

Note

Molecular constants of the ground state of oxygen ($^{16}\text{O}_2$) accounting for new experimental data

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The spectrum of the oxygen molecule is a subject of permanent interest in view of the importance of the molecule. The most recent paper devoted to its molecular constants is dated 2003 [1]. The aim of [1], as can be seen from its title, was to obtain molecular constants for oxygen using all the available experimental data. However, the newest and most accurate measurements [2–4] were not taken into account in that analysis. In the present Note, the oxygen rotational spectrum has been refitted, with the inclusion of the newly measured lines, and the results compared with previous values [1,2,5,6]. Improved values for the rotational constants of the $X^3\Sigma_g^-(v=0)$ state of the oxygen molecule ($^{16}\text{O}_2$) are presented.

We begin with a brief review of the history of the oxygen rotational spectrum since many of the lines have been measured several times. The first measurements of rotational transitions of oxygen were performed by McKnight and Gordy [7] who measured the frequency of the $(N, J) = (3, 2) - (1, 2)$ line as 424763.80(20) MHz. In a subsequent paper by Steinbach and Gordy [8], this frequency was corrected to 424763.210(100) MHz (600 kHz downshift). There was some confusion with this value: in the abstract of [8], it is given as 424763.120(100) (which is the value quoted, for example, in the JPL catalog [9]) while in the text it appears as 424763.210(100) MHz. This value 424763.210(100) MHz was repeated later in the book by Gordy and Cook [10] and used then by many researchers to obtain spectroscopic constants of the $X^3\Sigma_g^-(v=0)$ state of $^{16}\text{O}_2$. Zink and Mizushima [6] measured five new rotational lines and improved the values of B_0 and D_0 considerably. Later Park et al. [11], using the same tunable far-infrared spectrometer, mea-

sured a new line at 1525130.648(34) MHz and corrected a line previously measured in [6] as 2502323.923(92)–2502324.021(39) MHz.

In [4], we revised the frequency of the $(N, J) = (3, 2) - (1, 2)$ line to 424763.023(20) MHz—about 200 kHz below the previous value of Steinbach and Gordy [8]. In our next paper [2], we measured another seven pure rotational lines up to 1.12 THz; one of them had been measured earlier in [6] as 773839.691(64) MHz, but our re-measurement gave 773839.510(60) MHz (i.e., about 180 kHz downshift). Papers by Rouillé et al. [5] and more recently by Brodersen and Bendtsen [1], have also given oxygen molecular constants. Their values for B_0 and D_0 differed from those that we obtained by fitting the microwave, submillimeter wave, and far-infrared transitions [2] because they used older values and a smaller number of pure rotation lines. The constants of [2] were derived by combining the previously measured frequencies [6–8,12] with the new ones and represent improved values for the rotational and centrifugal constants B_0 and D_0 , even though some previously measured rotational frequencies were included in our fit together with re-measured ones. In [3], we re-investigated some fine structure lines. The present Note summarizes all known results. We have also added some lines from [13] which were somehow missed in all previous fits, bringing the total number of ground state lines used in the present fit to 46, of which 13 are rotational transitions in the submillimeter and far infrared ranges.

It is important to consider the control measurements used in the recent investigations. To check the reliability and accuracy of our spectrometer, we carried out four tests. (a) In [2], we measured lines of CO throughout the whole range studied, since these provide frequency standards known to sub-kHz accuracy. Our measurements agree with previous Lamb dip measurements to

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better than 10 kHz in the range up to 1 THz (Table 2 in [2]). (b) We checked the combination differences from our rotational lines, comparing them to the previously measured fine structure frequencies, and found agreement in the kHz range (Table 3 in [2]). (c) We found internal consistency in our measurements to about 5 kHz from the residuals of the fit (Tables 4 and especially 5 in [2]), other than for the line $(N, J) = (5, 4) - (3, 3)$, where the discrepancy of 67.38 kHz is far from our prediction but still within the experimental error. (d) Using the same spectrometer [3], we measured some of the fine structure lines of $^{16}\text{O}_2$ and found

agreement with previous measurements by other authors to within a few kHz, thus making a second test of the accuracy of our spectrometer and the consistency of all our measurements.

