

## Rotational Structure of $^{16}\text{O}_2$ , $^{16}\text{O}^{17}\text{O}$ , and $^{16}\text{O}^{18}\text{O}$ ( $X^3\Sigma_g^-$ ) from Laser Magnetic Resonance Spectra

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Improved values of the rotational constants  $B$  and  $D$  of  $^{16}\text{O}^{17}\text{O}(v=0)$  and  $D$  of  $^{16}\text{O}_2(v=1)$  were obtained from an analysis of the laser magnetic resonance spectra at 765 and 4252 GHz.

### INTRODUCTION

Laser magnetic resonance (LMR) commenced with the observation of  $N = 5 \leftarrow 3$  transitions of the  $^{16}\text{O}_2$  molecule in the  $X^3\Sigma_g^-, v = 0$  state (1). Subsequently, many other LMR spectra of the oxygen molecule were observed;  $N = 5 \leftarrow 3$  (more transitions were observed because of increased sensitivity) (2),  $N = 15 \leftarrow 13$  and  $N = 23 \leftarrow 21$  (3), and  $N = 17 \leftarrow 15$  and  $N = 21 \leftarrow 19$  (4).

The LMR technique was improved considerably with the additional frequencies available from optically pumped lasers (5), and the sensitivity increased with the use of an InSb bolometer (6). The improved sensitivity ( $10^{-9} \text{ cm}^{-1}$  at 428.6285 GHz) permitted the detection of LMR spectra of the  $^{16}\text{O}^{17}\text{O}(v=0)$ ,  $^{16}\text{O}^{18}\text{O}(v=0)$ , and  $^{16}\text{O}_2(v=0, 1)$  molecules for the rotational transitions  $N = 3 \leftarrow 1$  (6). These isotopic and vibrationally excited molecules were at room temperature, and occurred in their natural isotopic abundances (0.204% for  $^{18}\text{O}$  and 0.037% for  $^{17}\text{O}$ ). Using the 764.6426- and 4251.6740-GHz lines of the  $\text{CH}_3\text{OH}$  molecule pumped by  $\text{CO}_2$  laser lines, we have now observed  $N = 5 \leftarrow 3$  transitions in these four species and  $N = 25 \leftarrow 23$  transitions in  $^{16}\text{O}_2(v=0)$ . These measurements have yielded improved rotational constants for the  $^{16}\text{O}_2(v=1)$  and  $^{16}\text{O}^{17}\text{O}(v=0)$  molecules, and confirmed those for  $^{16}\text{O}_2(v=0)$  and  $^{16}\text{O}^{18}\text{O}(v=0)$ .

### EXPERIMENTAL RESULTS

The observed LMR spectra of the oxygen molecules at 764.6426 GHz are shown in the first column of Table I. All but three of these are due to  $N = 5 \leftarrow 3$

TABLE I  
 LMR Spectra of the Oxygen Molecules at 764.6426 GHz  
 [(a)  $\Delta M = 0$  transitions; (b)  $\Delta M = \pm 1$  transitions]

