 | 5→6 | 0.70 | 0.3 |
| 5455 | 5472.5 | | | | | 3 | 4 | −2→−1 | 0.42 | 0.1 |
| 5482 | 5491.7 | | | | | 5 | 6 | 4→5 | 0.61 | 0.2 |
| 5827 | 5835.5 | | | | | 5 | 6 | 3→4 | 0.53 | 0.3 |
| 5965 | 5976.3 | −12.8 | 3.1 | 1.6 | 0.6 | 5 | 4 | −1→−2 | 0.39 | 0.2 |
| 6017 | 6026.4 | | | | | 7 | 6 | −5→−6 | 0.58 | 0.1 |
| 6276 | 6286.1 | −8.9 | −2.1 | −0.9 | −0.4 | 5 | 6 | 2→3 | 0.44 | 0.4 |
| 7190 | 7196.1 | | | | | 9 | 8 | −7→−8 | 0.52 | 0.1 |
| 7510 | 7520.4 | | | | | 9 | 10 | 9→10 | 0.55 | 0.1 |
| 8210 | 8217.1 | | | | | 11 | 10 | −9→−10 | 0.48 | 0.1 |
| 9235 | 9248.1 | | | | | 9 | 10 | 6→7 | 0.33 | 0.3 |

paper and in TSI. The system of interrelations which enable these parameters to be determined from the experimental data and compared with the theory are discussed in this section.

## A. Source of Results

### Direct Experimental Results

The spin coupling constants $\lambda_{(0)}$, $\lambda_{(1)}$, $\lambda_1$, and $\mu$ were determined directly by fitting the field-free spectrum with the theoretical formulas derived in TSI. The quantities $\lambda_e$ and $\lambda_2$ follow immediately from the theory presented there, and may be considered on firm ground. Similarly, $g_r$ and $g_l^e$ were determined by fitting the microwave spectrum in the presence of a magnetic field, under the assumption that $g_s^e = -2.00229$. On these quantities the quoted errors are the expected standard errors in a least-squares fit.

### Derived Results

To separate the various physical mechanisms contributing to the parameters, we use the assumption (discussed in TSI) that the spin-orbit coupling parameter $A$ and the reciprocal moment of inertia $B$ can be treated as constants in the sums of matrix components which enter in the theory. Denoting the common factor $\sum_n |(0|L_x|n)|^2/(E_n-E_0)$ by $L(L+1)/hv$, and taking $B=1.44$ cm$^{-1}$, one may readily deduce values for $\lambda_r'$, $\lambda_e''$, $\mu'$, $\mu''$, $A$, $L(L+1)/hv$, $\chi_{H-F}$, and $R_e$ (as corrected for electronic contributions to $B$) from the above direct experimental results. These results are also tabulated. The quoted errors reflect only the errors in the direct experimental results. No attempt has been made to allow for the error introduced by our theoretical assumption.

### Calculated Results

Finally, we also list the values for $\lambda_e'$, $\lambda_1'$, $\mu'$, and $\chi_{dia}$ which were obtained by direct calculation, using Meckler's expression for the molecular oxygen wave function. The method of calculation of $\lambda'$ and $\mu'$ is given in TSI. No limit of error was assigned to these quantities for lack of any sound manner of estimation.

## B. Discussion of Individual Results

### Rotational Moment

A key to unraveling the entire problem experimentally was the fact that our precise Zeeman-effect measurements and theory have allowed us to determine

the rotational $g$-factor $g_r$ defined in Eq. (17). Admittedly, the measurement is not of high accuracy, since it is based on small shifts superposed on the enormously larger splittings caused by the full Bohr magnetons of electron spin moment. Still, there is enough data to give reasonable assurance.

The magnitude and even the sign of $g_r$ are rather unexpected. It is well known that in $H_2$ the electrons make almost no contribution to $g_r$, leaving $g_r = +0.883m/M = 0.883g_r{}^n$.[14] As another example,[8] OCS has $g_r = -0.025m/M$. There appear to be no examples of so large a negative $g$-factor as the $-0.25m/M$ which we find in $O_2$ in any of the molecules previously studied.

It is of interest to compare the oxygen result with the resulting moment if the electronic charge cloud merely rotated rigidly with the nuclei. One can readily show that in this case, we have

$$g_r = g_r{}^n + g_r{}^e = \frac{Z}{A} - \frac{\sum_i \langle x_i^2 + z_i^2 \rangle}{A(R/2)^2}, \qquad (27)$$

where $z$ is the internuclear axis and $R$ is the internuclear distance. These one-electron averages $\langle x_i^2 + z_i^2 \rangle$ are readily carried out with the use of Meckler's molecular orbitals (MO's) made up of Gaussian atomic orbitals (AO's). A simple integration shows that these Gaussian AO's have a value of $\langle r^2 \rangle$ which agrees with that of the Hartree-Fock atomic wave function[15] within 10 percent. This indicates that for a calculation of this type Meckler's MO's should give reasonably close approximations to the true values. The results are given in Table VI for each orbital. If we assumed that the electrons in all orbitals moved rigidly with the molecule, the resultant $g_r{}^e$ would be $-0.758m/M$, and $g_r$ would be $-0.258m/M$. This only slightly exceeds the experimental value. The agreement would still be within the experimental error and the error due to the wave functions if one assumed that the eight inner $1s$ and $2s$ electrons moved with unhindered precession about their nuclei, simply cancelling nuclear charge, while the eight outer $2p$ electrons moved rigidly. This is a more reasonable semiclassical model, since it is the asphericity of the charge distribution which causes it to rotate with the molecule.[16]