In the second column of Table 1, we present our frequency measurements of the oxygen lines [2,3] together with all previously measured values [6,7,11–14] from the microwave to the far-infrared regions. The data set was then fitted using the program *spfit.exe* from JPL [9]. The calculated frequencies are given in the third column of Table 1 and the residuals (Obs. – Calc.) in the fourth column.

Table 1
Observed and calculated frequencies of oxygen lines ($^{16}\text{O}_2$, $X^3\Sigma_g^-, v = 0$)

Transition $N', J' - N, J$ ($N^\pm = N', J' - N, J \pm 1$)	Observed frequency (MHz), [2,3,6,7,11–14]	Calculated frequency (MHz)	Obs. – calc. (MHz)
1 ⁻	118750.340(7) [3]	118750.338(5)	0.002
1 ⁺	56264.785(40) [3]	56264.776(3)	0.009
3 ⁻	62486.255(10) [7]	62486.254(3)	0.001
3 ⁺	58446.590(20) [7,14]	58446.591(3)	-0.001
5 ⁻	60306.052(8) [3]	60306.057(3)	-0.005
5 ⁺	59590.978(10) [14]	59590.985(3)	-0.007
7 ⁻	59164.215(20) [14]	59164.203(3)	0.012
7 ⁺	60434.777(8) [3]	60434.780(3)	-0.003
9 ⁻	58323.885(10) [14]	58323.874(3)	0.011
9 ⁺	61150.570(10) [14]	61150.565(3)	0.005
11 ⁻	57612.49(1) [13]	57612.481(3)	0.009
11 ⁺	61800.157(7) [3]	61800.161(3)	-0.004
13 ⁻	56968.180(20) [12]	56968.204(4)	-0.024
13 ⁺	62411.223(10) [14]	62411.225(3)	-0.002
15 ⁻	56363.391(7) [3]	56363.389(4)	0.002
15 ⁺	62998.00(1) [13]	62997.989(4)	0.011
17 ⁻	55783.819(20) [12]	55783.802(4)	0.017
17 ⁺	63568.520(10) [14]	63568.532(4)	-0.012
19 ⁻	55221.372(10) [12]	55221.369(5)	0.003
19 ⁺	64127.777(20) [12]	64127.782(4)	-0.005
21 ⁻	54671.145(20) [12]	54671.162(5)	-0.017
23 ⁻	54129.97(2) [13]	54130.005(6)	-0.035
23 ⁺	65224.120(10) [14]	65224.089(6)	0.031
25 ⁻	53595.72(3) [13]	53595.755(6)	-0.035
25 ⁺	65764.744(20) [12]	65764.791(6)	-0.047
31 ⁻	52021.423(9) [12]	52021.416(6)	0.007
33 ⁻	51503.348(18) [12]	51503.356(7)	-0.008
33 ⁺	67900.867(11) [12]	67900.879(7)	-0.012
35 ⁻	50987.760(19) [12]	50987.752(10)	0.008
35 ⁺	68431.005(17) [12]	68431.013(6)	-0.008
37 ⁻	50474.223(27) [12]	50474.239(16)	-0.016
37 ⁺	68960.312(12) [12]	68960.312(7)	0.000
39 ⁺	69489.030(15) [12]	69489.019(11)	0.011
3, 2–1, 1	368498.245(20) [2]	368498.245(11)	0.000
3, 2–1, 2	424763.023(20) [2]	424763.021(10)	0.002
3, 3–1, 2	487249.270(30) [2]	487249.275(11)	-0.005
5, 4–3, 3	715392.980(70) [2]	715392.901(15)	0.079
5, 4–3, 4	773839.510(60) [2]	773839.491(15)	0.019
5, 5–3, 4	834145.560(50) [2]	834145.548(15)	0.012
7, 6–5, 5	1061123.857(100) [2]	1061123.829(16)	0.028
7, 6–5, 6	1120714.836(50) [2]	1120714.815(16)	0.021
9, 8–7, 8	1466807.133(60) [6]	1466806.911(22)	0.222
9, 9–7, 8	1525130.648(34) [11]	1525130.785(22)	-0.137
11, 10–9, 10	1812405.539(112) [6]	1812405.242(32)	0.297
13, 12–11, 12	2157577.773(52) [6]	2157577.745(33)	0.028
15, 14–13, 14	2502324.021(39) [11]	2502324.030(38)	-0.009