(a) $\Delta M = 0$ transitions							
B <sub>obs.</sub> (T)	B <sub>calc.</sub> (T)	N=5 J' M' + J M	N=3 J M	rel. slope (T/THz)	SQDP	peak int. (cm <sup>-1</sup> )	species
0.0158	0.01570	4 4	4 4	-20.0	0.0780	7.76E-9	v=1
0.0210	0.02094	4 3	4 3	-26.7	0.0439	4.37E-9	v=1
0.0315	0.03136	4 2	4 2	-39.9	0.0196	1.95E-9	v=1
0.0624	0.06237	4 1	4 1	-78.9	0.0050	4.96E-10	v=1
	0.14487	6 4	4 4	-98.6	1.6E-8	1.63E-15	v=1
0.18267	0.18271	4 4	4 4	-19.7	0.0789	2.15E-5	1616
	0.19224	4 -2	4 -2	-36.1	1.1E-8	1.10E-15	v=1
	0.19328	6 3	4 3	-132.2	7.5E-8	7.46E-15	v=1
0.24306	0.24313	4 3	4 3	-26.2	0.0445	1.21E-5	1616
0.27339*	0.27347	6 -4	4 -4	20.7	0.0747	7.34E-8/6	1617
	0.29239	6 2	4 2	-205.1	3.1E-7	3.06E-14	v=1
	0.34547	6 2	2 2	38.4	2.7E-7	2.63E-14/6	1617
	0.34971	4 0	4 0	-166.2	1.5E-4	1.46E-11	v=1
0.36061	0.36070	4 2	4 2	-38.5	0.0201	0.547E-5	1616
	0.36171	4 -1	4 -1	-66.4	1.6E-6	1.64E-13	v=1
0.3679**	0.36794	6 -3	4 -3	28.2	0.0403	3.96 E-8/6	1617
0.5007	0.50078	4 -2	4 -2	-35.2	1.7E-6	4.74E-10	1616
	0.55425	6 -2	2 -2	42.1	0.0163	1.60E-9/6	1617
	0.61748	6 1	2 1	58.8	1.7E-5	1.71E-12/6	1617
	0.62646	6 -2	4 -2	-134.4	8.4E-8	8.39E-14	v=1
0.63588	0.63598	4 1	4 1	-58.1	0.0059	1.61E-6	1616
0.70317	0.70308	6 -4	4 -4	22.3	0.0675	3.57E-8	1618
	0.78731	6 1	4 1	-1036.8	1.8E-6	1.77E-13	v=1
0.81465	0.81459	6 4	4 4	-65.0	1.0E-5	2.80E-9	1616
0.85315	0.85324	4 -1	4 -1	-50.5	9.0E-5	2.45E-8	1616
	0.89849	6 -1	2 -1	53.6	3.9E-3	3.83E-10/6	1617
0.96630	0.96635	6 -3	4 -3	31.7	0.0318	1.68E-8	1618
0.99688	0.99698	4 0	4 0	-54.1	0.00111	3.02E-7	1616
	0.99663	6 0	2 0	54.6	5.0E-4	4.950E-11/6	1617
	1.03926	5 -3	3 -3	55.7	4.3E-5	4.19E-12	1617
	1.15336	6 2	2 2	39.9	1.3E-5	6.62E-12	1618
1.23687	1.23686	6 3	4 3	-131.6	3.4E-5	9.16E-8	1616
1.39618	1.39618	6 -2	2 -2	41.2	0.0116	6.14E-9	1618
	1.62104	6 1	2 1	43.6	1.7E-4	8.95E-11	1618
1.82880	1.82881	6 -1	2 -1	42.0	0.00369	1.95E-9	1618
	1.86485	5 4	4 4	-149.8	4.60E-9	2.43E-13	1618
	1.92695	6 0	2 0	41.5	9.9E-3	5.23E-10	1618
	1.97384	5 -3	3 -3	41.3	2.7E-4	1.41E-10	1618
	1.97857	5 3	4 3†	-21.1	0.0225	1.12E-8	1618
1.9992	1.99848	5 2	4 2†	-20.6	0.0162	8.07E-9	1618
2.0147	2.01400	5 4	4 4†	-22.1	0.0285	1.42E-8	1618
2.0399	2.03896	5 1	4 1†	-20.2	0.0103	5.11E-9	1618
	2.11766	5 -1	4 -1†	-20.3	0.0023	1.14E-9	1618
	2.16413	5 -2	4 -2†	-20.7	0.79E-3	3.93E-10	1618

\* Hfs components are seen at 0.26425, 0.26775, 0.27139, 0.27505, 0.27925, and 0.28263 Tesla.

\*\* 5 Hfs components are seen at 0.3590, 0.3664, 0.3700, 0.3737, and 0.3774 Tesla. It is assumed that a component at 0.3609 Tesla is hidden in the very strong resonance at 0.36072 Tesla.

† Transitions N=6+4.

