FINE STRUCTURE OF THE RED SYSTEM OF ATMOSPHERIC OXYGEN BANDS*

Harold D. Babcock and Luise Herzberg
Mount Wilson and Yerkes Observatories
Received May 12, 1948

ABSTRACT

Improved high-dispersion spectrograms of the red bands of atmospheric oxygen have been obtained, with air paths ranging from 30 meters to about 100 km. For unblended lines of medium intensity the wave lengths have been determined with an accuracy of about one part in seven million, and as a result the molecular constants of the molecules, O_2^{16}, $O^{16}O^{18}$, and $O^{16}O^{17}$ in the $^3\Sigma_g^-$ ground state and the $^1\Sigma_g^+$ excited state, have been evaluated much more precisely than previously.

Careful analysis shows a variation in the triplet splitting of the $^3\Sigma_g^-$ state which is dependent both on the vibrational quantum number and on the mass of the molecule, in addition to the variation due to the change of rotational energy.

A. INTRODUCTION

The most extensive and accurate measurements of the atmospheric oxygen bands previously published are those by Dieke and Babcock,[1] which were based on wave lengths obtained with interferometers by H. D. Babcock.[2] Dieke and Babcock discussed the 0–0, 1–0, 2–0, and 3–0 bands of O_2^{16} and also a new weak band, which was shown to belong to O_2 but which seemed independent of the main system. They called this weak band "A'" because it is intermingled with the 0–0 band, long designated "A" in the solar spectrum. Their paper served as a basis for R. S. Mulliken's[3] interpretation of the band system as a $^1\Sigma - {}^3\Sigma$ transition of the oxygen molecule and also for the theoretical discussion of the triplet-splitting in the $^3\Sigma$ ground state by H. A. Kramers[4] and by R. Schlapp.[5]

The new weak band, A', which Dieke and Babcock[1] described, was shown by Giauque and Johnston[6] to arise from an isotopic molecule, $O^{16}O^{18}$—a result which stimulated the search for other isotopes through spectroscopic observation. From additional data specially obtained by H. D. Babcock,[7] Giauque and Johnston[8] also established the existence of the molecule $O^{16}O^{17}$; and, following the later determination of the mass ratios of $O^{16} : O^{18} : O^{17}$ and the relative abundance of these isotopes, a new system of physical atomic weights, based on $O^{16} = 16$, was distinguished from the familiar system of chemical atomic weights in which O (natural mixture of isotopes) $= 16$.

The work of Dieke and Babcock was also used by Giauque and Johnston[9] in their determination of the entropy of oxygen, from which we quote:

It is suggested that entropy values deduced from reliable spectroscopic data are preferable as a basis for thermodynamic calculations to the less accurate values obtained from heat capacity measurements and the third law [of thermodynamics]. . . . The general agreement of the various physical facts concerning the oxygen molecule in relation to entropy and particularly the close agreement of the entropy as obtained by the two methods support our confidence that the third law of thermodynamics is an exact law.

[1] *Proc. Nat. Acad. Sci.*, **13**, 670, 1927.

[2] *Mt. W. Contr.*, No. 328; *Ap. J.*, **65**, 140, 1927.

[3] *Phys. Rev.*, **32**, 880, 1928.

[4] *Zs. f. Phys.*, **53**, 422, 1929.   [7] *Proc. Nat. Acad. Sci.*, **15**, 471, 1929.

[5] *Phys. Rev.*, **51**, 342, 1937.   [8] *J. Amer. Chem. Soc.*, **51**, 3528, 1929.

[6] *J. Amer. Chem. Soc.*, **51**, 1436, 1929.   [9] *Ibid.*, pp. 2319–2321.

The exact calculation of free energy and other properties of gases has been discussed by Giauque,[10] who took into account molecular rotation, vibration, nuclear spin, and electronic excitation.

In the present paper further measurements of the red bands of oxygen, made with air paths up to a maximum of the order of 100 km, are combined with the earlier Mount Wilson data. The results are more precise and more complete than are those in preceding papers. Besides the bands described by Dieke and Babcock and the 1–1 band of O_2^{16}, which was first observed by Babcock[11] and later studied by Mecke and Baumann,[12] the weaker 2–1 and 3–1 bands are now observed and also the 1–0 bands of both $O^{16}O^{18}$ and $O^{16}O^{17}$.

Refinement of the observations and also of the theoretical treatment now permits a more critical analysis (by L. H.), from which improved values of the molecular constants are derived. The accuracy of the new constants for O_2^{16} in the ground state, $^3\Sigma_g^-$, and in the electronically excited state, $^1\Sigma_g^+$, surpasses that for the constants of any other molecule.

B. OBSERVATIONAL DATA

Most of the later measurements have been obtained on Mount Wilson with the Snow telescope and a plane-grating spectrograph of 30-foot focus. A few plates were made with the 75-foot spectrograph of the 150-foot tower telescope and others in the laboratory at Pasadena, where interferometers were used to observe the absorption in 30 meters of air. This short air path permitted precise measurements of the principal lines of the 0–0 band of O_2^{16}, which are much too wide in the solar spectrum for satisfactory measurement, even with the midday summer sun on Mount Wilson.

All wave lengths in the present compilation of data were referred ultimately to the secondary standards in the spectrum of neon.[13]

Three excellent gratings were available, two ruled by Michelson at the University of Chicago and one by Anderson at the Johns Hopkins University. Second-, third-, and fourth-order spectra were used, with dispersions ranging from 0.88 to 0.12 A per millimeter.

Because of the range of intensity among the lines of O_2 and the overlapping of the bands from different isotopic molecules, spectrograms were made with various air paths. The weakest lines, i.e., most of those due to $O^{16}O^{17}$, part of those belonging to $O^{16}O^{18}$, and those with greatest K'' in the other bands, are seen only when the sun is close to the horizon. Under this condition, however, the strongest lines become so wide that they obscure many weak lines. The best that can be done is to observe the sun at various altitudes and to hunt for the close faint companions of the stronger lines.

At the lowest solar altitudes the weakening of the light, even in the deep red, is rapid and variable; at the same time the rate of change of the intensities of telluric lines with respect to length of air path varies rapidly. Since spectrographs having high dispersion usually do not provide high brightness, each exposure made with very low sun corresponds to an integration through the range of the variables. It will be apparent, therefore, that the labor of producing a consistent set of estimated line intensities throughout such a system of bands is very great. Photometric measures for numerous lines in the bands of O_2 have been published by various observers, and H. C. van de Hulst[14] has given a theoretical discussion of the intensities of atmospheric lines.

Readers interested in the obscuration of lines in spectra of celestial objects by telluric absorption will find a convenient arrangement of the wave lengths of oxygen band lines ($\lambda > 6600$ A) in *The Solar Spectrum*, $\lambda 6600–\lambda 13495$.[15] The work cited contains also

[10] *J. Amer. Chem. Soc.*, **52**, 4808, 1930.

[11] *Phys. Rev.*, **35**, 125, 1930.   [13] *Trans. I.A.U.*, **1**, 40, 1922.

[12] *Zs. f. Phys.*, **72**, 139, 1931.   [14] *Ann. d'ap.*, **8**, 1–25, 1945.