Viewed in terms of the rigorous quantum-mechanical picture, the unusually large $g_r{}^e$ is probably a result of the fact that $p$ orbitals, which would tend to have larger angular momentum matrix elements than $s$ orbitals, are prominent in oxygen. This effect might be anticipated[17] by noting that the atomic correspondence at large $R$ is to atomic $P$ states, whereas in $H_2$ it is to $S$-states.

[14] N. J. Harrick and N. F. Ramsey, Phys. Rev. **88**, 228 (1952).

[15] Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) **A238**, 229 (1939). A very useful analytic approximation is given by P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

[16] G. C. Wick, Phys. Rev. **73**, 51 (1948).

[17] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), Chap. X.

TABLE IV. Survey of other $S$-band lines. The first column gives the observed magnetic field for resonance at the experimental frequency of 2987.0 Mc/sec. The limit of error is estimated to be $\pm 0.06$ percent. The signal amplitude column has the same significance as in Table III.

| Experimental $H$ (gauss) | Signal amplitude |
|---|---|
| 2493 | 0.1 |
| 2743 | 0.1 |
| 2826 | 0.05 |
| 3159 | 0.2 |
| 3187 | 0.08 |
| 3398 | 0.2 |
| 3423 | 0.3 |
| 3440 | 0.3 |
| 3529 | 0.2 |
| 3587 | 0.1 |
| 3608 | 0.15 |
| 3830 | 0.2 |
| 4086 | 0.08 |
| 4322 | 0.06 |
| 4339 | 0.06 |
| 4436 | 0.2 |
| 4456 | 0.08 |
| 4493 | 0.2 |
| 4522 | 0.35 |
| 4713 | 0.3 |
| 4761 | 0.2 |
| 4819 | 0.2 |
| 6421 | 0.15 |
| 6481 | 0.2 |
| 6827 | 0.3 |
| 6937 | 0.2 |
| 7047 | 0.15 |
| 7083 | 0.15 |
| 7281 | 0.3 |
| 7320 | 0.15 |
| 7748 | 0.1 |
| 7828 | 0.3 |
| 7987 | 0.1 |
| 8010 | 0.2 |
| 8318 | 0.1 |
| 8401 | 0.2 |
| 8450 | 0.1 |
| 8485 | 0.1 |
| 8576 | 0.15 |
| 8612 | 0.15 |
| 8750 | 0.15 |
| 8876 | 0.15 |
| 9090 | 0.15 |

## Spin-Orbit Coupling

The other key in the solution was the experimental measurement of $g_l{}^e$. With $\sum_n |(0|L_x|n)|^2/(E_n - E_0)$ evaluated from $g_r{}^e$, this gives us the spin-orbit coupling parameter $A$, and hence the second-order spin-orbit contribution $\lambda''$ to the parameter $\lambda$. As is clear from the table, $\lambda''$ is less than 1 percent of $\lambda$. Thus, even if this evaluation of $\lambda''$ has a serious fractional error, we are still assured that the first-order spin-spin contribution, $\lambda'$, is the overwhelming one. This makes $\lambda_e'$ and $\lambda_1'$ firmly known quantities the calculation of which would serve as a test for the quality of a proposed electronic wave function. Since the calculation of TSI gave only 60 percent of $\lambda_e'$, it is clear that the Gaussian MO's are not too good an approximation (even when adjusted as described there). On the other hand, the calculated $\lambda_1'$ is roughly 16 percent too high. This is really as good agreement as one could expect.

TABLE V. Parameters of the oxygen molecule as determined in this work. As explained in the text, the quoted errors are standard errors based on least-squares fits of the experimental data. They include no estimates of the theoretical errors in the assumed interrelations and thus are not necessarily limits of error.