TABLE I—Continued

B <sub>obs.</sub> (T)	B <sub>calc.</sub> (T)	(b) ΔM=±1 transitions		rel. slope (T/THz)	SQDP	peak int. (cm <sup>-1</sup> )	species
		N=5 J' M' + J M	N=3 J M				
0.01763	0.01764	4 3	4 4	-22.5	0.0097	9.7E-10	v=1
0.01825	0.01825	4 4	4 3	-23.3	0.0097	9.7E-10	v=1
0.02450	0.02452	4 2	4 3	-31.2	0.0170	1.70E-9	v=1
0.02568	0.02572	4 3	4 2	-32.8	0.0170	1.70E-9	v=1
0.04026	0.04017	4 1	4 2	-51.0	0.0219	2.18E-9	v=1
0.04353	0.04348	4 2	4 1	-55.4	0.0219	2.18E-9	v=1
	0.09805	6 3	4 4	-68.1	5.4E-7	5.4E-13	v=1
0.1088	0.10872	4 0	4 1	-130.7	0.0240	2.39E-9	v=1
	0.11806	6 2	4 3	-82.6	5.6E-6	5.54E-13	v=1
0.13645	0.13656	4 1	4 0	-165.4	0.0241	2.39E-9	v=1
	0.14869	6 1	4 2	-105.6	5.8E-5	5.77E-12	v=1
	0.16540	4 -3	4 -2	-31.4	5.1E-7	5.07E-14	v=1
0.20321	0.20326	4 3	3 4	-21.7	0.0097	2.70E-6	1616
0.21431	0.21436	4 4	4 3	-23.4	0.0098	2.66E-6	1616
	0.22802	4 -1	4 -2	-42.0	1.6E-6	1.60E-13	v=1
	0.26890	4 -1	4 0	-159.3	1.3E-3	1.33E-10	v=1
	0.27698	6 5	3 4	-177.5	3.9E-5	3.87E-12	v=1
	0.27804	4 -2	4 -1	-61.4	1.1E-4	1.05E-11	v=1
0.28034	0.28047	4 2	4 3	-29.7	0.0168	4.57E-6	1616
	0.29177	6 3	2 2	32.2	2.8E-7	2.70E-14/6	1617
0.30191	0.30198	4 3	4 2	-33.0	0.0169	4.59E-6	1616
	0.31333	6 -3	4 -4	24.2	0.0095	9.33E-10/6	1617
	0.31395	6 -4	4 -3	23.5	0.0098	9.65E-10/6	1617
	0.36682	6 -1	4 -2	-79.4	6.7E-5	6.65E-12	v=1
	0.40232	4 0	4 -1	-69.1	1.4E-3	1.43E-10	v=1
	0.41859	6 1	2 2	45.8	1.4E-7	1.34E-14/6	1617
0.43738	0.43752	4 -3	4 -2	-31.5	4.6E-6	1.27E-9	1616
0.44171	0.44180	4 1	4 2	-44.6	0.0204	5.55E-6	1616
0.44180 <sup>1</sup>	0.44176	6 -2	4 -3	34.4	0.0161	1.58E-9/6	1617
0.44424 <sup>2</sup>	0.44428	6 -3	2 -2	33.5	0.0165	1.62E-9/6	1617
	0.48676	6 2	2 1	50.7	1.8E-5	1.72E-12/6	1617
0.49611	0.49622	4 2	4 1	-51.6	0.0202	5.50E-6	1616
	0.53208	6 4	4 3	-333.0	3.6E-4	3.58E-10	v=1
0.5732	0.57309	4 -1	4 -2	-38.1	8.3E-6	2.29E-9	1616
0.60180	0.60190	6 3	4 4	-52.6	3.67E-5	1.00E-8	1616
0.69637 <sup>3</sup>	0.69630	6 -1	2 -2	49.5	0.0180	1.77E-8/6	1617
0.70725 <sup>4</sup>	0.70727	6 -2	2 -1	49.2	0.0157	1.55E-9/6	1617

(1) Hfs components are observed at 0.43290, 0.43638, 0.44711, 0.45079 Tesla. Two components are hidden in strong lines at 0.43738 and 0.44171 Tesla due to <sup>16</sup>O<sub>2</sub>.

(2) Hfs components are observed at 0.43519, 0.43881, 0.44603, 0.44969, and 0.45332 Tesla. One component is hidden.

(3) Hfs components are observed at 0.68915, 0.69203, 0.69490, 0.69784, 0.70069, and 0.70364 Tesla.

(4) Hfs components are observed at 0.69975, 0.70286, 0.70580, 0.70875, 0.71173, and 0.71463 Tesla.

† Transitions N=6+4.

transitions of the four above-stated O<sub>2</sub> species. The three lines near 2 Tesla in the ΔM = 0 case are due to N = 6 ← 4 transitions of the <sup>16</sup>O<sup>18</sup>O(v = 0) molecule.

The LMR data at 4251.6740 GHz are shown in the first column of Table II.

