TABLE II. Energies of Hf^{176} transitions.

Energy (kev)	I_{upper}	$4I$-2	B (kev)
89	2	6	14.8
203	4	14	14.5
306	6	22	13.9
(420)[a]	(8)	(30)	(14)

[a] Estimated value.

of Lu^{176} is based on Klinkenberg's[10] theoretical statement that the parity is odd, and the ft value of the β^- decay indicating a third-forbidden transition.[9]

One may infer the possible presence of other odd-odd nuclei of high spin in this region. Such species, if their

[10] P. F. A. Klinkenberg, Revs. Modern Phys. 24, 63 (1952).

half-lives were too short for occurrence in nature, would be difficult to excite by ordinary means. Even first-forbidden transitions would be of rather long life, with correspondingly low intensity. Thus a number of the activities now known in this region may be isomeric states.

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Microwave Spectrum of O$_2$†

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Twenty-four lines of the microwave spectrum of oxygen molecule have been carefully measured. The theoretical origin of this spectrum is reexamined and the effect of centrifugal distortion is taken into account. The agreement between theory and experiment is satisfactory. It is pointed out that this spectrum is not suitable to determine the velocity of light.

I. INTRODUCTION

THE microwave spectrum of oxygen is due to its $^3\Sigma$ ground state. The rotational levels are split into triplets by the interaction of the spins of the unpaired electrons and the end-over-end rotation. Magnetic dipole transitions within these triplets give rise to 25 observable lines centered near 60 000 Mc/sec and one line at approximately double the center frequency.

An expression for the energy levels of this so-called ρ-type triplet was first given by Kramers,[1] who considered the spin-spin interaction, and showed it to be equivalent to a coupling of the total electron spin S and the figure axis of the molecule proportional to $3\cos^2\theta - 1$, where θ is the angle between S and the figure axis.

Hebb[2] considered the interaction of a component of electronic angular momentum, perpendicular to the figure axis and precessing about it, and the electron

spin. This interaction was found to have exactly the same form as that considered by Kramers.

Schlapp[3] recalculated the energy levels including the magnetic interaction $\mu\mathbf{K}\cdot\mathbf{S}$, of the electron spin and the end-over-end rotation, where $\mathbf{K}$ is the angular momentum of the end-over-end rotation and μ is the coupling constant. His formulas for the frequencies are

$$\nu_+(K) = (W_{J=K} - W_{J=K+1})/h = -(2K+3)B+\lambda$$
$$-(K+1)\mu+[(2K+3)^2B^2+\lambda^2-2\lambda B]^{\frac{1}{2}}, \quad (1a)$$

$$\nu_-(K) = (W_{J=K} - W_{J=K-1})/h = (2K-1)B+\lambda$$
$$+K\mu-[(2K-1)^2B^2+\lambda^2-2\lambda B]^{\frac{1}{2}}, \quad (1b)$$

where B is the usual rotational constant and λ is the coupling constant of the Kramers' interaction. Using these formulas he could explain the infrared data obtained by Dieke and Babcock.[4]

The unresolved microwave transitions near 60 000 Mc/sec were first observed by Beringer[5] and then by Strandberg, Meng, and Ingersoll.[6] The low-pressure, resolved lines were observed and measured by Burk-

[1] H. A. Kramers, Z. Physik 53, 422 (1929).
[2] M. H. Hebb, Phys. Rev. 49, 610 (1936).
[3] R. Schlapp, Phys. Rev. 51, 342 (1937).
[4] G. H. Dieke and H. D. Babcock, Proc. Natl. Acad. Sci. U. S. 13, 670 (1927).
[5] R. Beringer, Phys. Rev. 70, 53 (1946).
[6] Strandberg, Meng, and Ingersoll, Phys. Rev. 75, 1524 (1949).

halter, Anderson, Smith, and Gordy.[7] A few of these same lines were also measured by Gokhale and Strandberg.[8] The one high-frequency line was measured by Anderson, Johnson, and Gordy.[9] Burkhalter et al.[7] noticed that while Schlapp's formulas (1) give $\nu_+(K-1)+\nu_-(K+1)=2\lambda+\mu$, which does not depend on K, their experimental value of this sum increases with K.