[15] Babcock and Moore, *Pub. Carnegie Inst. Washington*, No. 579 (Washington, 1947).
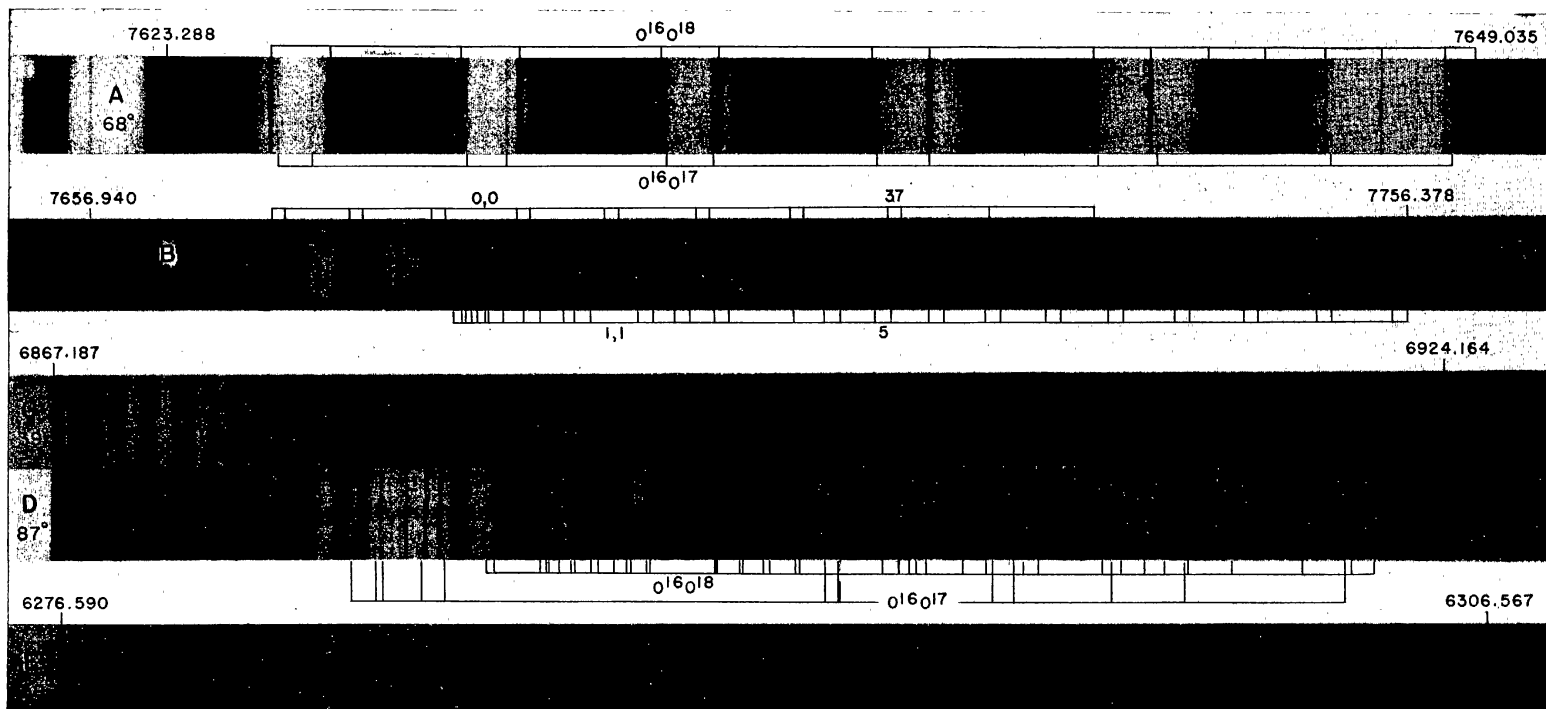
Fig. 1.—Parts of the $^1\Sigma \leftarrow {}^3\Sigma$ system of oxygen bands, observed at Mount Wilson. Zenith distances of sun at mid-exposure at the left. A, 0, 0 P-branches, O_2^{16}, $O^{16}O^{18}$, $O^{16}O^{17}$; B, 0, 0 and 1, 1 lines of O_2^{16} (note nearly complete absorption toward the origin and near-equality of intensity for pairs marked 37 and 5); C and D, 1, 0 of O_2^{16}, $O^{16}O^{18}$, and $O^{16}O^{17}$; E, 2, 0 of O_2^{16}.

the wave lengths of the O_2 lines in the $^1\Delta - {}^3\Sigma$ system: 1, 0 $\lambda\lambda$ 10584–10720, and 0,0 $\lambda\lambda$ 12493–12782.

In Tables 1, 2, and 3 are given wave lengths, wave numbers, and rotational assignments, K'', of lines observed in the bands 0–0, 1–0, 2–0, 3–0, 1–1, 2–1, and 3–1 of O_2^{16}, and in the 0–0 and 1–0 bands of $O^{16}O^{18}$ and of $O^{16}O^{17}$. Visual estimates of intensity are included for the first two bands mentioned; but even within a single band these estimates are chiefly useful as an indication of the range and for showing some small but real differences between ^PP and ^PQ lines or ^RQ and ^RP lines that have the same values of K''. For each of the other bands a note shows the range of intensity, but the numbers stated usually have different meanings from band to band. Intensities indicated in Tables 1, 2, and 3 relate to high sun on Mount Wilson. Weak lines were measured at low sun.

No data appear in Table 1 for two bands of O_2^{16} reported by others: the 4–0 band (head $= \lambda$ 5378), described by O. C. Lester,[16] and the 0–1 band (near λ 8624), suggested by Mecke and Baumann,[17] and observed in emission in the laboratory by J. Kaplan.[18]

From accurate predictions of the wave lengths of the lines in the 4–0 band, we conclude that our spectrograms do not show this band and that it is absent from the extensive observations of L. Becker.[19] Lester believed that his relative wave lengths were reliable to ± 0.05 A, and it is possible that, among some twenty lines which he assigned to this band, a few were due to O_2^{16}. But the evidence is too weak to permit further statements.

Positions of lines in the 0–1 band of O_2^{16} are accurately predictable, but our spectrograms do not show this band. On the other hand, some of the lines which Mecke and Baumann assigned to the 0–1 band are now found[15] to originate in the sun. Further observation is required to establish the occurrence of this band in absorption.

The wave numbers in the tables were computed to 0.0001 cm^{-1}, with the refractivity of air as given by Barrell and Sears,[20] and were rounded off to 0.001 cm^{-1} for tabulation. In order to avoid the accumulation of arithmetical errors, the computation of the band constants (secs. D and E) was based on the wave numbers as computed to 0.0001 cm^{-1}. These numbers are systematically smaller than those calculated from the refractivity of air as determined by Meggers and Peters[21] and used in Kayser's *Schwingungszahlen*, by 0.0135 cm^{-1} at λ 5500 and by 0.0045 cm^{-1} at λ 8000.

In Figure 1 are shown spectrograms illustrating the appearance of portions of various oxygen bands.

Within the tabular range of K'' in Tables 1, 2, and 3 every blank space is accounted for either as a forbidden line (e.g., $K'' = 1$ in ^PQ) or by masking attributable to another oxygen line, a solar line, or a telluric line presumably due to water vapor.

<center>C. BAND STRUCTURE</center>

The characteristic structure of the red atmospheric oxygen bands—two R-form branches forming a head and two P-form branches, separated from the former by a zero gap—has been interpreted by R. S. Mulliken[22] as a transition from the $^3\Sigma_g^-$ ground state of the O_2 molecule to a $^1\Sigma_g^+$ excited state. As was pointed out by J. H. Van Vleck,[23] a $\Sigma_g-\Sigma_g$ transition, though strictly forbidden as electric dipole radiation, is possible as

[16] *Ap. J.*, **20**, 81, 1904.

[17] *Das ultrarote Sonnenspektrum* (Leipzig, 1934).

[18] *Phys. Rev.*, **71**, 274, 1947.   [19] *Trans. R. Soc. Edinburgh*, Vol. **36**, Part I, 1900.

[20] *Phil. Trans. R. Soc. London, A*, **238**, 1, 1939.

[21] *Bull. Nat. Bureau Standards*, **14**, 697, 1917.

[22] *Phys. Rev.*, **32**, 880, 1928; and *Rev. Mod. Phys.*, **4**, 1, 1932.   [23] *Ap. J.*, **80**, 161, 1934.

TABLE 1

LINES IN THE $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ SYSTEM OF O_2^{16}

0–0 BAND

λλ 7593.695–7733.738

K''	λ_{air}	ν_{vac}	INT.	λ_{air}	ν_{vac}	INT.
	^PP Branch			^PQ Branch		
1....	7620.996	13118.034	25 a*	....	....	....
3....	24.500	12.005	32 a	7623.288	13114.089	30 a
5....	28.225	05.602	35 a	27.054	07.614	32 a
7....	32.168	13098.831	38 a	31.016	00.809	35 a
9....	36.328	91.695	38 a	35.192	13093.643	35 a
11....	40.707	84.193	35 a	39.585	86.114	32 a
13....	45.312	76.312	30 a	44.200	78.214	30 a
15....	50.135	68.068	20 a	49.035	69.947	20 a
17....	55.182	59.452	18 a	54.094	61.308	18 a
19....	60.454	50.465	12 a	59.370	52.311	15 a
21....	65.944	41.118	10	64.872	42.942	12
23....	71.670	31.385	10	70.600	33.203	10
25....	77.618	21.289	9	76.563	23.079	9
27....	83.800	10.813	8	82.756	12.581	8
29....	90.217	12999.956	6	89.177	01.715	6
31....	96.868	88.723	4	95.836	12990.465	4
33....	7703.759	77.105	3	7702.739	78.823	3
35....	10.874	65.131	− 1	09.871	66.817	− 1
37....	18.257	52.729	− 2	17.251	54.417	− 2
39....	25.862	39.978	− 4	24.880	41.623	− 4
41....	7733.738	12926.801	− 2†	7732.746	12928.459	− 4
	^RR Branch			^RQ Branch		
1....	7616.146	13126.387	17 a	7615.061	13128.257	20 a
3....	13.194	31.477	20 a	12.060	33.433	25 a
5....	10.455	36.203	25 a	09.302	38.193	50 a
7....	07.933	40.557	30 a	06.767	42.572	30 a
9....	05.635	44.528	30 a	04.453	46.571	40 a
11....	03.556	48.122	30 a	02.363	50.185	30 a
13....	01.697	51.337	25 a	00.493	53.420	25 a
15....	00.066	54.159	25 a	7598.847	56.269	25 a
17....	7598.650	56.611	25 a	97.438	58.709	30 a†
19....	97.438	58.709	30 a†	96.228	60.806	20 a
21....	96.503	60.329	12	95.235	62.526	14 †
23....	95.768	61.603	12	94.507	63.788	12 a
25....	95.235	62.526	13 †	93.997	64.672	10 a
27....	94.974	62.979	6 †	93.695	65.195	10 †
29....	7594.974	13162.979	6 †	93.695	65.195	10 †
31....	....	....	....	7593.850	13164.927	2

* Lines marked "a" were observed with artificial light and an air path of 30 meters. All lines not having this mark were observed in the solar spectrum.

† Either unresolved blend with another oxygen line, with a solar line, or with a telluric line (probably due to water vapor) or so close to such a line that the wave length is probably affected by it.