TABLE I—Continued

$\nu_{\text{obs.}}$ (T)	$\nu_{\text{calc.}}$ (T)	(b) $\Delta M = \pm 1$ transitions				rel. slope (T/THz)	SQDP	peak int. ( $\text{cm}^{-1}$ )	species
		N=5 J' M' + J M	N=3 J M						
	0.71439	6 0	2 1		58.4	8.1E-5	7.99E-12/6	1617	
0.73106	0.73113	4 -2	4 -1		-49.2	3.0E-4	8.40E-8	1616	
0.75495	0.75504	4 0	4 1		-56.8	0.0140	3.81E-6	1616	
0.78504	0.78512	6 2	4 3		-79.6	3.5E-4	9.40E-8	1616	
0.79820	0.79831	6 -4	4 -3		25.0	0.0105	5.55E-9	1618	
0.83029	0.83039	6 -3	4 -4		27.6	0.0087	4.60E-9	1618	
0.87370	0.87379	4 1	4 0		-57.6	0.0123	3.35E-6	1616	
0.88810	0.88820	4 0	4 -1		-49.4	0.00112	3.05E-7	1616	
	0.89599	6 1	2 0		57.3	0.00161	1.58E-10/6	1617	
	0.90628	6 -1	2 0		56.4	0.00288	2.83E-10/6	1617	
	0.91448	5 -2	3 -3		51.5	2.8E-5	2.79E-12/6	1617	
0.95952	0.95960	4 -1	4 0		-56.0	0.00456	1.25E-6	1616	
	0.97798	6 3	2 2		34.8	3.1E-5	1.64E-11	1618	
	0.98500	6 0	2 -1		52.9	0.0107	1.05E-9/6	1617	
	1.10186	6 0	4 -1		-573.7	1.7E-3	1.71E-10	$\nu=1$	
1.14047	1.14050	6 -3	2 -2		36.0	0.0143	7.55E-9	1618	
1.16808	1.16808	6 -2	4 -3		37.4	0.0136	5.20E-9	1618	
	1.21023	4 -2	2 -1		-3273.4	0.00202	2.01E-10	$\nu=1$	
1.23886	1.23892	6 -1	4 -2		-150.2	3.7E-4	1.02E-7	1616	
	1.25992	6 5	4 4		-80.9	0.00145	3.95E-7	1616	
	1.29651	5 -4	3 -3		62.5	4.7E-4	4.65E-11/6	1617	
	1.32096	6 1	2 2		42.4	7.4E-6	3.93E-12	1618	
1.32901	1.32910	6 1	4 2		-225.2	0.00245	6.70E-7	1616	
1.39127	1.39131	5 5	4 4		-71.7	0.0138	7.25E-9	1618	
1.42869	1.42856	6 2	2 1		42.6	0.00062	3.25E-10	1618	
	1.58547	4 -3	4 -4		240.3	9.4E-5	9.22E-12/6	1617	
1.60710	1.60721	6 -1	2 -2		42.3	0.0143	7.55E-9	1618	
1.60867	1.60878	6 -2	2 -1		41.8	0.0091	4.80E-9	1618	
	1.70398	6 0	2 1		43.3	2.5E-4	1.33E-10	1618	
	1.80223	5 -2	3 -3		40.0	1.88E-4	1.00E-10	1618	
1.8468	1.84663	6 1	2 0		41.8	0.00433	2.29E-9	1618	
1.8498	1.84968	6 -1	2 0		41.8	0.00238	1.26E-9	1618	
	1.88877	5 4	4 3†		-21.1	9.78E-4	4.86E-10	1618	
1.90660	1.90633	6 0	2 -1		41.6	0.0107	5.65E-9	1618	
	1.91598	5 5	4 4†		-22.0	2.44E-3	1.21E-9	1618	
	1.91883	5 3	4 2†		-20.6	3.59E-4	1.79E10	1618	
	1.91883	5 3	4 2†		-20.6	3.59E-4	1.79E-10	1618	
	1.97805	5 2	4 1†		-20.4	1.08E-4	5.39E-11	1618	
	2.05145	5 1	4 0†		-20.2	2.38E-5	1.18E-11	1618	
	2.06060	5 2	4 3†		-21.1	5.56E-3	2.76E-9	1618	
	2.06011	5 1	4 2†		-20.5	5.58E-3	2.77E-9	1618	
	2.06845	5 0	4 1†		-20.2	4.51E-3	2.24E-9	1618	
	2.07052	5 -1	4 0†		-20.2	2.91E-3	1.45E-9	1618	
	2.07215	5 -2	4 -1†		-20.5	1.59E-3	7.90E-10	1618	
	2.09477	5 -3	4 -2†		-20.8	7.65E-4	3.80E-10	1618	
	2.10984	5 3	4 4†		-22.0	4.51E-3	2.24E-9	1618	
	2.12785	5 0	4 -1†		-20.2	3.20E-6	1.59E-12	1618	
	2.17905	5 -4	4 -3†		-21.2	3.09E-4	1.54E-10	1618	

These lines are due to  $N = 25 \leftarrow 23$  transitions of the  $^{16}\text{O}_2(v = 0)$  molecule. Lines from the other isotopic species are too weak to be observed for these high rotational values.

## THEORY

The Hamiltonian of this molecule is (7)

$$\begin{aligned}
 H = & BN^2 - DN^4 + \frac{2}{3} \{ \lambda(3S_z^2 - S^2) + (\lambda_D/2)(N^2(3S_z^2 - S^2) + (3S_z^2 - S^2)N^2) \\
 & + (\lambda_{DD}/2)(N^4(3S_z^2 - S^2) + (3S_z^2 - S^2)N^4) \} + \gamma \vec{N} \cdot \vec{S} + \gamma_D N^2 \vec{N} \cdot \vec{S} \\
 & + (\mu_B/\hbar) \{ g_{\perp} \vec{S} \cdot \vec{B} + (g_z - g_{\perp}) S_z B_z - g_N (\vec{N} \cdot \vec{B} - N_z B_z) \}, \quad (1)
 \end{aligned}$$

where  $\vec{N}$  and  $\vec{S}$  are rotational and electronic spin angular momenta;  $N_z$  and  $S_z$  are their components along the molecular axis;  $B$  and  $D$  are rotational constants;  $\lambda$ ,  $\lambda_D$ ,  $\lambda_{DD}$ ,  $\gamma$ , and  $\gamma_D$  are coupling constants,  $\mu_B$  is the Bohr magneton, and

$$g_{\perp} = 2.004838 \quad g_z = 2.002025 \quad \text{and} \quad g_N = 0.000126 \quad (2)$$

are the magnetic  $g$  factors (8) for the  $^{16}\text{O}_2(v=0)$  molecule. These values of the  $g$  factors may be slightly different for other isotopic molecules and excited vibrational states, but we assumed that the differences are not significant and used the same  $g$  factors throughout.