A recent paper by Miller and Townes[10] reexamined the fine structure theory and obtained the formulas:

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

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

which can be obtained from the formulas (1) by replacing B by $B-\tfrac{1}{2}\mu$. The same formulas were also obtained by one of the present authors.[11]

The revised formulas (2) still give a constant value for $\nu_+(K-1)+\nu_-(K+1)$, namely $2\lambda+\mu$, which does not agree with experiment. Miller and Townes[10] assumed that B and λ in the formulas (2) are not constant but are expressed as

$$B=B_0-0.14K(K+1) \text{ Mc/sec}, \quad (3a)$$

$$\lambda=\lambda_0-\lambda_1 K(K+1), \quad (3b)$$

respectively. Using the values cited in the last column of Table II of this paper, they were able to obtain a satisfactory agreement with experiment. By combining their value of B_0 and the value obtained by infrared[12] work, Miller and Townes arrived at a value of 299 781 ±33 km/sec for the velocity of light. The difference between our theory and that of Miller and Townes will be pointed out in Secs. III and V.

II. EXPERIMENT

The line measurements were made on a Zeeman modulation spectrometer very similar to that described by Burkhalter et al.[7] A factor of ten increase in the signal-to-noise ratio was obtained by using Sylvania Type 1-N-53 crystals as detectors. A similar gain was made by slotting the coaxial cavity in the Type 1-N-26 multiplier crystal and matching its doubled output directly into the wave guide of the cell. The standard coaxial probe was used in the wave guide carrying the fundamental frequency. This increased signal-to-noise ratio permitted the use of small time constants with lock-in amplifier and recorder, eliminating any chance of possible shift in the line shape due to the time delay of the recorder network. Frequency measurements were made with a frequency standard monitored by W. W. V. Each line was measured as the tube was mechanically tuned in each direction, as a check on the lock-in time constant. The results are listed in Table I.

III. REEXAMINATION OF THE THEORY

The Hamiltonian for the ρ-type triplet is given as

$$H=B|\mathbf{K}|^2+2\lambda(S_z{}^2-|\mathbf{S}|^2)+\mu\mathbf{K}\cdot\mathbf{S}, \quad (4)$$

where S_z is the component of S along the molecular axis. The first term is the usual rotational energy, the second term represents the spin-spin interaction averaged over the space coordinates,[1] while the last term is the magnetic interaction between $\mathbf{S}$ and $\mathbf{K}$.[3]

If the constants B, λ, and μ are assumed independent of K, the matrix elements of H for the case $|S|=1$ are found to be:

$$H=B\begin{bmatrix} J(J-1) & 0 & 0 \\ 0 & (J+1)(J+2) & 0 \\ 0 & 0 & J(J+1) \end{bmatrix}+\lambda\begin{bmatrix} -2J/(2J+1) & 2\{J(J+1)\}^{\frac{1}{2}}/(2J+1) & 0 \\ 2\{J(J+1)\}^{\frac{1}{2}}/(2J+1) & -2(J+1)/(2J+1) & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
$$+\mu\begin{bmatrix} J & 0 & -(J-1)(J+1)^{\frac{1}{2}} \\ 0 & -(J+1) & -J\{J(2J+3)/(2J+1)\}^{\frac{1}{2}} \\ -(J-1)(J+1)^{\frac{1}{2}} & -J\{J(2J+3)/(2J+1)\}^{\frac{1}{2}} & 0 \end{bmatrix},$$
$$J=|\mathbf{K+S}|, \quad (5)$$

where the bases are chosen so as to make $|\mathbf{K}|^2$ diagonal.