| Symbol | Explanation | Numerical value Experimental | Calculated |
|---|---|---|---|
| $\lambda_{(0)}$ | $\lambda_{\text{eff}}(v=0)$ | $59\ 501.57 \pm 0.15$ Mc/sec | |
| $\lambda_{(1)}$ | $\lambda_{\text{eff}}(v=1)$ | $59\ 730 \pm 40$ Mc/sec | |
| $\lambda_e$ | $\lambda_e{}' + \lambda_e{}''$ | $59\ 386 \pm 20$ Mc/sec | |
| $\lambda_e{}'$ | spin-spin part | $58\ 920 \pm 60$ Mc/sec | $35\ 000$ Mc/sec |
| $\lambda_e{}''$ | $\frac{1}{2}\sum_n \dfrac{\|(n\|AL_x\|0)\|^2}{E_n-E_0}$ | $465 \pm 50$ Mc/sec | |
| $\lambda_1$ | $[R(d\lambda/dR)]_e$ | $16\ 896 \pm 150$ Mc/sec | |
| $\lambda_1{}'$ | $[R(d\lambda'/dR)]_e$ | | $19\ 600$ Mc/sec |
| $\lambda_2$ | $[\frac{1}{2}R^2 d^2\lambda/dR^2]_e$ | $(5\pm2)\times10^4$ Mc/sec | |
| $\mu$ | $\mu' + \mu''$ | $-252.67 \pm 0.05$ Mc/sec | |
| $\mu'$ | spin-nuclear part | $1 \pm 4$ Mc/sec | $10.0$ Mc/sec |
| $\mu''$ | $4\ \mathrm{Re}\sum_n \dfrac{(0\|AL_x\|n)(n\|BL_x\|0)}{E_n-E_0}$ | $(-254\pm4)$ Mc/sec | |
| $g_l{}^e$ | $2\ \mathrm{Re}\sum_n \dfrac{(0\|L_x\|n)(n\|AL_x\|0)}{E_n-E_0}$ | $-(2.94\pm0.05)\times10^{-3}$ | |
| $g_r$ | $g_r{}^n + g_r{}^e$ | $-(1.35\pm0.30)\times10^{-4} = -(0.25\pm0.05)m/M$ | |
| $g_r{}^n$ | $(Z/A)(m/M)$ | | $2.72\times10^{-4} = 0.500m/M$ |
| $g_r{}^e$ | $-4\ \mathrm{Re}\sum_n \dfrac{(0\|L_x\|n)(n\|BL_x\|0)}{E_n-E_0}$ | $-(4.1\pm0.3)\times10^{-4} = -(0.75\pm0.05)m/M$ | |
| $R_e$ | | $1.20741 \pm 0.00002$A | |
| $\dfrac{L(L+1)}{h\nu}$ | $\sum_n \dfrac{\|(0\|L_x\|n)\|^2}{E_n-E_0}$ | $(7.1\pm0.5)\times10^{-6}/\text{cm}^{-1}$ | |
| $A$ | spin-orbit coupling parameter | $-(21\pm2)$ cm$^{-1}$ | |
| $\chi_{\text{dia}}$ | $\dfrac{-N_0 e^2}{6mc^2}\sum_i \langle r_i^2\rangle$ | | $-29.5\times10^{-6}$ cm$^3$/mole |
| $\chi_{H-F}$ | $\dfrac{4N_0\beta^2}{3}\sum_n \dfrac{\|(0\|L_x\|n)\|^2}{E_n-E_0}$ | $(24.6\pm1.7)\times10^{-6}$ cm$^3$/mole | |
| $\chi_{\text{orb}}$ | $\chi_{\text{dia}} + \chi_{H-F}$ | $-(4.9\pm1.7)\times10^{-6}$ cm$^3$/mole | |
| $\chi_{\text{spin}}$ | $2N_0(g_s{}^e)^2\beta^2/3kT$ | | $1.003/T$ cm$^3$/mole |

From $g_l{}^e$ we directly find $\mu''$, using the relation $\mu'' = 2Bg_l{}^e$. This second-order interaction of the rotation-induced orbital angular momentum with the spin gives essentially the entire spin-rotation coupling constant $\mu$, leaving $1\pm4$ Mc/sec for the first order $\mu'$. Direct calculation of $\mu'$ (see TSI) gave 10.0 Mc/sec, and appeared insensitive to detailed choice of wave function. Since the experimentally deduced value is the difference of two large numbers, this agreement is reasonably good. A more informative check is to compare $\mu''$ computed as above with the value obtained by subtracting the reliably computed $\mu'$ from the experimental $\mu$. These results check to within 3.5 percent. Since the standard deviation in the least-squares fit is only 1.7 percent, this indicates that an error of the order of 1 or 2 percent may be introduced in removing $B$ from the summation and giving it its value in the ground electronic state. This is a reasonable magnitude of error

since a more detailed examination shows that the expected error is of the same order of magnitude as the effect of zero-point vibration, which is 0.6 percent in O$_2$. It does not seem possible to make any equally simple estimate of the error introduced by removing $A$ from the sum of matrix elements, nor, lacking a reliable calculated value for $\lambda'$, can we check it experimentally. The error is no doubt greater with $A$ than with $B$, but our partial check is still encouraging.