The values of the coupling constants for  $^{16}\text{O}_2(v=0, 1)$  (9),  $^{16}\text{O}^{17}\text{O}$  (10), and  $^{16}\text{O}^{18}\text{O}$  (11) are presented in Table III. We used these values to compute the magnetic field strength of transitions and found good agreement with the measured values (see Tables I and II, columns 1 and 2).

The rotational transitions of the  $^{16}\text{O}_2(v=1)$  and  $^{16}\text{O}^{17}\text{O}(v=0)$  molecules have not been observed before, and the existing values of  $B$  and  $D$  determined from microwave data (9, 11) are not accurate. New values for them were determined by fitting our previous (6) and present LMR data and the results are shown in Table III.

The relative slope, SQDP (matrix element of magnetic moment/Bohr Magnetron)<sup>2</sup>, and peak intensity are defined in our previous paper (6), and they are calculated now with the new sets of molecular parameters. The results are shown in Tables I and II. The last column of these tables indicate the molecular species; 1616, 1617, 1618, and  $v=1$  correspond to  $^{16}\text{O}_2(v=0)$ ,  $^{16}\text{O}^{17}\text{O}(v=0)$ ,  $^{16}\text{O}^{18}\text{O}(v=0)$ , and  $^{16}\text{O}_2(v=1)$ , respectively.

 HYPERFINE STRUCTURE OF  $^{16}\text{O}^{17}\text{O}$ 

Each of the  $^{16}\text{O}^{17}\text{O}(v=0)$  lines splits into six hfs components with nearly constant spacings, indicating that the hfs is almost completely decoupled by the external field. In the representation in which  $I_z$  (component of the nuclear spin  $I$  along the external field) is diagonal, we have (6)

$$\begin{aligned}
 \langle N'J'MIM_I | H_{\text{hfs}} | NJMIM_I \rangle = & (-1)^{J'-M} M_I \sqrt{6(2J'+1)(2J+1)} \begin{pmatrix} J & J & 1 \\ M & -M & 0 \end{pmatrix} \\
 \times & \left[ (-1)^{J+N}(b+c/3) \begin{Bmatrix} 1 & 1 & 1 \\ J & J & N \end{Bmatrix} \delta_{N',N} + \sqrt{10}(c/3) \begin{Bmatrix} 1 & 1 & 1 \\ N' & N & 2 \\ J & J & 1 \end{Bmatrix} \langle N' || C_2 || N \rangle \right]
 \end{aligned}$$

TABLE II  
 LMR Spectra of the Oxygen Molecule  $^{16}\text{O}_2(X^3\Sigma_g^-, v = 0)$  at 4251.6740 GHz  
 [(a)  $\Delta M = 0$  transitions, (b)  $\Delta M = \pm 1$  transitions]