170

TABLE 1—*Continued*

½–0 BAND

λλ 6867.187–6967.650

K''	λ_{air}	ν_{vac}	INT.	λ_{air}	ν_{vac}	INT.
		^PP Branch			^PQ Branch	
1.....	6883.833	14522.783	11	....	....	....
3.....	86.743	16.646	15	6885.754	14518.733	13†
5.....	89.903	09.989	17	88.948	12.001	15
7.....	93.309	02.821	19	92.369	04.798	17
9.....	96.965	14495.133	20	96.037	14497.083	18
11.....	6900.868	86.935	19	99.954	88.853	17
13.....	05.023	78.218	17	6904.117	80.117	15
15.....	09.431	68.979	13	08.534	70.860	12
17.....	14.090	59.230	10	13.200	61.091	10
19.....	19.002	48.966	8	18.122	50.803	8
21.....	24.164	38.193	9†	23.286	40.026	6†
23.....	29.599	26.870	5	28.727	28.685	5
25.....	35.280	15.051	3	34.422	16.837	3
27.....	41.218	02.721	5†	40.375	04.470	0
29.....	....	....		46.590	14391.582	− 2
31.....	53.912	14376.429	− 4	53.072	78.167	− 4
33.....	60.647	62.520	− 3?	59.812	64.243	− 3?
35.....	6967.650	14348.085	− 4†	6966.837	14349.758	− 4
		^RR Branch			^RQ Branch	
1.....	6879.928	14531.027	10	6879.041	14532.900	12
3.....	77.637	35.867	12	76.715	37.816	14
5.....	75.590	40.195	14	74.653	42.177	16
7.....	73.798	43.985	14	72.843	46.006	16
9.....	72.247	47.268	14	71.285	49.304	15
11.....	70.946	50.022	13	70.007	52.011	12
13.....	69.887	52.265	12	68.915	54.324	12†
15.....	69.096	53.947	11	68.105	56.040	11
17.....	68.525	55.152	8†	67.547	57.226	8
19.....	68.245	55.750	5	67.252	57.856	6
21.....	68.208	55.828	4	67.187	57.993	4
23.....	68.421	55.372	2	67.394	57.548	3
25.....	68.915	54.324	12†	67.856	56.575	2
27.....	69.627	52.816	2	68.577	55.042	2†
29.....	70.620	50.712	− 1	69.567	52.945	− 3†
31.....	71.872	48.062	− 3	6870.819	14550.291	− 3†
33.....	6873.392	14544.844	− 4	....	....	....

TABLE 1—*Continued*

2–0 BAND

λλ 6276.590–6353.099; Intensity −4 to 3

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	^PP Branch		^PQ Branch	
1........	6287.749	15899.546	....	....
3........	90.222	93.294	6289.397	15895.379
5........	92.959	86.381	92.162	88.394
7........	95.962	78.806	95.179	80.780
9........	99.230	70.567	98.457	72.515
11........	6302.764	61.668	6302.000	63.591
13........	06.567	52.104	05.810	54.006
15........	10.636	41.883	09.886	43.766
17........	14.977	30.993	14.235	32.854
19........	19.591	19.434	18.853	21.282
21........	24.479	07.208	23.750	09.030
23........	29.636	15794.329	28.913	15796.134
25........	35.072	80.777	34.358	82.555
27........	40.791	66.544	40.078	68.316
29........	46.796	51.626	46.086	53.388
31........	6353.099	15735.997	6352.379	15737.781
	^RR Branch		^RQ Branch	
1........	6284.536	15907.674	6283.795	15909.550
3........	82.726	12.257	81.956	14.207
5........	81.178	16.178	80.393	18.168
7........	79.896	19.427	79.101	21.443
9........	78.878	22.008	78.073	24.049
11........	78.126	23.916	77.312	25.982
13........	77.638	25.153	76.818	27.234
15........	77.419	25.709	76.590	27.813
17........	77.470	25.580	76.633	27.704
19........	77.785	24.781	76.938	26.930
21........	78.374	23.286†	77.525	25.440
23........	79.233	21.108	78.374	23.286†
25........	....	....	79.506	20.416
27........	81.781	14.650	80.910	16.856
29........	6283.468	15910.378	6282.588	15912.606

TABLE 1—*Continued*

3-0 BAND

λλ 5788.102–5829.917; Intensity −4 to 0

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
		^PP Branch		^PQ Branch
1........	5796.092	17248.221†	....	....
3........	98.195	41.965†	5797.530	17243.943
5........	5800.640	34.698	99.963	36.710
7........	03.327	26.718	5802.663	28.689
9........	06.289	17.930	05.631	19.882
11........	09.523	08.345	08.878	10.256
13........	13.041	17197.931	12.400	17199.828
15........	16.833	86.720†	16.263	88.404†
17........	20.912	74.677	20.278	76.547
19........	25.272	61.822	24.636	63.696
21........	5829.917	17148.148	5829.288	17149.999
		^RR Branch		^RQ Branch
1........	5793.411	17256.203†	5792.769	17258.115
3........	91.946	60.568	91.293	62.514†
5........	90.769	64.076	90.101	66.068
7........	89.865	66.771	89.189	68.788
9........	89.234	68.653	88.549	70.697
11........	88.877	69.718	88.187	71.777
13........	88.801	69.945	88.102	72.031
15........	88.995	69.366	88.289	71.473
17........	89.489	67.893†	88.763	70.059
19........	90.227	65.692	89.489	67.893†
21........	5791.293	17262.514†	5790.534	17264.777

173

TABLE 1—*Continued*

1–1 BAND

λλ 7684.331–7768.513; Intensity −4 to −3

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	*P*P Branch		*P*Q Branch	
1........	7710.099	12966.434	....	....
3........	13.658	60.451	7712.416	12962.538
5........	17.450	54.083	16.251	36.096
7........	21.482	47.319	20.304	49.294
9........	25.746	40.173	24.586	42.116
11........	30.254	32.627	29.101	24.556
13........	34.995	24.700	33.854	26.607
15........	39.978	16.379	38.848	18.265
17........	45.202	07.667	44.080	09.537
19........	50.670	12898.561	49.554	00.418
21........	56.378	89.069	55.275	12890.902
23........	62.334	79.179	61.232	81.008
25........	7768.513	12868.935	7767.458	12870.683
	*R*R Branch		*R*Q Branch	
1........	7705.207	12974.666	7704.076	12976.571
3........	02.240	79.664	01.078	81.622
5........	7699.506	84.273	7698.322	86.270
7........	96.996	88.507	....	....
9........	94.748	92.301	93.530	94.358
11........	92.722	95.723	91.487	97.810
13........	90.939	98.736	89.703	13000.825
15........	89.387	13001.360	88.127	03.491
17........	88.127	03.491	86.830	05.684
19........	87.034	05.339	85.764	07.488
21........	86.203	06.745	84.964	08.842
23........	85.629	07.717	7684.331	13009.914
25.... ..	7685.281	13008.306	....	....

TABLE 1—*Continued*

2–1 BAND

λλ 6954.014–6996.310; Intensity −4 to −3

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	^PP Branch		^PQ Branch	
1........	6970.055	14343.133	....	....
3........	73.207	37.020†	....	....
5........	....	....	6975.239	14332.473
7........	79.705	23.303	78.740	25.283
9........	83.452	15.617	82.501	17.667
11........	87.482	07.361	....	....
13........	....	....	90.839	00.491
15........	6996.310	14289.312	6995.378	14291.212
	^RR Branch		^RQ Branch	
3........	6963.773	14356.072	6962.804	14358.070
5........	61.707	60.332	60.746	62.315
7........	59.946	63.966	....	....
9........	58.462	67.029	....	....
11........	57.204	69.627	56.214	71.672†
13........	56.214	71.672†	....	....
15........	6955.621	14373.104	54.494	75.226
17........	....	....	6954.014	14376.219

3–1 BAND

λλ 6360.045–6390.320; Intensity −4

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	^PP Branch		^PQ Branch	
7........	6379.270	15671.44	6378.520	15673.29
9........	82.728	62.95	81.876	65.05
11........	86.268	54.27	85.597	55.92
13........	6390.320	15644.34	6389.599	15646.11
	^RR Branch		^RQ Branch	
7........	6363.135	15711.18	....	....
9........	62.122	13.68	....	....
11........	61.453	15.33	6360.593	15717.46
13........	6360.981	15716.50	....	....
15........	....	....	6360.045	15718.81

175

TABLE 2

LINES IN THE $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ SYSTEM OF $O^{16}O^{18}$