For a homonuclear diatomic molecule like $(O^{16})_2$ the nuclear functions for $K=$odd and $K=$even states have different symmetry properties for the permutation of the nuclei. Therefore, the matrix element between $K=$even and $K=$odd states vanishes, and the last

term in the formula (5) becomes[13]

$$\mu\begin{bmatrix} J & 0 & 0 \\ 0 & -(J+1) & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (6)$$

The secular equation given by the formulas (5) and (6) can be easily solved and gives the formulas (2) for the absorption frequencies.

The constants B, λ, and μ can depend on K, since the molecule is deformed by the centrifugal force. Since the perturbation due to the centrifugal potential is proportional to $K(K+1)$, the electronic and vibrational part of the wave function can be expanded as follows under

[7] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. **79**, 651 (1950).

[8] B. V. Gokhale and M. W. P. Strandberg, Phys. Rev. **84**, 844 (1951).

[9] Anderson, Johnson, and Gordy, Phys. Rev. **83**, 1061 (1951).

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

[11] M. Mizushima, Phys. Rev. **91**, 222 (1953).

[12] H. D. Babcock and L. Herzberg, Astrophys. J. **108**, 167 (1948).

[13] For the case of $O^{16}O^{17}$ or $O^{16}O^{18}$ formula (5) should be used.

the adiabatic assumption:

$$\psi(K)=\psi_0+AK(K+1)\psi_1+\cdots, \quad (7)$$

where ψ_0 and ψ_1 are the unperturbed wave functions and A is a small numerical factor. Thus, the rotational constant B becomes

$$B(K)=B_0+B_1K(K+1)+\cdots, \quad (8)$$

and B_1 is known from infrared data[14] to be approximately 5×10^{-6} cm^{-1}.

From the expansion (7), the matrix elements of the coupling constant λ are seen to be

$$\int\psi(K)\lambda\psi(K)=\int\psi_0\lambda\psi_0+2AK(K+1)\int\psi_1\lambda\psi_0$$

$$\equiv\lambda_0+K(K+1)\lambda_1, \quad (9)$$

and

$$\int\psi(K-1)\lambda\psi(K+1)=\lambda_0+(K^2+K+1)\lambda_1. \quad (10)$$

$$H=\begin{bmatrix} B_0J(J-1)+B_1J^2(J-1)^2 & 0 & 0 \\ 0 & B_0(J+1)(J+2)+B_1(J+1)^2(J+2)^2 & 0 \\ 0 & 0 & B_0J(J+1)+B_1J^2(J+1)^2 \end{bmatrix}$$

$$+\begin{bmatrix} -2\{\lambda_0+\lambda_1J(J-1)\}J/(2J+1) & 2\{\lambda_0+(J^2+J+1)\lambda_1\}\{J(J+1)\}^{\frac{1}{2}}/(2J+1) & 0 \\ 2\{\lambda_0+(J^2+J+1)\lambda_1\}\{J(J+1)\}^{\frac{1}{2}}/(2J+1) & -2\{\lambda_0+\lambda_1(J+1)(J+2)\}(J+1)/(2J+1) & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$+\begin{bmatrix} J\mu & 0 & 0 \\ 0 & -(J+1)\mu & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (11)$$

When the secular equation obtained from the above formula is solved, the following expressions for the absorption frequencies are found:

$$\nu_+(K)=-B_0(2K+3)-B_12(2K+3)(K^2+3K+3)$$
$$+\lambda_0+\lambda_1(K+1)(K-2)+\tfrac{1}{2}\mu+f(K+1), \quad (12a)$$

$$\nu_-(K)=B_0(2K-1)+2B_1(2K-1)(K^2-K+1)$$
$$+\lambda_0+\lambda_1K(K+3)+\tfrac{1}{2}\mu+f(K-1), \quad (12b)$$