$B_{\text{obs}}$ (T)	$B_{\text{calc}}$ (T)	(a) $\Delta M=0$ transitions.		rel. slope (T/THz)	SQDP	peak int. ( $\text{cm}^{-1}$ )
		N=25 J' M' +	N=23 J M			
	0.35001	26 -22	23 -22	-40.51	9.44E-10	2.77E-13
	0.37911	26 -21	23 -21	-45.82	4.70E-9	1.38E-12
	0.41576	26 -20	23 -20	-53.42	1.52E-8	4.45E-12
	0.46469	26 -19	23 -19	-65.66	4.15E-8	1.22E-11
	0.53780	26 -18	23 -18	-90.75	1.10E-7	3.23E-11
0.6113	0.61151	25 -24	24 -24	18.61	2.93E-3	8.60E-7
0.6418	0.64183	25 -23	23 -23	19.75	2.63E-3	7.71E-7
0.6752	0.67530	25 -22	22 -22	21.02	2.34E-3	6.88E-7
0.7127	0.71239	25 -21	22 -21	22.43	2.08E-3	6.09E-7
0.7540	0.75366	25 -20	22 -20	24.01	1.82E-3	5.35E-7
	0.78861	26 24	24 24	-41.30	6.17E-6	1.81E-9
0.7999	0.79973	25 -19	22 -19	25.77	1.59E-3	4.67E-7
0.8515	0.85134	25 -18	22 -18	27.72	1.38E-3	4.03E-7
	0.88346	26 23	23 23	-51.51	1.10E-5	3.22E-9
0.9091	0.90927	25 -17	22 -17	29.85	1.18E-3	3.46E-7
0.9743	0.97435	25 -16	22 -16	32.16	9.99E-4	2.93E-7
	1.03030	26 22	23 22	-73.99	1.38E-5	4.03E-9
1.0472	1.04735	25 -15	22 -15	34.58	8.40E-4	2.46E-7
	1.05308	26 -17	23 -17	230.16	1.24E-6	3.62E-10
1.1288	1.12887	25 -14	22 -14	37.03	6.99E-4	2.05E-7
	1.17367	25 22	22 22	22.41	8.08E-10	2.37E-13
1.2194	1.21914	25 -13	22 -13	39.39	5.77E-4	1.69E-7
	1.23648	25 21	22 21	23.88	4.45E-9	1.31E-12
	1.30416	25 20	22 20	25.39	1.47E-8	4.32E-12
1.3179	1.31785	25 -12	22 -12	41.51	4.74E-4	1.39E-7
	1.37673	25 19	22 19	26.93	3.77E-8	1.11E-11
1.4239	1.42394	25 -11	22 -11	43.22	3.87E-4	1.13E-7
	1.43944	26 21	23 21	-399.23	1.11E-5	3.26E-9
	1.45399	25 18	22 18	28.46	8.27E-8	2.43E-11
	1.53557	25 17	22 17	29.93	1.63E-7	4.77E-11
1.5355	1.53559	25 -10	22 -10	44.43	3.15E-4	9.25E-8
	1.62079	25 16	22 16	31.32	2.95E-7	8.65E-11
1.6503	1.65034	25 -9	22 -9	45.10	2.57E-4	7.54E-8
	1.70874	25 15	22 15	32.58	5.02E-7	1.47E-10
1.7656	1.76534	25 -8	22 -8	45.26	2.10E-4	6.16E-8
	1.79819	25 14	22 14	33.68	8.11E-7	2.38E-10
1.8778	1.87770	25 -7	22 -7	45.03	1.72E-4	5.04E-8
	1.88780	25 13	22 13	34.62	1.25E-6	3.68E-10
	1.97596	25 12	22 12	35.40	1.87E-6	5.49E-10
	1.98474	25 -6	22 -6	44.50	1.41E-4	4.14E-8
	2.06104	25 11	22 11	36.02	2.70E-6	7.93E-10

where

$$\langle N \| C_2 \| N \rangle = -\sqrt{N(N+1)(2N+1)(2N-1)(2N+3)},$$

and

$$\langle N+2 \| C_2 \| N \rangle = \sqrt{6(N+1)(N+2)(2N+3)}.$$

TABLE II—Continued.

$\nu_{\text{obs}}$ (T)	$\nu_{\text{calc}}$ (T)	(b) $\Delta M = \pm 1$ transitions				SQDP	peak int. ( $\text{cm}^{-1}$ )	
		N=25		N=23				rel. slope (T/THz)
		J'	M'	J	M			
	0.34470	26	-23	23	-22	-39.27	6.96E-10	2.04E-13
	0.35535	26	-21	23	-22	-41.80	5.18E-11	1.52E-14
	0.37250	26	-22	23	-21	-44.13	2.03E-9	5.96E-13
	0.38582	26	-20	23	-21	-47.58	3.53E-10	1.04E-13
	0.40715	26	-21	23	-20	-50.96	3.73E-9	1.09E-12
	0.42462	26	-19	23	-20	-56.06	1.52E-9	4.47E-13
	0.45260	26	-20	23	-19	-61.54	4.97E-9	1.46E-12
	0.47746	26	-18	23	-19	-70.31	5.57E-9	1.63E-12
	0.51798	26	-19	23	-18	-81.44	3.75E-9	1.10E-12
0.6222	0.62229	25	-24	23	-23	18.89	7.87E-5	2.31E-8
0.6302	0.63029	25	-23	24	-24	19.44	6.10E-5	1.79E-8
	0.63710	26	-18	23	-17	-147.08	6.10E-10	1.79E-13
0.6539	0.65380	25	-23	22	-22	20.07	1.52E-4	4.47E-8
0.6623	0.66246	25	-22	23	-23	20.66	1.18E-4	3.45E-8
0.6887	0.68865	25	-22	22	-21	21.38	2.20E-4	6.46E-8
0.6981	0.69804	25	-21	22	-22	22.02	1.69E-4	4.97E-8
0.7270	0.72735	25	-21	22	-20	22.86	2.83E-4	8.29E-8
0.7374	0.73753	25	-20	22	-21	23.53	2.16E-4	6.35E-8
0.7665	0.76628	26	25	24	24	-38.75	4.03E-4	1.18E-7
0.7704	0.77049	25	-20	22	-19	24.50	3.39E-4	9.94E-8
0.7814	0.78155	25	-19	22	-20	25.22	2.59E-4	7.59E-8
	0.81203	26	23	24	24	-44.09	6.46E-9	1.90E-12
0.8189	0.81877	25	-19	22	-18	26.34	3.88E-4	1.14E-7
0.8305	0.83075	25	-18	22	-19	27.09	2.96E-4	8.70E-8
0.8522	0.85162	26	24	23	23	-47.12	4.00E-4	1.17E-7
0.8730	0.87294	25	-18	22	-17	28.37	4.31E-4	1.26E-7
0.8859	0.88589	25	-17	22	-18	29.14	3.29E-4	9.66E-8
	0.91804	26	22	23	23	-56.65	4.05E-8	1.19E-11
0.9336	0.93384	25	-17	22	-16	30.59	4.66E-4	1.37E-7
0.9475	0.94776	25	-16	22	-17	31.37	3.57E-4	1.05E-7
0.9768	0.97646	26	23	23	22	-63.40	3.97E-4	1.16E-7
1.0019	1.00230	25	-16	22	-15	32.96	4.92E-4	1.44E-7
1.0171	1.01716	25	-15	22	-16	33.73	3.81E-4	1.12E-7
1.0795	1.07907	25	-15	22	-14	35.43	5.09E-4	1.49E-7
1.0951	1.09473	25	-14	22	-15	36.16	4.00E-4	1.17E-7
	1.09500	26	21	23	22	-89.56	1.65E-7	4.83E-11