0–0 BAND

λλ 7594.287–7684.964; Intensity −4 to 3

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}	K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	$^P P$ Branch		$^P Q$ Branch			$^R R$ Branch		$^R Q$ Branch	
1....	7619.698	13120.268	....	....	1....	....	....	7614.026	13130.042
2....	21.323	17.471	7620.077	13119.615	2....	7613.705	13130.595	12.578	32.539
3....	23.012	14.564	21.801	16.648	3....	12.314	32.995	11.194	34.927
4....	....	....	23.552	13.635	4....	11.007	35.250	09.868	37.216
5....	26.524	08.525	25.353	10.538	5....	09.746	37.427	08.586	39.430
6....	....	....	....	....	6..	08.530	39.526	07.366	41.537
7....	30.245	02.133	29.092	04.113	7....	07.366	41.537	06.198	43.555
8....	....	....	....	....	8....	06.238	43.486	05.076	45.494
9....	34.170	13095.396	33.036	13097.342	9....	05.186	45.304	04.013	47.331
10....	....	....	....	....	10....	....	....	02.996	49.090
11....	38.308	88.302	37.183	90.230	11....	03.216	48.710	02.036	50.751
12....	40.457	84.621	39.339	86.536	12....	....	....	01.127	52.323
13....	42.651	80.865	41.535	82.775	13....	01.470	51.730	....	....
14....	44.900	77.016	43.793	78.910	14....	....	....	7599.463	55.203
15....	47.204	73.076	46.098	74.967	15....	....	....	....	....
16....	49.552	69.064	48.454	70.940	16....	7599.228	55.610	98.006	57.726
17....	51.963	64.946	50.894	66.771	17....	....	....	....	....
18....	54.428	60.739	53.343	62.590	18....	98.006	57.726	96.768	59.870
19....	56.940	56.454	55.847	58.318	19....	....	....	....	....
20....	....	....	58.420	53.931	20....	96.975	59.511	....	....
21....	62.122	47.623	61.05	49.449	21....	....	....	....	....
22....	....	....	63.726	44.893	22....	....	....	....	....
23....	67.518	38.441	66.447	40.263	23....	....	....	....	....
24....	70.31	33.696	69.233	35.526	24....	....	....	....	....
25....	73.127	28.910	72.09	30.671	25....	95.590	61.911	94.287	64.169
26....	76.026	23.990	74.962	25.795	26....	95.590	61.911	94.287	64.169
27....	78.953	19.025	....	....	27....	7595.590	13161.911	7594.287	13164.169
28....	81.953	13.941	7680.912	13015.705					
29....	7684.964	13008.842	....	....					

TABLE 2—*Continued*

1–0 BAND

λλ 6885.279–6938.548; Intensity −4 to −3

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	^PP Branch		^PQ Branch	
1	6901.271	14486.088*	....	....
2	02.620	83.257	6901.607	14485.383
3	....	....	03.040	82.376*
4	05.494	77.229	04.531	79.246
5	07.023	74.025	06.059	76.045*
6	....	....	07.655	72.700*
7	10.250	67.265	09.32	69.218*
8	11.952	63.703	11.015	65.664
9	13.713	60.019	12.786	61.958*
10	15.533	56.213	....	....
11	17.409	52.293	16.475	54.245*
12	19.327	48.287*	18.429	50.162
13	21.338	44.089	20.426	45.993
14	23.369	39.852*	22.478	41.710
15	25.497	35.415*	24.597	37.290
16	27.675	30.876	....	....
17	....	....	....	....
18	32.150	21.560*	....	....
19	34.531	16.610	....	....
20	6936.962	14411.557	36.066	13.418
21	....	....	6938.548	14408.451
	^RR Branch		^RQ Branch	
1	6897.562	14493.879	6896.664	14495.765
2	96.445	96.225	95.521	98.168
3	95.382	98.460	94.451	14500.418
4	94.397	14500.569*	93.40	02.628*
5	93.40	02.628*	92.57	04.375*
6	92.57	04.375*	91.593	06.431
7	91.719	06.166	90.760	08.185
8	90.948	07.789	90.10	09.574*
9	90.240	09.279	89.271	11.320
10	89.585	10.659	88.612	12.709
11	....	....	88.000	13.998*
12	88.457	13.035	87.476	15.102
13	88.000	13.998*	87.000	16.105*
14	87.564	14.917	86.579	16.993*
15	87.196	15.692	86.209	17.774*
16	87.000	16.105*	....	....
17	86.579	16.993*	....	....
18	86.476	17.211	85.477	19.317
19	86.372	17.430*	85.349	19.587*
20	86.209	17.774*	85.279	19.734*
21	86.303	17.575	85.279	19.734*
22	6886.372	14517.430*	6885.349	14519.587*

* Either unresolved blend with another oxygen line, with a solar line, or with a telluric line (probably due to water vapor) or so close to such a line that the wave length is probably affected by it.

177

TABLE 3

LINES IN THE $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ SYSTEM OF $O^{16}O^{17}$

0–0 BAND

λλ 7599.550–7675.240; Intensity −4 to −3

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	^PP Branch		^PQ Branch	
1........	7620.322	13119.194	....	....
2........	21.988	16.326	....	....
3........	23.715	13.355	7622.503	13115.440
4........	25.475	10.328	....	....
5........	....	....	26.157	09.156
6........	29.196	03.934	....	....
7........	....	....	29.988	02.574
8........	33.131	13097.179	....	....
9........	....	....	34.052	13095.599
10........	37.276	90.071	....	....
11........	....	....	....	....
12........	41.644	82.588	....	....
13........	....	....	42.786	80.633
14........	46.209	74.777	....	....
15........	48.580	70.725	47.460	72.639
16........	....	....	....	....
17........	53.47	62.373	52.383	64.229
18........	56.00	58.057	....	....
19........	58.50	53.624	....	....
20........	....	....	....	....
21........	63.90	44.597	62.84	46.401
22........	66.669	39.885	....	....
23........	69.47	35.123	68.399	36.944
24........	72.32	30.281	....	....
25........	7675.240	13025.324	7674.183	13027.117
	^RR Branch		^RQ Branch	
1........	7615.552	13127.412	....	....
2........	14.15	29.828	....	....
3........	12.745	32.251	7611.584	13134.254
4........	11.364	34.634	....	....
5........	10.06	36.885	08.91	38.870
6........	7608.82	13139.025	....	....
14........	....	....	01.240	52.128
17........	....	....	7599.550	13155.053

178

TABLE 3—*Continued*

1–0 BAND

λλ 6876.972–6920.149; Intensity −4

K''	λ_{air}	ν_{vac}	λ_{air}	ν_{vac}
	ᴾP Branch		ᴾQ Branch	
4........	6897.352	14494.319	....	....
5........	98.918	91.029	6897.946	.14493.071*
6........	6900.543	87.616	99.596	89.605
7........	02.230	84.075	6901.271	86.088*
8........	....	....	03.040	82.376*
9........	05.786	76.617	....	....
10.......	07.655	72.700*	06.728	74.643
11.......	....	....	....	....
12.......	....	....	10.648	66.432
13.......	13.615	60.224	6912.73	14462.075*
14.......	....	....	....	....
15.......	....	....	....	....
16.......	6920.149	14444.484*	....	....
	ᴿR Branch		ᴿQ Branch	
1........	....	....	6888.323	14513.317
2........	6888.000	14513.998*	87.154	15.781
3........	87.000	16.105*	86.048	18.112
4........	....	....	85.004	20.314*
5........	85.004	20.314*	84.041	22.345*
6........	84.041	22.345*	83.108	24.313*
7........	83.230	24.056	82.277	26.067
8........	82.447	25.708*	81.463	27.785*
9........	....	....	80.757	29.276
10.......	81.054	28.649*	80.08	30.705
11.......	80.446	29.933	79.481	31.971*
12.......	....	....	....	....
13.......	79.393	32.157*	78.436	34.179
14.......	....	....	77.991	35.119*
15.......	78.630	33.769	....	....
16.......	78.315	34.434	....	....
17.......	6877.991	14535.119*	6876.972	14537.273

* Either unresolved blend with another oxygen line, with a solar line, or with a telluric line (probably due to water vapor) or so close to such a line that the wave length is probably affected by it.

magnetic dipole or electric quadrupole radiation. The observed four branches of the red atmospheric oxygen bands can be accounted for only by the selection rules for magnetic dipole radiation,

$$\Delta J = 0, \pm 1 \qquad (J = 0 \longleftrightarrow J = 0) \quad + \longleftrightarrow +, \quad - \longleftrightarrow -, \quad - \longleftrightarrow + . \qquad (1)$$

The corresponding transitions are indicated in Figure 2 by full lines. There is an ^{R}R branch ($\Delta J = +1$, $\Delta K = +1$), a ^{P}P branch ($\Delta J = -1$, $\Delta K = -1$), an ^{R}Q branch ($\Delta J = 0$, $\Delta K = +1$), and a ^{P}Q branch ($\Delta J = 0$, $\Delta K = -1$). In the $O^{16}O^{18}$ and $O^{16}O^{17}$ molecules the alternate rotational levels, with even values of K'', are present on account of the unequal masses of the atomic nuclei, but these even levels are absent in the symmetrical O_2^{16} molecule.

The over-all intensity of the bands is even less than that expected for ordinary magnetic dipole radiation. As Van Vleck[12] pointed out, this is due to the fact that, in addition, they represent a singlet-triplet intercombination.
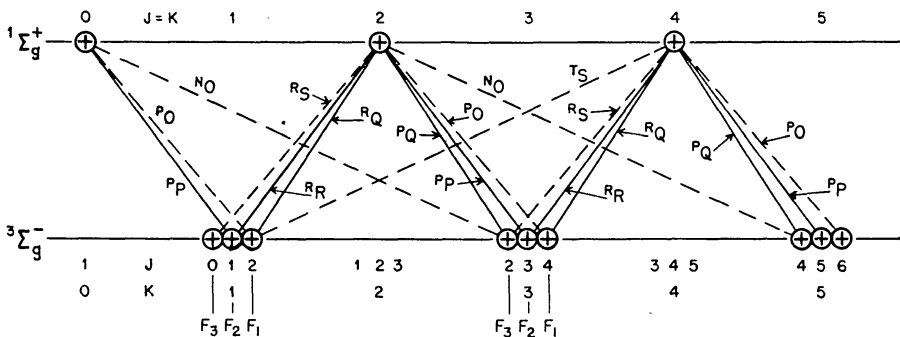
Fig. 2.—Combinations associated with branches of the red system of atmospheric oxygen bands of O_2^{16}. Branches corresponding to the dashed lines have not been observed. Spectra of $O^{16}O^{18}$ and $O^{16}O^{17}$ contain additional combinations, homologous to the full lines in the figure, among the alternate levels.