where

$$f(K)=[(B_0-\tfrac{1}{2}\mu)^2(2K+1)^2-2(B_0-\tfrac{1}{2}\mu)\lambda_0$$
$$+\lambda_0^2+6(B_0-\tfrac{1}{2}\mu)\lambda_1K(K+1)$$
$$+4(B_0-\tfrac{1}{2}\mu)B_1(2K+1)^2(K^2+K+1)$$
$$-4\lambda_0B_1(K^2+K+1)+2\lambda_0\lambda_1K(K+1)$$
$$+4B_1^2(2K+1)^2(K^2+K+1)^2$$
$$+\lambda_1^2K(K+1)(K^2+K+4)$$
$$+12B_1\lambda_1K(K+1)(K^2+K+1)]^{\frac{1}{2}},$$

and

$$\nu_-(1)=2\lambda_0+4\lambda_1+\mu. \quad (12c)$$

For $B_1=\lambda_1=0$, the above formulas reduce to the formulas (2). From the formulas (12) we see that the sum relationship has become

$$\nu_+(K-1)+\nu_-(K+1)=2\lambda_0+\mu+2\lambda_1(K^2+K+2). \quad (13)$$

[14] G. Herzberg, Ann. Physik **19**, 800 (1934).

TABLE I. Experimental and calculated frequencies (Mc/sec).

K	$\nu_{+\text{obs}}$	$\nu_{+\text{calc}}$	$\nu_{-\text{obs}}$	$\nu_{-\text{calc}}$
1	56 265.6±0.6	56 264.7	118 750.5±0.5	118 750.0
3	58 446.2±0.2	58 446.7	62 487.2±0.4	62 485.7
5	59 591.4±0.2	59 591.1	60 308.0±0.2	60 305.4
7	60 433.4±0.2	60 435.0	59 163.4±0.2	59 163.6
9	61 149.6±0.2	61 150.8	58 323.2±0.1	58 323.3
11	61 799.8±0.4	61 800.4	57 611.4±0.2	57 612.1
13	62 413.8±0.4	62 411.4	56 970.8±0.4	56 968.0
15	62 996.6±0.2	62 998.0	56 364.0±0.4	56 363.5
17	63 567.2±0.2	63 568.3	55 784.6±0.4	55 784.3
19	64 128.0±0.8	64 127.2	55 221.6±0.4	55 222.4
21	64 678.2±0.2	64 677.9		54 672.8
23	65 224.2±0.8	65 222.6	54 129.4±0.4	54 132.4
25			53 599.4±0.8	53 599.0

The coupling constant μ may be also K dependent, but a small K-dependent term of a function as small as μ may be neglected. Thus, considering centrifugal distortion the matrix of the Hamiltonian (4) becomes, for $(O^{16})_2$,

This formula shows a slight dependence upon K which Schlapp's did not.

If we use the value 299 776 km/sec for the velocity of light, the infrared data[12] give $B_0=43$ 100.9 Mc/sec. Adopting this B_0 value, we obtain the set of values shown in the column 1 of Table II which gives satisfactory agreement between our formulas (12) and experimental data. The comparison between calculated and experimental values is made in Table I.

The present theory differs from that of Miller and Townes in the method of taking into account the centrifugal effect. Miller and Townes have used in the formulas (2) a value of B arrived at from considerations of centrifugal distortion and an empirical value of λ, whereas we have included the effects of centrifugal

TABLE II. Values of the coupling constants (Mc/sec).

	Present paper I[a]	Present paper II[b]	Miller and Townes[c]
B_0	43 100.9	43 097.8	43 101.6
B_1	−0.141	−0.141	−0.14
λ_0	59 501.0	59 501.3	59 501.6
λ_1	0.05996	0.05996	0.0575
μ	−252.29	−252.53	−252.72

[a] This column lists the set of values which gives $c=299$ 776 km/sec and which gives the calculated values shown in Table I.
[b] This column lists one of the other sets which also give good agreement between theory and experiment.
[c] Reference 10.

FIG. 1. 9_ line ($p = 1.22$-mm Hg).

distortion, under the adiabatic assumption, in the Hamiltonian. It is natural that their values of the coupling constants are different from ours, as can be seen in Table II, since they differ in definition. Numerically, however, they are not so different, due to the fact that in the present case the centrifugal effect is very small. But in other states where this effect is large a marked difference will appear.