Another viewpoint would be to assume from the start that $g_l^e = (\mu - \mu')/2B$. In this, $B$ and $\mu$ are known from the field-free spectrum, and $\mu'$ is easily calculated to good accuracy. Thus $g_l^e$ is determined a priori. Since the contributions of $g_r$ to the spectrum are small and of a distinctive form they are easily eliminated. The only free parameter then left for the Zeeman spectrum is $g_s^e$, the electron spin g-factor. Our excellent agreement of theory and experiment then demonstrates that this has the theoretical value[18] $-2.0023$ with a precision of 60 ppm (parts per million). This precision is two orders of magnitude less than that obtained by Koenig, Prodell, and Kusch[19] with atomic hydrogen. It is also an order of magnitude less than that of Abragam and Van Vleck[20] in their interpretation of the data on the atomic oxygen Zeeman effect taken by Rawson and Beringer.[21] Nevertheless, it is a reassuring check that there is no unexpected difficulty in treating the case of two coupled spins in a molecular, as opposed to an atomic, environment.[22]

### Susceptibilities

Starting with a general formula of Van Vleck,[17] the molar susceptibility of a diatomic molecule with electronic spin $S$ but no diagonal orbital angular momentum is seen to be

$$\chi = \chi_{\text{spin}} + \chi_{H-F} + \chi_{\text{dia}}$$

$$= \frac{N_0(g_s^e)^2\beta^2 S(S+1)}{3kT} + \frac{4N_0}{3}\beta^2 \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_0}$$

$$- \frac{N_0 e^2}{6mc^2} \sum_i \langle r_i^2 \rangle. \quad (28)$$

Evidently the first term is dominant since $kT \ll (E_n - E_0)$ in most cases and the diamagnetic term is always small. It is still of some interest to know the magnitudes of the temperature-independent terms, however, in making detailed comparison of precise experimental data with the theory. The $\chi_{\text{dia}}$ is easily calculated from Meckler's wave function, and the expected accuracy is again

TABLE VI. Integrals over oxygen molecular orbitals. The occupation numbers apply to the lowest-energy configuration (Meckler's $\phi_c$). $R$ is the internuclear distance, $z$ is the internuclear axis, and $r$ is measured from the center of mass of the molecule.

| Orbital | Meckler notation | Occupation number | $\frac{\langle x^2+z^2\rangle}{(R/2)^2}$ | $\langle r^2\rangle \times 10^{16}$ cm$^2$ |
|---|---|---|---|---|
| $1s\ \sigma_g$ | $\varphi_s$ | 2 | 1.02 | 0.375 |
| $1s\ \sigma_u$ | $\chi_s$ | 2 | 1.02 | 0.375 |
| $2s\ \sigma_g$ | $\varphi_\sigma$ | 2 | 1.36 | 0.585 |
| $2s\ \sigma_u$ | $\chi_\sigma$ | 2 | 1.69 | 0.710 |
| $2p\ \sigma_g$ | $\varphi_0$ | 2 | 1.96 | 0.800 |
| $2p\ \sigma_u$ | $\chi_0$ | 0 | 2.62 | 1.038 |
| $2p\ \pi_u^\pm$ | $\varphi_\pm$ | 4 | 1.61 | 0.760 |
| $2p\ \pi_g^\pm$ | $\chi_\pm$ | 2 | 1.87 | 0.855 |

moderately good because the function $r^2$ puts no particular weight on the detailed behavior near the nucleus. The results are given for each orbital in Table VI. The high-frequency paramagnetic contribution $\chi_{H-F}$ is evaluated by using the value for $L(L+1)/h\nu$ determined from $g_r^e$. These two contributions nearly cancel, the diamagnetic term slightly exceeding the paramagnetic one. This remainder provides a correction of $5 \times 10^{-6}$ cm$^3$/mole to the spin susceptibility, which is $3.42 \times 10^{-3}$ cm$^3$/mole at $T = 20°C$. This correction is small compared to the spread in the experimentally obtained values, but might be useful in explaining small departures from Curie's law. Since it is definitely too small a correction to explain the deviation found by Woltjer, Coppoolse, and Weirsma,[17] that deviation must be ascribed to experimental error.

## V. LINE INTENSITIES

### A. Theory

It is easily verified that the $1/Q$ increment caused by absorption in a gas-filled cavity is equal to $4\pi\chi''$ or to $c/\omega$ times the absorption coefficient $\alpha$ of the gas for a plane wave of suitable polarization. Further, in these Zeeman-effect studies all degeneracies are lifted, so there is no summation over $M$ states. The standard analysis[23] then yields

$$\left(\frac{1}{Q}\right)_{ij} = \frac{4\pi\omega N}{kT} |(\mu_r)_{ij}|^2 \frac{\tau^{-1}}{(\omega - \omega_{ij})^2 + \tau^{-2}} \frac{e^{-E_i/kT}}{\sum_n e^{-E_n/kT}}, \quad (29)$$

where $|(\mu_r)_{ij}|^2$ is the average squared matrix element of $g_s^e\beta S_r$ or $\langle |g_s^e\beta H_{rf} \cdot S_{ij}|^2 \rangle / \langle H_{rf}^2 \rangle$, $S_r$ being the component of $S$ along $H_{rf}$. Also $\tau^{-1}$ is $2\pi\Delta\nu$, $\Delta\nu$ being the frequency half-width at half-power absorption. Eliminating $N$ by using the ideal gas law, approximating the partition sum by its classical value[24] $3kT/2B$, and setting $\omega = \omega_{ij}$, we find the maximum absorption to be

$$\left(\frac{1}{Q}\right)_{ij} = \frac{32\pi}{3} \frac{B\beta^2\nu}{(\Delta\nu/P)} \frac{e^{-BK(K+1)/kT}}{(kT)^3} |(S_r)_{ij}|^2. \quad (30)$$