The selection rules for electric quadrupole radiation are:

$$\Delta J = 0, \pm 1, \pm 2 ; \qquad J = 0 \longleftrightarrow J = 0 , \qquad J = 1 \longleftrightarrow J = 0 ;$$

$$+ \longleftrightarrow +, \quad - \longleftrightarrow -, \quad + \longleftrightarrow - . \qquad (2)$$

Accordingly, all the branches which are observed as magnetic dipole transitions are also possible as quadrupole radiation. In addition, branches with $\Delta J = \pm 2$ should occur. The latter are indicated in Figure 2 by broken lines. Of these, the transitions with $\Delta J = \pm 2$, $\Delta K = \pm 1$, almost coincide with the magnetic dipole ^{R}Q and ^{P}Q lines, since the F_1 and F_3 levels of the $^{3}\Sigma_g^{-}$ state lie very close together (see sec. F). These lines could hardly be observed even under the most favorable circumstances, since the intensity of the electric quadrupole lines is only one-thousandth to one ten-thousandth[23] the intensity of the magnetic dipole lines. On the other hand, the electric quadrupole lines with $\Delta J = +2$, $\Delta K = \pm 3$, are about three times as widely spaced as are the magnetic dipole lines and are well separated from them. In fact, lines of the ^{T}S branch ($\Delta J = +2$, $\Delta K = +3$) should occur in the region beyond the band head, where no masking is possible by the much stronger magnetic dipole lines. However, they have not as yet been observed.

D. DETERMINATION OF THE ROTATIONAL AND VIBRATIONAL CONSTANTS OF O_2^{16}

As indicated in Figure 2, the three components of the $^{3}\Sigma_g^{-}$ ground state of oxygen are designated by F_1, F_2, and F_3, according as $J = K + 1$, $J = K$, and $J = K - 1$. The

^PP and ^RR branches of the red atmospheric bands correspond to transitions from the F_2 component, the ^RQ and ^PQ branches to transitions from the F_1 and F_3 components, respectively. According to the theory developed by Kramers[4] and by Schlapp[5] (see sec. F), the F_2 component follows the formula for the ordinary nonrigid rotator

$$F_2(K) = BK(K+1) - DK^2(K+1)^2 + \dots , \tag{3}$$

while F_1 and F_3 follow more complicated formulae containing F_2 and additional terms. The rotational constants B and D can therefore be determined by an analysis of the ^PP and ^RR branches only. The ^PQ and ^RQ branches have to be taken into consideration only for the discussion of the triplet-splitting in the ground state.

TABLE 4

SPACING OF ROTATIONAL LEVELS FOR O_2^{16}, $^3\Sigma_g^-$ STATE, $v''=0$

(Unit = 1 Cm^{-1})

K	$\Delta_2 F_2'$ (OBSERVED)*				$\Delta_2 F_2'$ (COMPUTED)	O−C
	0–0	1–0	2–0	Mean		
2.......	14.382	14.380	14.380	14.381	14.372	+0.009
4.......	25.875	25.878	25.875	25.876	25.876	0
6.......	37.371	37.374	37.372	37.372	37.371	+ .001
8.......	48.862	48.853	48.861	48.859	48.860	− .001
10.......	60.335	60.333	60.340	60.336	60.340	− .004
12.......	71.810	71.805	71.812	71.809	71.811	− .002
14.......	83.269	83.286†	83.270	83.270	83.270	0
16.......	94.707	94.710	94.717	94.711	94.716	− .005
18.......	106.146	106.186†	106.146	106.146	106.146	0
20.......	117.591†	117.557†	117.573	117.565	117.558	+ .007
22.......	128.944	128.958	128.957	128.953	128.951	+ .002
24.......	140.313	140.321	140.332	140.322	140.323	− .001
26.......	151.713†	151.603†	....	....	151.671	....
28.......	163.022†	....	163.025	163.025	·162.995	+ .030
30.......	174.256†	174.284	174.381†	174.284	174.292	− .008
32.......	....	185.542	....	185.542	185.560	− .018
34.......	....	196.760	....	196.760	196.797	−0.037

* $\Delta_2 F_2''(K) = {}^RR(K - 1) - {}^PP(K + 1)$.

† Omitted from the means or given low weight because one or both lines involved are blends.

For the determination of the rotational constants of O_2^{16}, only the most accurately measured bands, namely, 0–0, 1–0, 2–0, 3–0, and 1–1 were used. Of these, the rather weak 3–0 band was disregarded in the determination of the constants of the lower state, since these could be determined more accurately from the 0–0, 1–0, and 2–0 bands alone.

As is well known, the combination differences,

$$\Delta_2 F_2''(K) = {}^RR(K - 1) - {}^PP(K + 1) , \tag{4}$$

should agree for bands with the same lower state. Table 4, which contains these differences formed from the observed wave numbers of the 0–0, 1–0, and 2–0 bands, shows that this condition is very accurately fulfilled. With very few exceptions, the agreement is within 0.005 cm^{-1}, an accuracy only rarely obtained in measurements of band spectra.

From equation (3) it follows that

$$\Delta_2 F_2''(K) = F_2''(K + 1) - F_2''(K - 1)$$

$$= (4B'' - 6D'')(K + \tfrac{1}{2}) - 8D''(K + \tfrac{1}{2})^3 \tag{5}$$

and

$$\frac{\Delta_2 F_2''(K)}{K + \frac{1}{2}} = (4B'' - 6D'') - 8D''(K + \tfrac{1}{2})^2. \tag{5a}$$

By plotting $\Delta_2 F_2''(K)/(K + \frac{1}{2})$ against $(K + \frac{1}{2})^2$, using the mean values of $\Delta_2 F_2''(K)$ obtained from the 0–0, 1–0, and 2–0 bands, the rotational constants,

$$B_0'' = 1.437\,7\,7_0 \pm 0.000\,01\,5 \text{ cm}^{-1}$$

and

$$D_0'' = (4.91_3 \pm 0.0\,20) \times 10^{-6} \text{ cm}^{-1},$$

were obtained.[24]

In the two last columns of Table 4 the $\Delta_2 F_2''(K)$ values, computed with these constants according to equation (5), and their deviations from the mean observed values are given. For all K values up to $K = 24$ these deviations are well below 0.01 cm^{-1}.

The same method was less satisfactory when applied to the determination of the rotational constants B and D of the vibrational level $v'' = 1$ of the lower electronic state and of the levels $v' = 0, 1, 2,$ and 3 of the upper electronic state, because many fewer accurately measured lines were available to form the combination differences.

On the other hand, the *differences* between the rotational constants of the upper and lower states of a band, that is $B' - B''$ and $D' - D''$, can be determined from the sums of the lines of the R and P branches according to the equation

$$\tfrac{1}{2}[{}^R R(K) + {}^P P(K)] = (\nu_0 + B' - 2D') + (B' - B'' - 6D')K(K + 1)$$
$$- (D' - D'')K^2(K + 1)^2. \tag{6}$$

By plotting the observed values of the left-hand side of this equation against $K(K + 1)$, we obtain a curve whose intercept with the ordinate axis gives $(\nu_0 + B' - 2D')$, whose initial slope gives $(B' - B'' - 6D')$ and whose curvature gives $(D' - D'')$.

The values obtained in this way are only approximate. If, with their aid, again using the observed values $[{}^R R(K) + {}^P P(K)]$, the quantities

$$\frac{\tfrac{1}{2}[{}^R R(K) + {}^P P(K)] - (\nu_0 + B' - 2D')}{K(K + 1)}$$

are calculated and plotted against $K(K + 1)$, it is readily seen from equation (6) that a straight line is obtained whose slope is $(D' - D'')$ and whose intercept with the ordinate axis is $(B' - B'' - 6D')$.

If the improved values for B' and D' thus derived are substituted in the right-hand side of equation (6) and the differences between these calculated and the observed values of $\tfrac{1}{2}[{}^R R(K) + {}^P P(K)]$ are plotted against $K(K + 1)$, final corrections to the values $(\nu_0 + B' - 2D')$, $(B' - B'' - 6D')$, and $(D' - D'')$ are obtained.

The accuracy of the $(B' - B'')$ and $(D' - D'')$ values determined in this way is greater than the accuracy of the individual rotational constants obtained from the combination differences. It is therefore best to determine only one pair of rotational constants, B and D, from combination differences and all the others from the $(B' - B'')$ and $(D' - D'')$ values, especially if there is one state, as in the present case the one with $v'' = 0$, for which the combination differences are known with particular accuracy.

