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Absorption Spectrum of the Oxygen Molecule in the 55–65-Gc/sec Region*

BURNELL G. WEST† AND MASATAKA MIZUSHIMA
University of Colorado, Boulder, Colorado

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The theory of the rotational spectrum of the oxygen molecule developed elsewhere is revised by correcting the calculation of the effects of centrifugal distortion. Precise measurements of the center frequencies of 8 of the predicted absorption lines were made. These measurements are combined with measurement of 12 lines made elsewhere to obtain the values of 7 parameters appearing in the theory.

THEORY

THE ground-state configuration of the electronic wave function of the oxygen molecule is ${}^3\Sigma_g^-$. The spin of this state couples with end-over-end rotation to produce a molecular fine-structure splitting of the rotational energy levels. This splitting lies primarily in a band centered approximately at 60 Gc/sec.

The theory of the rotational spectrum of oxygen has been developed in considerable detail.[1–3] The first measurement of the absorption due to transitions between the levels of the triplet states was made by R. Beringer[4] in 1946; many other groups[3,5–10] made further and more detailed measurements. Zimmerer and Mizushima[10] measured 12 of the lines to approximately 2 parts in 10^7, using an improved version of a spectrometer designed by Richardson.[9]

In the present work, the theory developed by Mizushima and Hill[3] is revised by making a more careful analysis of the centrifugal distortion.

The Hamiltonian used here is

$$H=B\mathbf{N}^2+\tfrac{2}{3}\lambda(3S_z^2-\mathbf{S}^2)+\mu\mathbf{N}\cdot\mathbf{S},$$

where **N** and **S** are the angular momenta of end-over-end rotation and spin, respectively. This Hamiltonian differs slightly from that used by Mizushima and Hill, but the difference is not distinguishable in experiments of the type discussed here.

Using this Hamiltonian, we find the absorption frequencies to be[11]

$$\begin{aligned}\nu(N\pm)=\lambda_0+\mu_0/2-8\mu_1/2+(\lambda_1+5\mu_1/2)(n^2+n+2)\\ \pm\{f(n)-(2n+1)[B_0+2B_1(n^2+n+1)\\ +B_2(3n^4+6n^3+13n^2+10n+4)]\\ +2[\lambda_1/3-\mu_1/2]\},\end{aligned}$$

where

$$[f(n)]^2=A^2+n(n+1)D^2,$$

in which

$$\begin{aligned}A=(2n+1)[(B_0-\tfrac{1}{2}\mu_0)+(2B_1-\tfrac{1}{2}\mu_1)(n^2+n+1)\\ +B_2(3n^4+6n^3+13n^2+10n+4)-\tfrac{3}{2}\mu_1]\\ -[\lambda_0+\tfrac{2}{3}\lambda_1(7n^2+7n+4)]/(2n+1),\end{aligned}$$

and

$$D=[2\lambda_0+2\lambda_1(n^2+n+1)]/(2n+1).$$

Here, we have used $n=N\pm1$.

The differences between these expressions and those of Mizushima and Hill[3] lie in the approach used to obtain the centrifugal-distortion correction. In their computation, the quantity $(\frac{2}{3}\lambda-\mu)$ was subtracted from all diagonal elements of the matrix expression of the Hamiltonian in order to simplify it. This procedure is valid provided λ and μ do not depend on N. Since centrifugal distortion of these parameters is N-dependent, this approach is no longer valid.

RESULTS OF THE EXPERIMENT

Eight of the absorption lines were measured in this work. These 8 measurements were combined with the 12 made by Zimmerer and Mizushima[10] to provide sufficient data to give a least-squares fit on the 7 parameters B_0, B_1, B_2, λ_0, λ_1, μ_0, and μ_1. The values for the parameters are shown in Table I, compared to the values obtained by Zimmerer and Mizushima. The 20 lines measured are shown in Table II, where those meas-

TABLE I. Values of parameters of oxygen molecule (Mc/sec).

Parameter	This work	Zimmerer and Mizushima
B_0	43 100.3±0.2	43 100.5
B_1	−0.092±0.001	−0.147
B_2	$(5\pm2)\times10^{-6}$	...
λ_0	59 501.397±0.015	59 501.332
λ_1	0.05845±0.00004	0.05858
$\frac{1}{2}\mu_0$	−126.352±0.0005	−126.293
$\frac{1}{2}\mu_1$	$-0.000120\pm2\times10^{-6}$	−0.000117

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† Present address: Edgerton, Germeshausen, and Grier, Inc., Dublin, California.

