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Precise Measurement of the Microwave Absorption Frequencies of of the Oxygen Molecule and the Velocity of Light*

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Ten microwave absorption frequencies of the oxygen molecule in the 60-kMc/sec region have been measured with an accuracy of about 10 kc/sec. The result is interpreted by successfully refining the existing theory. Comparing the resultant value of the rotational constant B_0 with the value obtained in ultraviolet spectra, the velocity of light is calculated to be 299 773±12 km/sec.

I. INTRODUCTION

THE microwave absorption spectrum of the oxygen molecule was found by Beringer[1] in the early period of microwave spectroscopy and was interpreted by Van Vleck[2] as absorption due to the transitions among the members of the triplet given by the electronic spin 1, the spin being coupled to the end-over-end rotation in the manner of Hund's case (b). Burkhalter, Anderson, Smith, and Gordy[3] first succeeded in resolving it into individual lines. Mizushima and Hill[4] increased the accuracy and gave a refined theory which explained the data with a suitable choice of parameters. Miller and Townes[5] pointed out that the result, if combined with the ultraviolet data, can give the velocity of light. Mizushima and Hill,[4] however, found that the data does not have sufficient accuracy to determine the velocity of light to better than 60 km/sec.

The linewidth of each line has been measured by Gordy and his group,[6] Artman and Gordon,[7] and Gokhale and Strandberg.[8] The argreement between their results was not bad except for the last by Gokhale and Strandberg.

2. EXPERIMENT AND RESULTS

The details of the experimental technique used here is given in a paper by one of us.[9]

30-kMc/sec microwave power, generated by an EMI klystron, is multiplied by a diode to 60 kMc/sec. The klystron frequency is phase-locked to a harmonic of a quartz crystal oscillator at 2.5 Mc/sec. This transfers the frequency stability of the quartz crystal oscillator to the 30-kMc/sec klystron in the manner as described in the earlier paper.[9] Zeeman modulation of 70 cps is used with 25-foot absorption cell. A special waveform is used to eliminate the distortion caused by the conducting walls of the absorption cell as well as a fixed bias to eliminate the residual stray magnetic field. Careful testing was done to establish the independence of the center frequency from the magnitude of the Zeeman field and its modulation frequency. Detection of the signal is done by a bolometer and a recorder. A typical recorder trace is given in Fig. 1. The result of this experiment is given in Table I.

The measurement of the linewidth parameter was done to resolve the discrepancy between old data which are mentioned in Sec. 1 of this paper. The results are shown in Table II. It is found that our result is not far from previous data, but somewhat smaller than them in most cases. All measurements were done at room temperature.

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

Lines	Obs (this paper)	Obs (Mizushima and Hill)[a]	Calc
1_-		118 750.5	
3_-	62 486.255	62 487.2	62 486.256
5_-	60 306.044	60 308.0	60 306.055
7_-	59 164.215	59 163.4	59 164.205
9_-	58 323.885	58 323.2	58 323.885
11_-		57 611.4	57 612.505
13_-		56 970.8	56 968.245
15_-		56 364.0	56 363.448
17_-		55 784.6	55 783.884
19_-		55 221.6	55 221.449
23_-		54 129.4	
25_-		53 599.4	53 595.951
1_+		56 265.6	56 264.752
3_+	58 446.580	58 446.2	58 446.577
5_+	59 590.978	59 591.4	59 590.979
7_+	60 434.776	60 433.4	60 434.779
9_+	61 150.570	61 149.6	61 150.567
11_+	61 800.155	61 799.8	61 800.163
13_+	62 411.223	62 413.8	62 411.224
15_+		62 996.6	62 997.980
17_+	63 568.520	63 567.2	63 568.535
19_+		64 128.0	
21_+		64 678.2	
23_+	65 224.120	65 224.2	65 223.961

[a] See reference 4,

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TABLE II. Linewidth parameter (Mc/mm Hg).

Lines	This paper	Hill and Gordy[a]	Artman and Gordon[b]	Burkhalter *et al.*[c]	Anderson *et al.*[a]	Gokhale and Strandberg[d]
3_-	1.96			2.09	1.92	1.46
5_-	1.60		1.99		1.86	
7_-	1.70	2.01	1.82			1.11
9_-	1.64	1.94	2.00		1.97	0.83
3_+	1.96	2.07	2.23		1.71	1.11
5_+	1.56	1.80	1.96			
7_+	1.68		1.92		2.05	
9_+	1.42		1.93			
11_+	1.60				1.97	
13_+	1.54			0.87		0.99
17_+	1.50					

[a] See reference 6.
[b] See reference 7.
[c] See reference 3.
[d] See reference 8.