[18] R. Karplus and N. M. Kroll, Phys. Rev. **77**, 536 (1950).
[19] Koenig, Prodell, and Kusch, Phys. Rev. **88**, 191 (1952).
[20] A. Abragam and J. H. Van Vleck, Phys. Rev. **92**, 1448 (1953).
[21] E. B. Rawson and R. Beringer, Phys. Rev. **88**, 677 (1952).
[22] These orders of magnitude are indices of the increasing difficulty of the problem as one proceeds from the simplest atom to a more complex atom, and finally to a molecule. For a molecular problem, our agreement is quite satisfactory.

[23] J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. **17**, 227 (1945).
[24] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 139.

TABLE VII. Table of field-dependent transformations $U_K$.

| $K$ | $J$ | $M$ | $H$ (kilogauss) | $U_{1\tau}$ | $U_{2\tau}$ | $U_{3\tau}$ |
|---|---|---|---|---|---|---|
| 1 | 1 | $-1$ | 1.98 | 0.000 | 1.000 | 0.024 |
|   |   | $-1$ | 5.55 | 0.000 | 0.991 | 0.136 |
|   |   | 0 | 1.98 | $-0.038$ | 0.996 | 0.056 |
|   |   | 0 | 5.55 | $-0.103$ | 0.982 | 0.148 |
|   |   | 0 | 10.7 | $-0.176$ | 0.954 | 0.244 |
|   |   | 1 | 10.7 | 0.000 | 0.974 | 0.230 |
| 1 | 2 | $\pm2$ | — | 0.000 | 0.000 | 1.000 |
|   |   | $\pm1$ | 2.2 | 0.000 | $-0.054$ | 0.997 |
|   |   | $-1$ | 7.2 | 0.000 | $-0.171$ | 0.985 |
|   |   | $-1$ | 8.8 | 0.000 | $-0.204$ | 0.977 |
|   |   | 0 | 2.2 | 0.050 | $-0.062$ | 0.995 |
|   |   | 0 | 6.7 | 0.040 | $-0.171$ | 0.984 |
|   |   | 0 | 7.2 | 0.048 | $-0.178$ | 0.983 |
|   |   | 1 | 6.0 | 0.000 | $-0.146$ | 0.990 |
|   |   | 1 | 6.7 | 0.000 | $-0.159$ | 0.986 |
| 3 | 2 | $-1$ | 6.0 | 0.935 | $-0.122$ | $-0.331$ |
|   |   | $-1$ | 7.5 | 0.914 | $-0.152$ | $-0.377$ |
|   |   | 0 | 3.7 | 0.973 | $-0.138$ | 0.182 |
|   |   | 0 | 5.6 | 0.920 | $-0.216$ | 0.326 |
|   |   | 0 | 7.5 | 0.862 | $-0.281$ | 0.419 |
|   |   | 0 | 8.5 | 0.832 | $-0.316$ | 0.455 |
|   |   | 1 | 3.7 | 0.992 | $-0.114$ | 0.070 |
|   |   | 1 | 5.2 | 0.981 | $-0.163$ | 0.107 |
| 3 | 3 | $-3$ | 10.4 | 0.000 | 0.985 | 0.166 |
|   |   | $-2$ | 10.4 | 0.315 | 0.927 | 0.198 |