The coupling constants for the magnetic dipole hfs,  $b$  and  $c$ , are obtained by microwave spectroscopy (10) as  $-101.441$  and  $139.73$  MHz, respectively. The hfs splitting constants in our case can be calculated using these values in the above formulas and the relative slope given in Table I. We first calculated them assuming that the upper and the lower states are pure ( $N = 5, J = 4$ ) and ( $N = 3, J = 4$ ) states, respectively. The results are shown in the column indicated as calc.\* in Table IV. The calculation was repeated using the exact eigenfunctions which are the mixtures of different  $J$ - and  $N$ -states because of the external field and the spin interactions, and the results are shown in the last column indicated as calc.\*\* in Table IV. There is a reasonable agreement with experiment, but no remarkable improvement by using the exact eigenfunctions.

TABLE II—Continued

P <sub>obs</sub> (T)	B <sub>calc</sub> (T)	(b) $\Delta M = \pm 1$ transitions				rel. slope (T/Thz)	SQDP	peak int. (cm <sup>-1</sup> )
		N=25		N=23				
		J'	M'	J	M			
	1.13371	25	23	22	22	21.28	2.05E-8	6.02E-12
1.1641	1.16465	25	-14	22	-13	37.89	5.17E-4	1.52E-7
1.1806	1.18087	25	-13	22	-14	38.55	4.15E-4	1.22E-7
	1.19367	25	22	22	21	22.72	9.51E-8	2.79E-11
	1.21503	25	21	22	22	23.53	2.43E-11	7.14E-15
1.2181	1.21718	26	22	23	21	-125.38	3.84E-4	1.13E-7
	1.25847	25	21	22	20	24.22	2.76E-7	8.09E-11
1.2592	1.25906	25	-13	22	-12	40.20	5.15E-4	1.51E-7
1.2755	1.27551	25	-12	22	-13	40.75	4.27E-4	1.25E-7
	1.28063	25	20	22	21	25.02	2.01E-10	5.90E-14
	1.32822	25	20	22	19	25.76	6.41E-7	1.88E-10
	1.35107	25	19	22	20	26.54	9.63E-10	2.82E-13
1.3618	1.36169	25	-12	22	-11	42.18	5.04E-4	1.48E-7
1.3780	1.37792	25	-11	22	-12	42.62	4.35E-4	1.28E-7
	1.40290	25	19	22	18	27.32	1.30E-6	3.82E-10
	1.42621	25	18	22	19	28.06	3.49E-9	1.02E-12
1.4718	1.47113	25	-11	22	-10	43.72	4.83E-4	1.42E-7
	1.48222	25	18	22	17	28.85	2.42E-6	7.08E-10
1.4872	1.48664	25	-10	22	-11	44.03	4.40E-4	1.29E-7
	1.50576	25	17	22	18	29.54	1.06E-8	3.10E-12
	1.56569	25	17	22	16	30.31	4.19E-6	1.23E-9
1.5853	1.58518	25	-10	22	-9	44.71	4.55E-4	1.34E-7
	1.58917	25	16	22	17	30.94	2.81E-8	8.25E-12
1.5996	1.59948	25	-9	22	-10	44.92	4.43E-4	1.30E-7
	1.65252	25	16	22	15	31.67	6.87E-6	2.02E-9
	1.67564	25	15	22	16	32.23	6.78E-8	1.99E-11
1.7010	1.70112	25	-9	22	-8	45.16	4.21E-4	1.23E-7
1.7137	1.71382	25	-8	22	-9	45.28	4.43E-4	1.30E-7
	1.74166	25	15	22	14	32.89	1.08E-5	3.17E-9
	1.76408	25	14	22	15	33.38	1.51E-7	4.42E-11
1.8158	1.81597	25	-8	22	-7	45.13	3.82E-4	1.12E-7
1.8267	1.82681	25	-7	22	-8	45.20	4.40E-4	1.29E-7
	1.83177	25	14	22	13	33.95	1.63E-5	4.78E-9
	1.85320	25	13	22	14	34.37	3.13E-7	9.19E-11
	1.92138	25	13	22	12	34.83	2.37E-5	6.96E-9
1.9272	1.92685	25	-7	22	-6	44.75	3.40E-4	9.97E-8
1.9360	1.93569	25	-6	22	-7	44.79	4.33E-4	1.27E-7
	1.94155	25	12	22	13	35.20	6.13E-7	1.80E-10
	2.00883	25	12	22	11	35.55	3.35E-5	9.83E-9