[1] H. A. Kramers, Z. Physik **53**, 422 (1929).

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

[3] M. Mizushima and R. M. Hill, Phys. Rev. **93**, 745 (1954).

[4] R. Beringer, Phys. Rev. **70**, 53 (1946).

[5] J. H. Burkhalter, R. S. Anderson, W. V. Smith, and W. Gordy, Phys. Rev. **79**, 651 (1950).

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

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

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

[9] J. M. Richardson, J. Appl. Phys. **29**, 137 (1958).

[10] R. W. Zimmerer and M. Mizushima, Phys. Rev. **121**, 152 (1961).

[11] B. G. West, thesis, University of Colorado, 1965 (unpublished).

TABLE II. Observed and calculated frequencies (Mc/sec).

Line	Observed frequencies	Calculated frequencies
1+	56 264.766(W)	56 264.765
3+	58 446.580(Z)	58 446.580
5+	59 590.978(Z)	59 590.976
7+	60 434.776(Z)	60 434.773
9+	61 150.570(Z)	61 150.560
11+	61 800.169(W)	61 800.159
13+	62 411.223(Z)	62 411.225
15+	...	62 997.991
17+	63 568.520(Z)	63 568.534
19+	64 127.777(W)	64 127.782
21+	...	64 678.914
23+	65 224.12(Z)	65 224.073
25+	65 764.744(W)	65 764.760
3−	62 486.255(Z)	62 486.251
5−	60 306.044(Z)	60 306.056
7−	59 164.215(Z)	59 164.205
9−	58 323.885(Z)	58 323.879
11−	...	57 612.488
13−	56 968.180(W)	56 968.211
15−	56 363.393(W)	56 363.393
17−	55 783.819(W)	55 783.800
19−	55 221.372(W)	55 221.355
21−	54 671.145(W)	54 671.131
23−	...	54 129.949
25−	...	53 595.665
27−	...	53 066.779

ured in this work are followed by (W) and those measured by Zimmerer and Mizushima by (Z). The calculated frequencies using the parameter values of Table I are also shown in Table II.

The computations were done on an IBM 1620 digital computer, using a programming system developed by West[12] which overcame the inherent lack of accuracy in the Fortran system. The program made it possible to estimate the accuracy of the parameter values by a method related to computation of statistical variance.

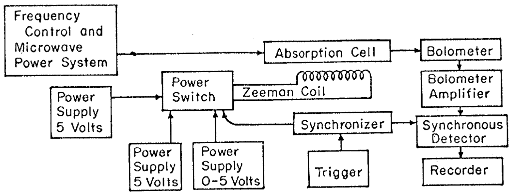

FIG. 1. Block diagram of spectrometer.

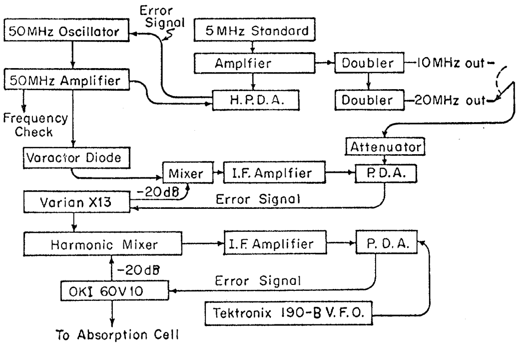

FIG. 2. Frequency control system.

It is this variance which is indicated by the error brackets of the parameter values in Table I.

There is no improvement on the value of the velocity of light over the one obtained by Zimmerer and Mizushima.[10] A very large discrepancy between the accepted value of the velocity of light and the one obtained from B_0 is still puzzling.

THE SPECTROMETER

The spectrometer used in this work was quite similar to that described by Zimmerer.[10] Frequency control was obtained by three successive stages of multiplication of a 5-Mc frequency standard. At each stage, an oscillator was phase-locked to the appropriate harmonic of the previous stage. The first stage was a phase-locked varicap-controlled Hartley oscillator, used to drive a varactor diode for generation of harmonics up to order 200. The second stage was a Varian X-13 klystron, phase-locked[13] to the desired harmonic generated by the varactor. The final stage was an OKI 60V10 klystron, phase-locked to the fifth, sixth, or seventh harmonic of the varian unit. A block diagram of the frequency control system is shown in Fig. 1, and a block diagram of the spectrometer is shown in Fig. 2.

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[12] R. L. West (private communication).

[13] M. Peter and M. W. P. Strandberg, Proc. Inst. Radio Engrs. 43, 869 (1955).