| $K$ | $J$ | $M$ | $H$ (kilogauss) | $U_{1\tau}$ | $U_{2\tau}$ | $U_{3\tau}$ |
|---|---|---|---|---|---|---|
| 3 | 4 | $-2$ | 6.0 | 0.089 | $-0.155$ | 0.984 |
|   |   | $-1$ | 3.6 | 0.378 | $-0.139$ | 0.915 |
|   |   | $-1$ | 8.5 | 0.338 | $-0.286$ | 0.895 |
|   |   | 0 | 3.6 | $-0.186$ | $-0.086$ | 0.978 |
|   |   | 0 | 5.2 | $-0.304$ | $-0.087$ | 0.924 |
|   |   | 0 | 8.5 | $-0.498$ | $-0.075$ | 0.863 |
|   |   | 1 | 5.6 | $-0.139$ | $-0.143$ | 0.980 |
|   |   | 2 | 3.9 | $-0.041$ | $-0.106$ | 0.993 |
|   |   | 3 | 3.9 | 0.000 | $-0.088$ | 0.995 |
|   |   | 3 | 9.3 | 0.000 | $-0.228$ | 0.974 |
|   |   | 4 | 9.3 | 0.000 | 0.000 | 1.000 |
| 5 | 4 | $-2$ | 4.1 | 0.984 | $-0.120$ | $-0.130$ |
|   |   | $-2$ | 5.9 | 0.968 | $-0.163$ | $-0.182$ |
|   |   | $-1$ | 3.8 | 0.958 | $-0.093$ | $-0.272$ |
|   |   | $-1$ | 6.0 | 0.922 | $-0.123$ | $-0.363$ |
|   |   | $-1$ | 6.5 | 0.914 | $-0.128$ | $-0.381$ |
|   |   | $-1$ | 8.2 | 0.884 | $-0.140$ | $-0.448$ |
|   |   | 0 | 3.8 | 0.834 | $-0.166$ | 0.523 |
|   |   | 0 | 8.2 | 0.726 | $-0.321$ | 0.608 |
|   |   | 0 | 9.1 | 0.711 | $-0.342$ | 0.602 |
| 5 | 6 | $-3$ | 4.1 | 0.059 | $-0.109$ | 0.993 |
|   |   | $-2$ | 6.5 | 0.164 | $-0.197$ | 0.966 |
|   |   | $-1$ | 5.9 | 0.328 | $-0.216$ | 0.920 |
|   |   | $-1$ | 8.7 | 0.388 | $-0.305$ | 0.872 |
|   |   | 0 | 8.6 | $-0.634$ | $-0.014$ | 0.774 |
|   |   | 0 | 9.1 | $-0.650$ | $-0.014$ | 0.759 |
|   |   | 2 | 6.3 | $-0.162$ | $-0.158$ | 0.974 |
|   |   | 3 | 6.3 | $-0.096$ | $-0.168$ | 0.981 |

Evidently lowering the temperature gives a rapid rise in intensity for the lower rotational levels. Since our experimental frequency is fixed by the cavity, $\nu$ is the same for all lines. Also, it is an experimental fact that in oxygen the normalized line breadth parameter $(\Delta\nu/P)$ at a given temperature has the same value for all lines within roughly $\pm10$ percent. (Beringer and Castle's[13] anomalous results were caused by their incorrect use of $\nu/H$ rather than $d\nu/dH$ to convert their field widths to frequency widths.) Thus at a given temperature, the variations of intensity from line to line come almost entirely from the factor $|(S_r)_{ij}|^2 \exp[-BK(K+1)/kT]$. Since the Boltzmann factor is readily calculated, we are left only with the task of computing the matrix elements.

To handle the general case, it is convenient to expand $H_{rf}$ as

$$H = H^+ u_+ + H^- u_- + H_Z u_Z,$$

where

$$H^{\pm} = (H_X \mp iH_Y)/\sqrt{2} \tag{31}$$

and

$$u_{\pm} = (u_X \pm iu_Y)/\sqrt{2}.$$

The $u_X$ and $u_Y$ are unit vectors in the $X$ and $Y$ directions. Then

$$H \cdot S_{ij} = H^+(S_+)_{ij}/\sqrt{2} + H^-(S_-)_{ij}/\sqrt{2} + H_Z(S_Z)_{ij}, \tag{32}$$

where $S_{\pm}$ are $S_X \pm iS_Y$. Since the selection rules on matrix elements of $S_+$, $S_-$, and $S_Z$ are all different ($\Delta M$ being $+1$, $-1$, and 0. respectively), only one term on the right will contribute to $(S_r)_{ij}$ for a given $ij$

transition. The $S$ matrix elements will have coefficients $f$, depending on the rf field and sample configurations, which give the fraction of the stored energy active in inducing each particular type of transition. For example

$$|(S_r)_{ij}|^2 = \frac{\int_{\text{sample}} |H^+|^2 d\tau}{\int_{\text{cavity}} H^2 d\tau} \frac{|(S_+)_{ij}|^2}{2} \equiv \frac{f_+|(S_+)_{ij}|^2}{2}. \tag{33}$$

Finally, we note that with cylindrical symmetry about the static field direction $Z$,

$$|(\tau M|S_{\pm}|\tau'M')|^2 = 4|(\tau M|S_X|\tau'M')|^2 \tag{34}$$

for elements which exist in the left member. This enables us to write, in general,

$$|(S_r)_{ij}|^2 = 2|(S_X)_{ij}|^2[f_+\delta(M_i, M_j+1) + f_-\delta(M_i, M_j-1)] + |(S_Z)_{ij}|^2 f_0\delta(M_i,M_j). \tag{35}$$

For nonrotating radiation perpendicular to $Z$ in a gas-filled cavity, $f_+ = f_- = \frac{1}{2}$. For localized samples, these numbers would obviously be reduced by filling factors. With pure circularly polarized radiation, one of the $f_{\pm}$ would be unity, all other $f$'s being zero. (Rotation is possible only when two degenerate modes are excited out of phase.)