## CONCLUSION

From the observed LMR spectra of O<sub>2</sub> in its natural abundance new values of *B* and *D* for <sup>16</sup>O<sup>17</sup>O and that of *D* for the <sup>16</sup>O<sub>2</sub>(*v* = 1) molecules were calculated. The sensitivity limit of our spectrometer at 765 GHz is found to be about  $3 \times 10^{-10}$  cm<sup>-1</sup>, significantly better than  $10^{-9}$  cm<sup>-1</sup> we found previously (6) at 429 GHz. At 4252 GHz it was considerably less, about  $10^{-8}$  cm<sup>-1</sup>. These results may be explained by a decreasing detector sensitivity with frequency, and somewhat lower *Q*'s of the LMR spectrometer at higher frequencies. In all cases the sensitivity became worse



TABLE III  
Oxygen Molecular Constants (GHz)

ref.	<sup>16</sup> O <sub>2</sub> v=0	<sup>16</sup> O <sup>17</sup> O v=0	
	4,9	10	present work
B=	43.1004608(75)	41.8306(1)	41.83114(10)
D=	1.4520(20)·10 <sup>-4</sup>	1.386·10 <sup>-4</sup>	1.343(20)·10 <sup>-4</sup>
λ=	59.5013489(38)	59.50009(1)	
λ <sub>D</sub> =	5.8305(19)·10 <sup>-5</sup>	5.75(2)·10 <sup>-5</sup>	
λ <sub>DD</sub> =	3.39(14)·10 <sup>-10</sup>		
γ=	-0.2525875(30)	-0.245114(5)	
γ <sub>D</sub> =	-2.4544(29)·10 <sup>-7</sup>	-2.4(3)·10 <sup>-7</sup>	

  

ref.	<sup>16</sup> O <sup>18</sup> O v=0	<sup>16</sup> O <sub>2</sub> v=1	
	11	9	present work
B=	40.707408(10)	42.626398(82)	
D=	1.29·10 <sup>-4</sup>	1.48865·10 <sup>-4</sup>	1.447(2)·10 <sup>-4</sup>
λ=	59.499097(43)	59.6460785(66)	
λ <sub>D</sub> =	5.312(80)·10 <sup>-5</sup>	6.326(10)·10 <sup>-5</sup>	
γ=	-0.238488(7)	-0.2531932(11)	
γ <sub>D</sub> =	-6.19(116)·10 <sup>-7</sup>	-2.524(36)·10 <sup>-7</sup>	

TABLE IV  
Hyperfine Constants in LMR of <sup>16</sup>O<sup>17</sup>O(v = 0)

resonance field (T)	transition M + M		hfs splitting constant (Gauss)		
			obs.	calc.*	calc.**
			0.2734	-4	-4
0.3679	-3	-3	-36.7	-37.4	-37.6
0.4418	-2	-3	-35.8	-37.2	-37.0
0.4442	-3	-2	-36.2	-36.9	-37.3
0.6964	-1	-2	-29.0	-28.1	-30.1
0.7073	-2	-1	-29.8	-27.1	-30.2

\* Calculated assuming that both upper and lower states are pure J=4 states. (N=5 and 3 for upper and lower states, respectively.)

\*\* First order perturbation calculation using exact eigenfunctions.

near the limit of our electromagnet, 2 Tesla, where magnetic field inhomogeneities are greater.

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