IV. INTERPRETATION OF λ_1

Since the centrifugal effect is small in our case, we may start from the harmonic oscillator approximation for the vibrational wave function. Thus, the vibrational parts of ψ_0 and ψ_1 are the harmonic oscillator wave functions of the ground state and first excited state, respectively. Because of the centrifugal potential, which is approximately

$$\frac{-h^2}{8\pi^2 m} K(K+1)\left(\frac{1}{r_e^2} - \frac{2\rho}{r_e^3}\right), \tag{13}$$

where r_e is the equilibrium interatomic distance and $\rho = r - r_e$, ψ_0 and ψ_1 will be mixed to give a distorted wave function:

$$\psi(K) = \psi_0 + h^{\frac{3}{2}}(8\pi^3 m^{\frac{3}{2}} \nu^{\frac{3}{2}} r_e^3 2^{\frac{1}{2}})^{-1} K(K+1)\psi_1, \tag{14}$$

where m is the reduced mass and ν is the vibrational frequency.

The coupling constant λ can be expanded at the equilibrium interatomic distance as

$$\lambda = \lambda_e + (\partial\lambda/\partial r)_{r=r_e}\rho + \cdots. \tag{15}$$

Thus

$$\int \psi(K)\lambda\psi(K) = \int \psi_0\lambda\psi_0 + 2AK(K+1)\int \psi_0\lambda\psi_1$$

$$\equiv \lambda_0 + \lambda_1 K(K+1), \tag{16}$$

from which we obtain

$$\lambda_0 = \int \psi_0\lambda\psi_0 = \lambda_e, \tag{17a}$$

$$\lambda_1 = 2A \int \psi_0\lambda\psi_1 = h^2 16(\pi^4 m^2 \nu^2 r_e^3)^{-1}(\partial\lambda/\partial r)_{r=r_e}. \tag{17b}$$

If we use the obtained values for the constants, we find

$$(\partial\lambda/\partial r)_{r=r_e} = +2.41 \times 10^3 \text{ Mc/sec Å}. \tag{18}$$

Thus, we obtain

$$\lambda = 59\ 501.0 + 2.41 \times 10^3\rho \text{ Mc/sec}, \tag{19}$$

with ρ in Å.

V. VELOCITY OF LIGHT

If we combine the B_0 value obtained here with that obtained in infrared spectra,[12] we shall be able to obtain the value of the velocity of light. However, it must be noted that the accuracy of the B_0 value obtained in the microwave spectrum is not so good.

Suppose $B_0 + \Delta B_0$ is adopted instead of B_0, where ΔB_0 is very small compared to B_0. Then from our equation (12) we obtain the increase of the calculated frequency as

$$\Delta\nu_+(K) = \Delta B_0[\{(2K+3)^2(B_0 - \tfrac{1}{2}\mu) - \lambda_0\}f(K+1)^{-1}$$

$$-2K - 3 + 16K^4 B_1] = \Delta\nu_-(K+2), \tag{20}$$

where f is the function defined in the Eq. (12). Using the numerical values obtained in Sec. III, we find that always $0 > \Delta\nu/\Delta B_0 > -0.1$, except in the $K=1$ case where the ratio is about -0.2. It means that a change of 5 Mc/sec in the value of B_0 amounts to a change of less than 0.5 Mc/sec in the calculated ν values, which is within the error limits. Readjustment of the other constants will make the latter change smaller. As an example, we have shown another set of values in the second column of Table II. This set is as good as the former one in explaining the experimental results. Thus, the value of the velocity of light obtained from the oxygen spectra may have a rather large flexibility. A crude estimation gives $c = 299\ 776 \pm 60$ km/sec, corresponding to the experimental error of ± 0.5 Mc/sec.

Fig. 1. 9_ line (*p* = 1.22-mm Hg).