The procedure for calculating the required matrix elements, starting from the simple elements of $S_\theta$

referred to the gyrating coordinates $g$, can be symbolized as

$$(S_F)_{ij} = (U^{-1}T^{-1}S_F TU)_{ij}$$
$$= [U^{-1}T^{-1}(\sum_g \Phi_{Fg}S_g)TU]_{ij}. \quad (36)$$

In this equation, the $\Phi_{Fg}$ are the direction cosines between fixed and gyrating axes; $T$ is the transformation between the Hund case (a) basis (in which $S_z = \Sigma$ is diagonal, and in which we express $\Phi_{Fg}$ and $S_g$) and the basis which diagonalizes the field-free Hamiltonian; $U$ is the transformation between the latter basis and the true eigenfunctions in the presence of the field. The transformations $T$ are derived and tabulated in TSI; $U$ is derived in Sec. I-B of this paper, and a number of specific cases are listed in Table VII.

For $F = Z$, $(T^{-1}S_F T)$ has been carried out in TSI and the result appears, multiplied by $-g_s{}^e\beta H$, as the terms linear in $H$ in (4) of this paper. As discussed in Sec. I-B, we neglect the part of $U$ which is off-diagonal

in $K$. The resulting transformed matrix elements $(S_Z)_{ij}$ are of the type $(KJM|S_Z|KJ'M)$. For transitions possible below 50 kMc/sec, $J' = J\pm2$. These would be forbidden in the absence of the magnetic field, but, as noted in Sec. I-B, $J$ breaks down as an angular momentum quantum number with increasing field and is kept only as a convenient label. On the other hand, at high fields $\mathfrak{IC}_{ms} = -g_s{}^e\beta HS_Z$ is such an important part of the Hamiltonian that when the total Hamiltonian is diagonalized, $S_Z$ is nearly diagonal also. Thus the $(J|J\pm2)$ elements of $S_Z$ never get very large. Detailed calculation verifies this conclusion, all $\Delta M = 0$ transitions having a calculated intensity less than one percent of that of the strong $\Delta M = \pm1$ transitions. The conclusion is further substantiated by the fact that $\Delta M = 0$ lines were not observed experimentally even when a cavity mode was used in which $f_0$ was 0.44.

The transformations are carried out in exactly the same manner for $S_X$. We can carry them analytically to

$$2(KJM|T^{-1}(\sum_g \Phi_{Xg}S_g)T|KJ'M-1) =$$

|  | $J' = K-1$ | $J' = K$ | $J' = K+1$ |
|---|---|---|---|
| $J=K-1$ | $[K(K-1)-M(M-1)]^{\frac{1}{2}}$ $\times g(K,K-1)/g_s{}^e$ | $C_{K-1}[(K-M)(K-M+1)]^{\frac{1}{2}}$ | $0$ |
| $J=K$ | $-C_{K-1}[(K+M)(K+M-1)]^{\frac{1}{2}}$ | $[K(K+1)-M(M-1)]^{\frac{1}{2}}$ $\times g(K,K)/g_s{}^e$ | $B_{K+1}[(K-M+1)(K-M+2)]^{\frac{1}{2}}$ |
| $J=K+1$ | $0$ | $-B_{K+1}[(K+M)(K+M+1)]^{\frac{1}{2}}$ | $[(K+1)(K+2)-M(M-1)]^{\frac{1}{2}}$ $\times g(K,K+1)/g_s{}^e$ |

$$(37)$$

In this, the $C_{K-1}$, $B_{K+1}$, and $g(K,J)$ are defined in Eq. (60) of TSI and listed in Table VIII of that paper. We note that since we are dealing with $(M|M-1)$ elements there is no symmetry of this matrix about the diagonal. Thus one must take extra care to read off the correct element. Inspection of this matrix shows that $\Delta J = \pm2$ transitions are forbidden between the field-free eigenfunctions which form the basis for (37). The $\Delta J = \pm1$ transitions contribute to the millimeter spectrum treated in TSI. The $\Delta J = 0$ elements are all proportional to $[J(J+1)-M(M-1)]^{\frac{1}{2}}$, and their squares will give the allowed transition probabilities in very weak fields.

For the fields of interest in this experiment, however, the departure of $U$ from a diagonal (unit) matrix are so large (i.e., the $J$'s are so mixed) that it is essential that the transformation $U$ be applied. When this is done, it turns out that $\Delta J = \pm2$ transitions have appreciable intensities even at a thousand gauss, and that their intensity is of the same order as that of the "allowed" lines for fields above roughly 6 kilogauss. Of course, the intensities of the "allowed" lines is also strongly modified by $U$.