3. THEORY

The same theory as given in Mizushima and Hill's paper[4] is used to interpret the present result. The parameters B and μ are refined here by including higher order terms, as

$$B(N)=B_0+B_1N(N+1)+B_2N^2(N+1)^2, \tag{1}$$

$$\mu(N)=\mu_0+\mu_1N(N+1), \tag{2}$$

where N is the quantum number for the end-over-end rotation.

The frequency of N_+ and N_- lines, which correspond to transitions $(N, J=N+1)\rightarrow(N, J=N)$ and $(N, J=N-1)\rightarrow(N, J=N)$, respectively, can be calculated in the same way as in Mizushima and Hill's case[4] and we obtain the following expression:

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

where

$$\begin{aligned}[f(n)]^2=\bigg[&(2n+1)\{(B_0-\mu_0/2)+(2B_1-\mu_1/2)(n^2+n+1)\\ &+B_2(3n^4+6n^3+13n^2+10n+4)\}\\ &-3\frac{\mu_1}{2}\frac{\lambda_0+\lambda_1(sn^2+sn+2)}{2n+1}\bigg]^2\\ &+\left[\frac{2\lambda_0+2\lambda_1(n^2+n+1)}{2n+1)}\right]^2 n(n+1),\end{aligned}$$

and

$$n=N\mp1.$$

In addition to B_2 terms and μ_1 terms, this expression differs from Mizushima and Hill's formula[4] due to a misprint in the latter.

Babcock and Herzberg[10] analyzed ultraviolet spectra of the atmospheric oxygen and obtained

$$\begin{aligned}B_0&=1.43777\pm0.000015\ \mathrm{cm}^{-1},\\ B_1&=(-4.91_3\pm0.020)\times10^{-6}\ \mathrm{cm}^{-1},\\ |B_2|&<0.3\times10^{-9}\ \mathrm{cm}^{-1}.\end{aligned} \tag{4}$$

Our parameters B_1 and B_2 are thus determined to be

$$\begin{aligned}B_1&=-0.1472\pm0.0006\ \mathrm{Mc/sec},\\ |B_2|&<10^{-5}\ \mathrm{Mc/sec}.\end{aligned} \tag{5}$$

From our formula (3) we can see that a value for B_2 of 10^{-5} Mc/sec can change the theoretical frequency by 0.01 Mc/sec even at $N\simeq20$ and the effect is much smaller for lower N lines. Since our experimental inaccuracy is about 0.01 Mc/sec for lines of N smaller than 20, the requirement (5) means we should neglect B_2 in this analysis. We found the set of parameters given in Table III gives a very close fit to our data as shown in Table I, except for the 23_+ line. This line 23_+, however, is a very weak one and the experimental error can be as large as 0.2 Mc/sec. The same set of parameters can reproduce previous less accurate data by Mizushima and Hill[4] within 1 Mc/sec in most cases. Although the inaccuracy of that previous measurement was claimed to be less than 0.8 Mc/sec the present measurement showed larger discrepancies from them in some cases. The deviation of more than 1 Mc/sec between the old data and the present theory can thus be acceptable.

4. VELOCITY OF LIGHT

If our value of B_0 is combined with Babcock and Herzberg's value, we obtain the velocity of light c as

$$c=299\,773\pm12\ \mathrm{km/sec}, \tag{6}$$

which deviates very much from the accepted value[11]

$$c=299\,793.0\pm0.3\ \mathrm{km/sec}. \tag{7}$$

FIG. 1. Recorder trace of 3_- line at 80 μ Hg pressure and room temperature. Line 1 is without Zeeman field; line 2 is with a 1.2-gauss Zeeman field. The vertical straight lines at the top are the theoretical Zeeman pattern.