The final values of B', B'', D', and D'' obtained by this method are given in Table 5, those of ν_0 in Table 6. The band origins of Table 6 refer to the nonexisting rotational F_2

---

[24] For a more detailed discussion of the method see G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. I (New York: Prentice-Hall Inc., 1939).

level, $K = 0$, $J = 0$. As indicated by the number of significant figures given, the accuracy of the values of B_3', D_3', $\nu_0(2, 1)$, and $\nu_0(3, 1)$ is appreciably smaller than that of the other constants.[25]

In order to check the accuracy of the calculations, the ^PP and ^RR branches of all the bands measured were computed with the constants given in Tables 5 and 6. The deviations from the observed values of well-measured lines (that is, all lines except blends and a few lines with high J values) are well within 0.01 cm⁻¹ for the 0–0 band and within 0.02 cm⁻¹ for the 1–0, 2–0, and 1–1 bands. For the weak 3–0, 2–1, and 3–1 bands

TABLE 5

INDIVIDUAL ROTATIONAL CONSTANTS OF THE
$^3\Sigma_g^-$ AND $^1\Sigma_g^+$ STATES OF O_2^{16}
(Unit = 1 Cm⁻¹)

	$^3\Sigma_g^-$ State	$^1\Sigma_g^+$ State
B_0	1.43777_0	1.39132_8
B_1	1.42197_9	1.37305_4
B_2	....	1.35473_1
B_3	....	1.33620
D_0	$4.91_3 \times 10^{-6}$	$5.40_9 \times 10^{-6}$
D_1	$4.82_5 \times 10^{-6}$	$5.45_8 \times 10^{-6}$
D_2	....	$5.56_7 \times 10^{-6}$
D_3	....	$5.6_1 \times 10^{-6}$

TABLE 6

ZERO LINES ν_0 OF THE $^1\Sigma_g^+$–$^3\Sigma_g^-$ BAND SYSTEM OF O_2^{16}
(Unit = 1 Cm⁻¹)

v'	v''	
	0	1
0	13120.9080	....
1	14525.6602	12969.274_4
2	15902.4156	14346.030
3	17251.109_6	15694.7_6

the agreement is not so good but is still satisfactory. No systematic trend is noticeable in the deviations. It is therefore unnecessary to introduce a term $HK^3(K + 1)^3$ in formula (3).

If, in the usual way, the values B_v and D_v of Table 5 are represented by the formulae,

$$B_v = B_e - a_e\left(v + \tfrac{1}{2}\right) + \gamma_e\left(v + \tfrac{1}{2}\right)^2 + \dots , \tag{7}$$

$$D_v = D_e + \beta\left(v + \tfrac{1}{2}\right) + \dots , \tag{8}$$

the rotational constants given in Table 7 are obtained.

The constants B_0, B_1, and B_2 of the $^1\Sigma_g^+$ state are represented by formula (7) with the values for B_e, a_e, and γ_e as given in Table 7 within an accuracy of 0.00001 cm⁻¹, the less accurately determined constant B_3 within 0.0001 cm⁻¹.

---

[25] The last decimal is printed in full size when the accuracy is well within one unit of the next to the last decimal. If the accuracy is less, the last decimal is a subscript.

The vibrational constants given in Table 7 correspond to the usual representation of the zero lines by a formula,

$$\nu_0(v'v'') = \nu_e + \omega_e'(v'+\tfrac{1}{2}) - \omega_e'x_e'(v'+\tfrac{1}{2})^2 + \omega_e'y_e'(v'+\tfrac{1}{2})^3 \ldots$$
$$- \omega_e''(v''+\tfrac{1}{2}) + \omega_e''x_e''(v''+\tfrac{1}{2})^2 - \omega_e''y_e''(v''+\tfrac{1}{2})^3 \ldots . \tag{9}$$

Since in the red atmospheric band system no bands occur with $v'' > 1$, ω_e'' was determined from $\Delta G_{1/2}''$ with the aid of the constants $\omega_e''x_e''$, $\omega_e''y_e''$, and $\omega_e''z_e''$, derived by Curry and Herzberg from an analysis of the Schumann-Runge bands.[26] The value $\Delta G_{1/2}''$ itself

TABLE 7
CONSTANTS OF THE O_2^{16} MOLECULE*†

	$^3\Sigma_g^-$ State	$^1\Sigma_g^+$ State
$A_0 = \nu_{00}$		13120.9080 cm^{-1}
ν_e		13195.2221 cm^{-1}
$\Delta G_{\frac{1}{2}}$	1556.3856 cm^{-1}	1404.7521 cm^{-1}
ω_e	1580.3613 cm^{-1}	1432.6874 cm^{-1}
$\omega_e x_e$	12.0730 cm^{-1}‡	13.95008 cm^{-1}
$\omega_e y_e$	0.0546 cm^{-1}‡	−0.01075 cm^{-1}
$\omega_e z_e$	−0.00143 cm^{-1}‡	
k_e	11.7664$_1 \times 10^5$ dynes/cm	9.6701$_7 \times 10^5$ dynes/cm
D_0 (diss. energy)	5.081 e.v.§	3.455 e.v.
B_0	1.43777$_0$ cm^{-1}	1.39132$_0$ cm^{-1}
B_e	1.44566$_6$ cm^{-1}	1.40041$_6$ cm^{-1}
a_e	0.01579$_1$ cm^{-1}	0.01817$_0$ cm^{-1}
γ_e		−0.00004$_3$ cm^{-1}
D_0 (rot. const.)	4.91$_3 \times 10^{-6}$ cm^{-1}	5.39$_5 \times 10^{-6}$ cm^{-1}
D_e (rot. const.)	4.95$_7 \times 10^{-6}$ cm^{-1}	5.35$_6 \times 10^{-6}$ cm^{-1}
β	0.08$_8 \times 10^{-6}$ cm^{-1}	0.07$_7 \times 10^{-6}$ cm^{-1}
I_0	19.4652$_1 \times 10^{-40}$ gm cm^2	20.1136$_3 \times 10^{-40}$ gm cm^2
I_e	19.3589$_0 \times 10^{-40}$ gm cm^2	19.9844$_2 \times 10^{-40}$ gm cm^2
r_0	1.21071$_5 \times 10^{-8}$ cm	1.23075$_9 \times 10^{-8}$ cm
r_e	1.20740$_4 \times 10^{-8}$ cm	1.22675$_6 \times 10^{-8}$ cm

* The last decimal is printed in full size when the accuracy is well within one unit of the next to the last decimal. If the accuracy is less, the last decimal is a subscript.

† R. T. Birge, *Phys. Soc. London, Reports on Progress in Physics*, **8**, 90, 1941.

‡ Curry and Herzberg, *Ann. d. Phys.*, **19**, 800, 1934.

§ G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. I.

could be obtained from the zero lines with considerable accuracy. The value obtained as difference between $\nu_0(1, 1)$ and $\nu_0(1, 0)$ and the value obtained as difference between $\nu_0(2, 1)$ and $\nu_0(2, 0)$ agree within 0.0002 cm^{-1}. Even though this perfect agreement may be accidental, it is believed that the $\Delta G_{1/2}''$ value is accurate within 0.001 cm^{-1}. Similar remarks hold for the vibrational quanta of the upper state.

The definition of the quantities given in Table 7 and the notation used are in agreement with general usage (see, e.g., G. Herzberg[24]). For example, quantities with subscript 0 refer to the lowest vibrational level; quantities with subscript e to the nonexisting vibrationless level. The first two entries in Table 7 refer to the energy of electronic excitation; the next six concern the vibrational energy. The dissociation energy, D_0'', for the $^3\Sigma_g^-$ state is the value given by G. Herzberg,[24] recalculated with the more recent values for the basic physical constants (see below). The dissociation energy, D_0', for the $^1\Sigma_g^+$ state was obtained by subtracting the electronic excitation energy ν_{00} from the dissociation energy of the $^3\Sigma_g^-$ state.

[26] *Ann. d. Phys.*, **19**, 800, 1934.

B, a, γ, D (rotational constant), and β concern the energy of rotation, including the effect of centrifugal stretching of the molecule with increase of angular momentum. The moments of inertia, I, and the internuclear distances, r, were determined from the rotational constants in the usual way. (Attention is called to the use of D in two different senses, a peculiarity of the notation which has become fixed in the literature.)

Values of the basic physical constants used in deriving Table 7 are those adopted by R. T. Birge,[27] such as wave length associated with one absolute volt $= 12395.4 \times 10^{-8}$ cm; and $h/8\pi^2 c = 27.9865 \times 10^{-40}$ gm. cm.