Table 2

Molecular constants of oxygen $^{16}\text{O}_2$ ($X^3\Sigma_g^-, v=0$) obtained in this work by the program *spfit.exe* [9] from the experimental lines [2,3,6,7,11–14]. For comparison the results of [1,5,6] are also given

Constant	Ref. [6] (MHz)	Ref. [5] (MHz)	Ref. [1] (MHz)	This work (MHz) [2,3,6,7,11–14]
B_0	43100.4519(23)	43100.4565(23)	43100.4569(26)	43100.4425(12)
D_0	0.14514(78)	0.145176(19)	0.145180(21)	0.145124(13)
H_0	—	$8.4(48) \times 10^{-8}$	$9.3(54) \times 10^{-8}$	$3.8(36) \times 10^{-8}$
λ	59501.346(21)	59501.3477(22)	59501.3473(16)	59501.3456(26)
λ_D	0.058309(61)	0.058316(15)	0.058329(11)	0.058344(17)
λ_{DD}	$3.34(146) \times 10^{-7}$	$3.31(12) \times 10^{-7}$	$3.214(87) \times 10^{-7}$	$3.13(14) \times 10^{-7}$
γ	−252.5867(21)	−252.58684(39)	−252.58666(30)	−252.58648(34)
γ_D	$−2.4530(18) \times 10^{-4}$	$−2.4301(96) \times 10^{-4}$	$−2.4343(63) \times 10^{-4}$	$−2.452(11) \times 10^{-4}$
γ_{DD}	$−1.44(30) \times 10^{-9}$	$−1.41(57) \times 10^{-9}$	$−1.20(36) \times 10^{-9}$	$−1.57(71) \times 10^{-9}$

One of the parameters employed to establish the goodness-of-fit is the r.m.s. error (the square root of the sum of the squared residuals divided by the number of degrees of freedom). This estimate is usually used when the experimental values have roughly the same measurement errors. Because of big differences between the experimental errors of the fine structure lines and the far infrared lines, and the difference in their numbers (33 and 13), we calculated the r.m.s. errors for the two types of transitions separately. For the fine structure lines, it is about 15 and 60 kHz for the far infrared lines.

Column 5 of Table 2 lists our new values of the nine rotational constants determined for the $X^3\Sigma_g^-(v=0)$ state of the oxygen molecule. The data set consists of all the experimental frequencies for the $X^3\Sigma_g^-(v=0)$ state known to the authors. For comparison, values of the constants obtained in [1,5,6] are presented in Columns 2, 3, and 4 of this Table. (The values listed for [1] are those given there as “Solution I.”) As can be seen, the main differences between the present and the previous values occur for the B_0 and D_0 constants, where they are several times the quoted errors. It is also worth noting that the values obtained in the present Note, $B_0 = 43100.4425(12)$ MHz and $D_0 = 0.145124(13)$ MHz, agree within the error limits with the values obtained in [2], $B_0 = 43100.4438(9)$ MHz and $D_0 = 0.145115(40)$ MHz, even though the constant H_0 was not varied in [2].

In summary, new rotational constants have been obtained for the $X^3\Sigma_g^-, v=0$ state of $^{16}\text{O}_2$, using a data set consisting of all the available line frequencies, including some new measurements. The new values of the rotational constants B_0 and D_0 agree within the error limits with those we obtained previously in [2].

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