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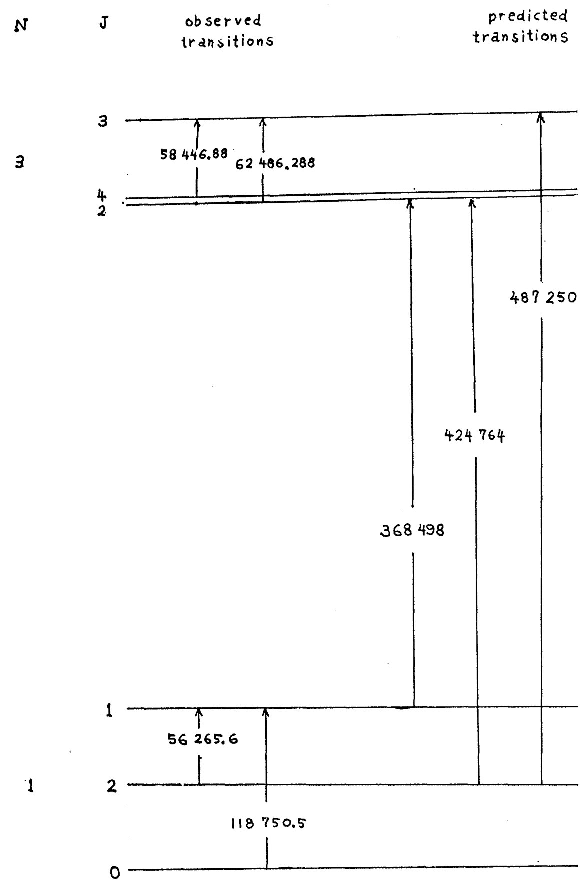

FIG. 2. Energy levels of the O_2 molecule with predicted transitions.

As a matter of fact, if we use values (7) and (4), we expect B_0 to be

$$B_0 = 43\ 103.3 \text{ Mc/sec}, \tag{8}$$

which is different from our value by 2.8 Mc/sec.

The deviation must be, to some extent, due to the fact that frequencies of the transitions we are dealing with here are insensitive to the value of B_0. We see from our formula (3) that change of 1 Mc/sec in the value of B_0 produces, for example, change of theoretical frequencies of 0.2, 0.05, and 0.03 Mc/sec for $n=2$, 10, and 18 lines, respectively. If the other parameters are suitably adjusted the frequency change can be even smaller. Although the present measurement is very accurate, we have not measured all lines, unfortunately. This means that we cannot utilize the accuracy of the present measurement completely to determine all the parameters.

Assuming that our choice of parameters is right and that our measured frequencies are accurate to 0.01 Mc/sec, the inaccuracy for each parameter is estimated as shown in Table III.

The inaccuracy of B_0 is thus estimated to be 1 Mc/sec here, and the inaccuracy of the ultraviolet spectra data given in (4) will give the additional inaccuracy of 0.5 Mc/sec for the B_0 value. The total inaccuracy 1.5 Mc/sec, however, is still much larger than the above-mentioned deviation 2.8 Mc/sec between our value of B_0 and the expected value given by (8). This means our value for the velocity of light given in (6) has an inaccuracy of 12 km/sec as indicated there, but the discrepancy from the accepted value given in (7) of 8 km/sec remains unexplained.

TABLE III. Values of parameters (Mc/sec).

	This work	Mizushima and Hill[a]
B_0	43 100.5±1.0	43 100.9
B_1	−0.1470±0.001	−0.141
B_2	0 ± 10^{-5}	
λ_0	59 501.332±0.005	59 501.0
λ_1	0.05858±0.0001	0.05996
$\mu_0/2$	−126.2930±0.001	−126.15
$\mu_1/2$	$-0.000\ 117\pm2\times10^{-6}$	...

[a] See reference 4.

5. PREDICTION ON $N=1\leftrightarrow3$ TRANSITIONS

In order to resolve the discrepancy about the value of the velocity of light pointed out in the last section, a measurement on transitions whose frequencies are more sensitive to B_0 is desirable. The $N=1\leftrightarrow3$ transition is of such a type since it is an end-over-end rotational transition. The frequency for this transition is essentially given by

$$10B_0+140B_1=430\ 984 \text{ Mc/sec}. \tag{9}$$

The details of energy levels calculated by our theory and transitions allowed by the selection rule $\Delta J=0, \pm1$ are shown in Fig. 2.