TABLE 8

CONSTANTS OF THE $^3\Sigma_g^-$ AND THE $^1\Sigma_g^+$ STATES OF $O^{16}O^{18}$

(Unit = 1 Cm^{-1})

	$^3\Sigma_g^-$ STATE		$^1\Sigma_g^+$ STATE	
	Observed	Computed	Observed	Computed
$A_0 = \nu_0(0, 0)$	....	....	13122.98$_6$	13123.0194
$\nu_0(1, 0)$	....	....	14488.8$_4$	14488.8741
$\Delta G_{\frac{1}{2}}$	....	....	1365.8$_5$	1365.8547
B_0	1.3579$_3$	1.357932	1.3141$_2$	1.314100
B_1	....	....	1.2974$_0$	1.297350
D_0	4.4$_2 \times 10^{-6}$	4.381$\times 10^{-6}$	5.0$_5 \times 10^{-6}$	4.811$\times 10^{-6}$

TABLE 9

CONSTANTS OF THE $^3\Sigma_g^-$ AND THE $^1\Sigma_g^+$ STATES OF $O^{16}O^{17}$

(Unit = 1 Cm^{-1})

	$^3\Sigma_g^-$ STATE		$^1\Sigma_g^+$ STATE	
	Observed	Computed	Observed	Computed
$A_0 = \nu_0(0, 0)$	....	....	13121.97$_8$	13122.0207
$\nu_0(1, 0)$	....	....	14506.2$_6$	14506.2820
$\Delta G_{\frac{1}{2}}$	....	....	1384.2$_8$	1384.2613
B_0	1.395$_8$	1.395417	1.352$_0$	1.350357
B_1	....	....	1.333$_1$	1.332906

E. DETERMINATION OF THE ROTATIONAL AND VIBRATIONAL CONSTANTS OF THE ISOTOPIC MOLECULES $O^{16}O^{18}$ AND $O^{16}O^{17}$

In the spectra of the isotopic molecules $O^{16}O^{18}$ and $O^{16}O^{17}$, only the 0–0 and 1–0 bands were measured (Tables 2 and 3). The rotational constants and zero lines given in Tables 8 and 9 were determined by the methods used in the analysis of the O_2^{16} bands. Because of the low intensity of the isotopic bands and the very frequent occurrence of blends, the accuracy as a whole is much lower than that of the constants of O_2^{16}.

In addition to the observed values of the molecular constants of $O^{16}O^{18}$ and $O^{16}O^{17}$,

---

[27] *Phys. Soc. London, Reports on Progress in Physics*, 8, 90, 1941.

Tables 8 and 9 contain the values computed from the theoretical formulae for the isotope effect by means of the constants of O_2^{16}. The following relations were used:

$$B_e^i = \rho^2 B_e ; \qquad a_e^i = \rho^3 a_e ; \qquad D^i = \rho^4 D ; \qquad \gamma_e^i = \rho^4 \gamma_e \qquad (10)$$

$$^i = \nu_e + \rho\omega_e' (v'+\tfrac{1}{2}) - \rho^2\omega_e'x_e' (v'+\tfrac{1}{2})^2 + \dots$$
$$- \rho\omega_e'' (v''+\tfrac{1}{2}) + \rho^2\omega_e''x_e'' (v''+\tfrac{1}{2})^2 - \dots , \qquad (11)$$

where the superscript i refers to the heavier isotopic molecule and where

$$\rho = \sqrt{\frac{\mu}{\mu^i}} \qquad (\mu = \text{reduced mass}) .$$

Using the mass values $O^{16} = 16.00000$, $O^{18} = 18.00485$,[28] and $O^{17} = 17.00450$,[28] we obtained and used the following values for ρ:

$$\rho (O^{16}O^{18}) = 0.9717637 ; \qquad \rho (O^{16}O^{17}) = 0.9851212 .$$

The agreement between the observed and the computed values of the molecular constants of the isotopic molecules (Tables 8 and 9) is very satisfactory. The very slight systematic deviations from the calculated values in the case of $\nu_0(0, 0)$ and $\nu_0(1, 0)$ are probably due to the fact that the value of $\omega_e''x_e''$ (Table 7), which had to be used in the determination of ν_e, is not exact. A more accurate value for $\omega_e''x_e''$ is not available, since no bands with v'' between 2 and 12 have yet been measured.

It should perhaps be emphasized that, with the exception of the values for $\nu_0(0, 0)$ and $\nu_0(1, 0)$, the computed values of the molecular constants of the isotopic molecules are of higher accuracy than are the observed ones.

If the values of the constants in Table 8 are recomputed, using $O^{18} = 18.00369$,[29] the agreement with observation is not quite so close as that shown in the table.

F. TRIPLET-SPLITTING OF THE $^3\Sigma_g^-$ GROUND STATE OF THE O_2 MOLECULE

Schlapp[5] has given theoretical expressions for the energy of the three component levels of a $^3\Sigma$ state:[30]

$$F_3 = W_0 - (2K-1)B - \lambda + [(2K-1)^2B^2 + \lambda^2 - 2\lambda B]^{1/2} - \gamma K$$
$$(J = K-1) ,$$

$$F_2 = W_0 , \qquad (J = K) , \qquad (12)$$

$$F_1 = W_0 + (2K+3)B - \lambda - [(2K+3)^2B^2 + \lambda^2 - 2\lambda B]^{1/2} + \gamma(K+1)$$
$$(J = K+1) .$$

Here $W_0 = F_2$ is given by formula (3); λ and γ are two numerical parameters: λ, in a first approximation, is a measure of the spin-spin interaction of the uncompensated electrons and γ of the interaction of the uncompensated electron spin with the magnetic field due to the rotation of the molecule. The symbol γ here is to be distinguished from γ as used in Table 7.

According to H. A. Kramers,[31] the spin-spin interaction of the uncompensated elec-

[28] Flügge and Mattauch, *Phys. Zs.*, **43**, 1, 1942.

[29] Livingston and Bethe, *Rev. Mod. Phys.*, **9**, 245, 1937.

[30] In Schlapp's paper the energy levels F_1, F_2, and F_3 are called "W_{K+1}," "W_K," and "W_{K-1}," respectively.

[31] *Zs. f. Phys.*, **53**, 422, 1929.

trons is mathematically equivalent to an interaction of the total spin with the axis of figure of the molecule. The presence of the parameter λ is therefore an indication of the fact that the molecule does not belong completely to Hund's case b.

In the case of the ground state of the O_2 molecule, Schlapp obtained the values

$$\lambda = 1.985 \text{ cm}^{-1} \quad \text{and} \quad \gamma = -0.008 \text{ cm}^{-1}$$

from Dieke and Babcock's[1] measurements of the red atmospheric band system. The new measurements presented here (Tables 1–3) make it possible to redetermine these constants with higher accuracy. This was done for the vibrational levels with $v'' = 0$

TABLE 10*
TRIPLET-SPLITTING OF THE $^3\Sigma_g^-$ GROUND STATE OF O_2^{16}: $v'' = 0$

K''	$F_2-F_3 = {}^PP(K) - {}^PQ(K)$			$F_2-F_1 = {}^RR(K) - {}^RQ(K)$		
	Observed Mean	Computed $\gamma = -0.008$ $\lambda = 1.985$	Computed $\gamma = -0.00837$ $\lambda = 1.984$	Observed Mean	Computed $\gamma = -0.008$ $\lambda = 1.985$	Computed $\gamma = -0.00837$ $\lambda = 1.984$
1...........	....	3.9620	3.9596	1.873$_2$	1.8770	1.8766
3...........	2.084$_8$	2.0850	2.0830	1.952$_0$	1.9485	1.9490
5...........	2.012$_3$	2.0135	2.0107	1.987$_2$	1.9856	1.9868
7...........	1.976$_4$	1.9764	1.9728	2.014$_8$	2.0128	2.0148
9...........	1.947$_8$	1.9492	1.9449	2.041$_9$	2.0357	2.0384
11...........	1.921$_0$	1.9263	1.9212	2.064$_5$	2.0564	2.0598
13...........	1.901$_3$	1.9056	1.8998	2.081$_8$	2.0758	2.0799
15...........	1.880$_7$	1.8862	1.8797	2.104$_2$	2.0944	2.0993
17...........	1.859$_5$	1.8676	1.8604	2.124$_4$	2.1124	2.1180
19...........	1.844$_2$	1.8496	1.8416	2.128$_0$	2.1300	2.1364
21...........	1.823$_0$	1.8320	1.8232	2.165$_6$	2.1473	2.1545
23...........	1.816$_5$	1.8147	1.8052	2.180$_3$	2.1645	2.1723
25...........	1.784$_7$	1.7975	1.7873	....	2.1814	2.1900
27...........	1.770$_4$	1.7806	1.7696	2.205$_5$	2.1982	2.2076
29...........	1.760$_3$	1.7638	1.7521	2.228$_2$	2.2149	2.2250
31...........	1.740$_0$	1.7471	1.7346	....	....	....
33...........	1.720$_5$	1.7305	1.7173	....	....	....
35...........	1.686$_5$	1.7140	1.7000	....	....	....
37...........	1.688$_4$	1.6974	1.6827	....	....	....
39...........	1.645$_0$	1.6810	1.6656	....	....	....

* Unit = 1 cm^{-1}.

and 1 of the electronic ground state of O_2^{16}, as well as for the levels with $v'' = 0$ of the ground states of $O^{16}O^{18}$ and $O^{16}O^{17}$.

The separations of the triplet components are given by the term differences,

$$ {}^PP(K) - {}^PQ(K) = F_2 - F_3 , $$
$$ {}^RR(K) - {}^RQ(K) = F_2 - F_1 . \tag{13}$$

These term differences are given for the $v'' = 0$ and $v'' = 1$ levels of O_2^{16} in Tables 10 and 11. The values given for $v'' = 0$ are mean values obtained from the 0–0, 1–0, and 2–0 bands; the values given for $v'' = 1$ are those obtained from the 1–1 band. Only unblended lines were used to form the term differences.