## B. Comparison with Experiment

In Table I we list the values of $4|(S_X)_{ij}|^2$ $\times \exp[-BK(K+1)/kT]$ evaluated at $T = 300°$K for

those lines for which the entire calculation indicated above was carried through. As remarked in connection with Eq. (30), these factors should be nearly proportional to the experimental signal strength. ["Signal strength" is defined as proportional to $(1/Q)_{ij}$. It differs from the (integrated) intensity by a factor of $(1/\Delta\nu)$.] Inspection of the last two columns of Table I shows that the proportionality holds to an average of roughly $\pm10$ percent over a range of almost 100:1 in absolute value. This agreement is highly satisfactory in view of the difficulty of the measurement and in view of the approximation that $\Delta\nu$ is the same for all lines.

An attempt was made to check (30) more completely by measuring the absolute intensity. Inserting the numerical values for $T = 300°$K, with $\nu = 9400$ Mc/sec and $(\Delta\nu/P) = 2$ Mc/sec-mm Hg, one finds

$$(1/Q)_{ij} = 1.46\times10^{-7}|(S_X)_{ij}|^2$$
$$\times \exp[-0.0069K(K+1)]$$
$$\times [f_+\delta(M_i, M_j+1)+f_-\delta(M_i, M_j-1)]. \quad (38)$$

For linear polarization and the strong $K = J = 1$, $M = -1\to0$ line, this formula gives[25] $1.36\times10^{-8}$. This

[25] Beringer and Castle (see reference 13) quote a calculated $1/Q$ of $0.46\times10^{-8}$ under these same conditions. The discrepancy apparently comes from their value of $\mathfrak{M}^2$ which is defined as $g^2(S_X{}^2+S_Y{}^2) = 8|(S_X)_{ij}|^2$. They use $\mathfrak{M}^2 = \frac{1}{2}$, which is the value

conveniently establishes the scale factor for Table I, and any other cases can be computed by proportionality.

To relate these predictions to experimental data, we note that the power reflection coefficient of a cavity at its resonant frequency is[26]

$$|r|^2 = [(\xi-1)/(\xi+1)]^2, \qquad (39)$$

where $\xi = Q_e/Q_0$, $Q_e$ being the external $Q$ and $Q_0$ the unloaded cavity $Q$. Thus

$$\Delta|r|^2 = 4\xi(\xi-1)(\xi+1)^{-3}Q_0(1/Q)_{ij}. \qquad (40)$$

The coefficient in this equation has a broad maximum at the optimum operating point $\xi = 2 \pm \sqrt{3}$ where $|r|^2 = \frac{1}{3}$ At that point

$$\Delta|r|^2 = 0.385 Q_0(1/Q)_{ij}. \qquad (41)$$

This change in reflection coefficient gives a proportional change in power at the bolometer detector, which gives rise to a proportional unbalance voltage in the bolometer bridge. Collecting all coefficients of proportionality for our apparatus, we find the open circuit bridge output to be

$$\epsilon_{rms} = 6.0 \times 10^{-3} Q_0 P_0 (1/Q)_{jj}, \qquad (42)$$

where $P_0$ is the power (in mw) reflected to the bolometer by a total reflection at the cavity under the operating conditions. This formula presumes optimum sinusoidal modulation of the field, in which case the 50-cps modu-

lation component of $|r|^2$ has a peak amplitude of roughly 0.46 of the total change given by (41). The $\epsilon_{rms}$ is measured by comparison with a GR microvolter which is substituted with appropriate attention to impedance considerations.

The absolute intensities of several lines were measured at both room temperature and 78°K by this method. In all cases the experimental values of $(1/Q)_{ij}$ were approximately a factor of two too low. In view of the difficulty in measuring all of the parameters accurately, it is quite possible that this represents only an accumulation of small errors. This seems rather unlikely, however, because of the high stability of the results with respect to changed conditions. It is worth noting that Beringer and Castle found a measured $(1/Q)_{ij}$ for the $K = J = 1$, $M = -1 \rightarrow 0$ line, mentioned above, of $1.39 \times 10^{-9}$, a factor of *ten* less than our calculated value. Thus our factor of two is tantalizing, but not too surprising.

The general theory given in Sec. V-A is profitably used in consideration of the experiments with circular polarization. With the $TE_{111}$ cavity used, integration over the field configuration shows that for a purely $(+)$ circular excitation at a hole in the center of one end, we have $f_+ = 0.68$, $f_- = 0.06$, and $f_0 = 0.26$. Thus on interchanging the sense of rotation with respect to the static magnetic field, the signals on $\Delta M = \pm 1$ transitions change by factors of 12 in opposite directions, whereas the $\Delta M = 0$ transitions are unaffected. Experimentally, the change in the $\Delta M = \pm 1$ transitions was very close to this theoretical limit for ideal adjustment. As remarked above, no $\Delta M = 0$ transitions could be observed.

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of $|(S_+)_{ij}|^2$ or $4|(S_X)_{ij}|^2$ evaluated before the transformation $U$ is applied. The transformation $U$ increases the result by a factor of 1.48 and if we also supply the factor of 2 which they omit, agreement with our value is obtained.

[26] J. C. Slater, Revs. Modern Phys. 18, 487 (1946).