The absorption intensity for a transition $i\rightarrow f$ can be expressed as

$$I=A(i|S_z|f)^2\nu^2, \tag{10}$$

where A is a constant, ν is the frequency, and S_z is the z component of the electron spin operator.

The wave function for states we are interested in now can be obtained by solving our secular equation,[4] with the following results:

$$\begin{aligned} &N=1, J=1 \text{ state:} && |111M),\\ &N=1, J=2 \text{ state:} && a|112M)+b|312M),\\ &N=3, J=3 \text{ state:} && |313M),\\ &N=3, J=2 \text{ state:} && b|112M)-a|312M), \end{aligned} \tag{11}$$

where $a=0.997$, $b=0.139$, and each term is $|NSJM)$.

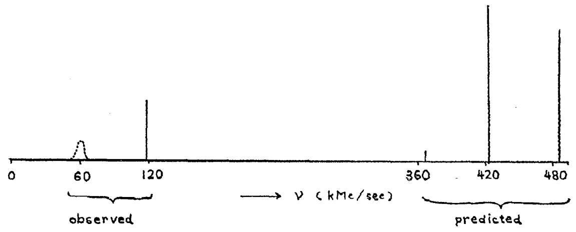

FIG. 3. Microwave absorption spectrum of the O_2 molecule.

The matrix elements of S_z can be calculated by using the above wave functions; and using formula (10) we obtain the theoretical absorption spectrum of the oxygen molecule as shown in Fig. 3.

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Antishielding and Contracted Wave Functions

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The antishielding factors, γ_∞, of several contracted negative ions are calculated and compared to the apparent experimental values. Although the use of contracted wave functions results in considerably smaller γ_∞'s, the agreement is still not encouraging for the negative ions. Interrelations are found among the wave functions contracted by different means. Also, γ_∞ of several closed-shell positive ions and two ^6S state ions (Mn^{+2} and Fe^{+3}) are calculated so that information from measured quadrupole coupling constants can be obtained. These positive-ion results with other published values should enable γ_∞ of all closed-shell ions to be estimated. The results are used to determine the nuclear quadrupole moment of Fe^{57m} from the published value of the quadrupole coupling constant in Fe_2O_3. This result is discussed.

I. INTRODUCTION

In calculations using atomic wave functions it is known that large differences can occur in the result if Hartree (H.) rather than Hartree-Fock (H.F.) functions are used. For example, calculations of the binding energies of alkali halide crystals[1] give better agreement with experiment when H.F. rather than more diffuse H. wave functions are used. Recently, various authors have calculated contracted wave functions.[2–6] These functions attempt to take into account the actual fields in which the ion is situated with the result that even better binding energies are obtained.

In this paper contracted wave functions are used to calculate atomic polarizabilities and the Sternheimer antishielding factors[7] for several ions. Comparison is made with the results obtained from the free ion H. and H.F. functions and with experimental results in order to obtain a more complete understanding of the applicability and interrelationship among the wave functions. Antishielding factors are also calculated for several closed shell positive ions and for Fe^{+3} and Mn^{+2}, which are in a ^6S state. These values are required to interpret quadrupole coupling data.

II. CONTRACTION OF WAVE FUNCTIONS

To obtain the wave functions used in this paper, several methods were needed and will be briefly described.

1. O^{-2}: Watson[6] has calculated analytic H.F. wave functions for O^{-2} ions that are in a sphere of charge with the radius of the sphere equal to the ionic radius. The wave functions were calculated for a charge of +2 and +1, on the stabilizing sphere. These wave functions are called $O^{-2}(+2w)$ and $O^{-2}(+1w)$, respectively. The $2p$ wave functions have five parameters and the $1s$ and $2s$ wave functions have seven parameters.

2. O^{-2}: Yamashita and Kajima[3] have calculated the wave functions for O^{-2} in $Mg^{+2}O^{-2}$ by assuming an analytic form for the $2p$ wave function with three parameters. The parameters are varied to minimize the energy of the entire crystal rather than the free ion alone. For the $1s$ and $2s$ wave function they took the H.F. O^{-1} wave function and used the H.F. wave function of Mg^{+2}. The calculation was done for the observed crystal spacing. The wave function is called $O^{-2}(MgO)$.

3. F^{-1}: Yamashita[4] has calculated the F^{-1} wave function in a manner similar to the O^{-2} calculation. The $2p$ wave function of F^{-1} has three parameters and

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