The third and sixth columns of Table 10 contain the triplet-splittings computed with the aid of equation (12) with the values of the parameters λ and γ given by Schlapp and the new B_0'' value from Table 7. It can be seen that there is a slight, but systematic,

difference between observed and computed values. This systematic difference can be made to disappear by choosing for the parameters the values

$$\lambda = 1.984 \text{ cm}^{-1}, \qquad \gamma = -0.00837 \text{ cm}^{-1}.$$

The splittings calculated according to equation (12) with these parameters are given in the fourth and seventh columns of Table 10.

The agreement between the observed and the computed values is very satisfactory indeed and gives confidence that the extrapolation of Schlapp's formula (12) to the F_3 state with $K = 1$, $J = 0$, is reliable. The position of this state cannot be obtained from the atmospheric oxygen bands but could be found from the ultraviolet bands, if lines with $K = 1$ were completely resolved.

TABLE 11*

TRIPLET-SPLITTING OF THE $^3\Sigma_g^-$ GROUND STATE OF O_2^{16}: $v'' = 1$

K''	$F_2-F_3 = {}^PP(K) - {}^PQ(K)$		$F_2-F_1 = {}^RR(K) - {}^RQ(K)$	
	Observed	Computed $\gamma = -0.00837$ $\lambda = 1.993$	Observed	Computed $\gamma = -0.00837$ $\lambda = 1.993$
1	....	3.9776	1.904_7	1.8895
3	....	2.1882	1.958_4	1.9601
5	2.012_8	2.0176	1.997_1	1.9973
7	1.975_5	1.9803	....	2.0249
9	1.943_2	1.9528	2.057_0	2.0483
11	1.929_3	1.9293	....	2.0696
13	1.906_5	1.9075	2.089_3	2.0897
15	1.886_0	1.8880	....	2.1089
17	1.870_1	1.8687	....	2.1276
19	1.857_5	1.8500	2.149_2	2.1459
21	1.833_0	1.8317	....	2.1639
23	1.828_6	1.8137	2.196_9	2.1818
25	1.74_8	1.7959	....	....

* Unit = 1 cm^{-1}.

The separations of the F_1 and F_3 levels from the F_2 levels have recently taken on new interest, since they give directly the wave lengths of the magnetic dipole spectrum of oxygen in the micro-wave region. This spectrum has been investigated experimentally by R. Beringer[32] and theoretically by J. H. Van Vleck.[33] Beringer found an absorption maximum of O_2 in the region $\lambda = 0.5$ cm ($\nu = 2$ cm^{-1}), and Van Vleck, using the data of Table 10, interpreted this absorption as an unresolved band consisting of the transitions $F_2(K) - F_1(K)$ for $K = 1, 3, 5, \ldots$, and $F_2(K) - F_3(K)$ for $K = 3, 5, 7, \ldots$. A secondary maximum, so far not investigated experimentally, ought to occur in the region $\lambda = 0.25$ cm ($\nu = 3.960$ cm^{-1}), corresponding to the transition $F_2(K) - F_3(K)$ for $K = 1$.

If the triplet-splittings in the $v'' = 1$ level are calculated with the same parameters λ and γ as for $v'' = 0$, but, of course, with B_1'' instead of B_0'', a slight systematic difference from the observed values of Table 11 is found. This can be corrected by changing the parameter λ to

$$\lambda = 1.993 \text{ cm}^{-1}.$$

[32] Phys. Rev., 70, 53, 1946.   [33] Phys. Rev., 71, 413, 1947.

The splittings computed with this changed value of λ and the same value of γ as before are given in the third and fifth columns of Table 11. The slight increase of λ in going from $v'' = 0$ to $v'' = 1$ corresponds to a strengthening of the coupling of the spin to the internuclear axis, that is, a greater deviation from Hund's case b.

In Table 12 the observed and computed triplet-splittings in the $v'' = 0$ level of the isotopic molecule $O^{16}O^{18}$ are given. The computed values were obtained by substituting $\lambda = 1.984$ cm^{-1}, $\gamma = -0.00740$ cm^{-1}, and $B = B_0'' = 1.35793$ cm^{-1} in equation (12).

TABLE 12*

TRIPLET-SPLITTING OF THE $^3\Sigma_g^-$ GROUND STATE OF $O^{16}O^{18}$: $v'' = 0$

| K | $F_2-F_3={}^PP(K)-{}^PQ(K)$ | | $F_2-F_1={}^RR(K)-{}^RQ(K)$ | |
	Observed	Computed $\gamma=-0.00740$ $\lambda=1.984$	Observed	Computed $\gamma=-0.00740$ $\lambda=1.984$
1	....	3.9606	1.886_3	1.8910
2	2.135_3	2.1515	1.943_3	1.9295
3	2.083_7	2.0696	1.945_2	1.9541
4	2.017_0	2.0311	1.966_0	1.9723
5	2.013_0	2.0066	2.002_9	1.9872
6	....	1.9883	....	2.0001
7	1.980_1	1.9734	2.018_9	2.0117
8	1.961_1	1.9605	2.008_2	2.0225
9	1.942_2	1.9489	2.034_3	2.0325
10	....	1.9382	2.049_5	2.0422
11	1.928_0	1.9281	2.040_9	2.0514
12	1.915_9	1.9185	2.067_0	2.0604
13	1.907_0	1.9092	....	....
14	1.893_9	1.9002	....	....
15	1.891_0	1.8914	....	....
16	1.876_2	1.8829	....	....
17	1.825_5	1.8744	....	....
18	1.851_6	1.8661	....	....
19	1.864_4	1.8579	....	....
20	1.861_1	1.8497	....	....
21	....	1.8416	....	....
22	....	1.8336	....	....
23	1.821_4	1.8257	....	....
24	1.830_0	1.8178	....	....
25	1.761_0	1.8099	....	....
26	1.805_2	1.8021	....	....
27	....	1.7943	....	....
28	1.763_9	1.7865	....	....

* Unit = 1 cm^{-1}.

The agreement between the observed and the computed values is within the accuracy of the measurements (which is lower than for O_2^{16}). If, instead of the above value for γ, the one used for O_2^{16} ($\gamma = -0.00837$ cm^{-1}) is substituted, a systematic deviation is found.

It is significant that the value of λ is unchanged, while γ changes in going from O_2^{16} to $O^{16}O^{18}$. This is in agreement with theoretical expectation. Since, in a first approximation, the electronic structure of a molecule and the nuclear separation are not affected by a small change in the masses of the nuclei, the interaction of the electron spin with the internuclear axis in the nonrotating and nonvibrating molecule and, consequently, the parameter λ should be the same for different isotopic molecules.[34] The influence of the

[34] The effect expected because of the change in the zero-point vibration is too small to be detected with the present accuracy.

nuclear masses on the rotational decoupling of the spin from the axis is accounted for by the changed value of B, substituted in formula (12).

On the other hand, the constant γ, representing the magnetic coupling between the electron spin and the axis of rotation, will be different for different isotopic molecules, since the magnetic moment produced by the rotation varies with the nuclear masses because of the change in angular velocity. N. F. Ramsey[35] found experimentally that the magnetic moments of the hydrogen isotopes, H_2, HD, and D_2, vary in proportion to the inverse reduced mass, that is, simply in proportion to the angular velocity of the molecule as a whole.

In the case of a molecule like O_2 with more than two electrons, one cannot expect such a simple relation to hold. As G. C. Wick[36] has shown, the electrons do not rotate rigidly with the molecule but "slip back." Therefore, the influence of the inner shells on the magnetic moments of isotopic molecules may be rather complicated.

TABLE 13*

TRIPLET-SPLITTING OF THE $^3\Sigma_g^-$ GROUND STATE OF $O^{16}O^{17}$

K	$F_2 - F_3 = {}^PP(K) - {}^PQ(K)$ Observed	$F_2 - F_1 = {}^RR(K) - {}^RQ(K)$ Observed
3	2.085_2	2.003_0
5	. . . .	1.985_7
6	1.988_6	. . . .
7	. . . .	2.011_0
15	1.897_1	. . . .
17	1.855_4	. . . .
21	1.770_4	. . . .
23	1.820_4	. . . .

*$v'' = 0$; unit = 1 cm^{-1}.

If one assumes that γ depends solely on the inverse reduced mass of the molecule, the constant γ for $O^{16}O^{18}$, calculated from the above value of γ for O_2^{16}, would be

$$\gamma_{\text{comp.}}(O^{16}O^{18}) = 0.00790 \, ,$$

while the observed value is

$$\gamma_{\text{obs.}}(O^{16}O^{18}) = 0.0074 \, .$$

The accuracy of the determination of the observed value for $O^{16}O^{18}$ is insufficient to decide whether the deviation from the computed value is significant.

In Table 13 the observed triplet-splitting of $O^{16}O^{17}$ is given. These data are not sufficiently accurate to warrant a separate determination of γ and λ.

We wish to thank Mr. G. Herzberg for his many helpful suggestions as to the methods of evaluation of the measurements and the interpretation of the results.

NOTE ADDED IN PROOF.—The measurements in this paper strongly support the conclusion of St. John and Babcock (*Mt. W. Contr.*, No. 223; *Ap. J.*, **55**, 36, 1922) that the measured wave lengths of atmospheric oxygen lines are remarkably constant.

[35] *Phys. Rev.*, **58**, 226, 1940.

[36] *Zs. f. Phys.*, **85**, 25, 1933.