

quantum must be closer to the kinetic energy of the electron *at the time of impact* than to Ve . In other words, in a large number of impacts, at least, the electron transfers almost if not all of its kinetic energy to the quantum of radiation when it produces that quantum, and the radiation thus produced is nearly if not exactly monochromatic.

THE STRUCTURE OF THE ATMOSPHERIC ABSORPTION
BANDS OF OXYGEN

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Although the atmospheric oxygen bands have been the subject of many investigations, the details of their structure have remained only partially explained. The earlier investigators² did not have any theory to guide them and it can readily be understood that they often came to contradictory results. In the present paper we have tried to account for the structure of the bands as completely as possible. Our progress has been based on new wave-length measurements which we believe to be more accurate than the previous ones.

1. A recent paper by one of us,³ gives details of the derivation with the interferometer of the wave-lengths of the lines in the α , B and A bands best suited to that method. With these lines as standards, the other lines in these bands have been measured on spectrograms obtained with a large Michelson plane grating used in the third and fourth orders at 30-foot focus. Such photographs were made at both high and low altitudes of the sun, since the faintest atmospheric lines are best observed with maximum air-path and the strongest ones with minimum air-path. At best the measurement of the widest lines is difficult and of relatively low accuracy. For example, some lines in the A band have a total width of about $1A$, even when observed on Mount Wilson with solar altitude exceeding 45° . The finer lines, on the other hand, can be seen only with high resolving power, and even with the sun close to the horizon they are faint and hard to measure. For the widest lines in the A band the usual micrometer measurements were supplemented by the use of a registering, thermoelectric microphotometer, giving a definite increase of accuracy. Some of these lines give evidence that under more favorable conditions of observation they might be resolved into close pairs.

For the α' band, $\lambda 5788 - \lambda 5834$, we have made no measurements, but have derived the wave-lengths on the International system by

subtracting 0.216A from the values given in Rowland's Table of Solar Wave-Lengths. The main part of this correction was obtained from the revision of the Rowland Table now in progress, with a slight alteration to allow for the difference between the standards of iron and those of neon. Throughout this paper all wave-lengths are expressed on the neon scale. Some small differences between wave-lengths stated here and those given in the work of Babcock to which reference has been made are accounted for by additional observations made specially for our purpose. The discordance between the values of Meggers⁴ and those given below is a natural result of the methods and approximations which he employed. The numerical data relating to the bands appear in table 1. The band designated A' is described later.

TABLE 1
A BAND

	λ	I	$\nu_{vac.}$	λ	I	$\nu_{vac.}$
	$P_1(\text{Å})$				$P_2(\text{Å})$	
0				7620.996	15	13,118.04
2	7624.493	23	13,112.02	23.289	22	14.11
4	28.203	25	05.64	27.050	24	07.63
6	32.150	25	13,098.87	31.021	24	00.81
8	36.317	25	91.72	35.196	24	13,093.64
10	40.694	23	84.22	39.583	22	86.12
12	45.297	19	76.34	44.197	18	78.22
14	50.120	16	68.10	49.032	15	69.96
16	55.172	13	59.47	54.078	12	61.34
18	60.447	10	50.48	59.359	9	52.34
20	65.938	6	41.13 _a	64.873	6	42.95 _S
22	71.664	5	31.40 _a	70.598	5	33.21 _a
24	77.617	4	21.29 _a	76.561	4	23.09 _a
26	83.798	3	10.82 _a	82.756	3	12.59 _a
28	90.215	2	12,999.37	89.175	2	01.72 _a
30	96.866	0	88.73 _a	95.836	0	12,990.47 _a
32	7703.756	0	77.11 _a	7702.733	0	78.83 _a
		$R_1(\text{Å})$			$R_2(\text{Å})$	
2	7616.143	10	13,126.40	7615.048	17	13,128.28
4	13.180	19	31.51	12.054	23	33.45
6	10.450	23	36.21	09.290	27	38.22
8	07.911	24	40.60	06.748	27	42.61
10	05.628	24	44.54	04.431	24	46.61
12	03.553	17	48.13	02.346	18	50.22
14	01.695	17	51.35	00.45	15	53.50
16	00.09	15	54.12	7598.760	24	56.43 _b
18	7598.760	24	56.43 _b	97.435	16	58.72 _b
20	97.435	16	58.72 _b	86.208	10	60.85
22	96.479	8	60.38	95.245	10 _d	62.51 _b
24	95.759	5	61.62	94.500	6	63.81 _a
26	95.245	10 _d	62.51 _b	93.988	3	64.70 _a
28	94.970	4	62.99 _b	93.695	3	65.20 _{b,a}
30	94.970	4	62.99 _b	93.695	3	65.20 _{b, a}

TABLE 1—Continued

A' BAND						
j	λ	I $P_1'(j)$	$\nu_{\text{VAC.}}$	λ	I $P_2'(j)$	$\nu_{\text{VAC.}}$
0	7619.691	00	13,120.29
2	7622.998	0	13,114.59	21.818	0	16.62
4	26.513	0	08.55	25.345	0	10.56
6	30.232	0	02.16	29.084	0	04.13
8	34.161	0	13,095.42	33.028	0	13,097.36
10	38.298	0	88.32	37.172	0	90.25
12	42.639	0	80.89	41.53	0	82.79
14	47.188	0	73.11	46.10	0	74.97
16	51.95	0	64.90	50.88	0 <i>d</i>	66.80
		$R_1'(j)$			$R_2'(j)$	
4	7611.002	0	13,134.94
6	7609.710	0	13,137.49	08.552	1 <i>d</i>	39.49
8	07.358	1	41.55	06.211	1 <i>d</i>	43.54
10	05.194	00	45.29	04.004	0	47.35
12	03.212	0	48.72	02.028	00	50.77
B BAND						
j	λ	I $P_1(j)$	$\nu_{\text{VAC.}}$	λ	I $P_2(j)$	$\nu_{\text{VAC.}}$
0	6883.832	10	14,522.792 <i>a</i>
2	6886.743	12	14,516.656 <i>a</i>	85.754	11	18.740 <i>a</i>
4	89.903	14	09.997 <i>a</i>	88.948	13	12.008 <i>a</i>
6	93.309	15	02.828 <i>a</i>	92.369	14	04.804
8	96.965	15	14,495.140 <i>a</i>	96.037	14	14,497.089 <i>a</i>
10	6900.868	15	86.941 <i>a</i>	99.954	14	88.860 <i>a</i>
12	05.023	14	78.224 <i>a</i>	6904.117	14	80.123 <i>a</i>
14	09.431	13	68.988 <i>a</i>	08.534	13	70.865 <i>a</i>
16	14.090	11	59.235 <i>a</i>	13.200	11	61.099 <i>a</i>
18	19.002	9	48.972 <i>a</i>	18.122	9	50.810 <i>a</i>
20	24.172	9	38.183 <i>a</i> (<i>S</i>)	23.302	9	39.998 <i>a</i>
22	29.598	4	26.88	28.728	4	28.69
24	35.283	2	15.05	34.421	2	16.84
26	41.231	1	02.70	40.381	1	04.46
28	47.45	0	89.81	46.614	0	14,391.54
		$R_1(j)$			$R_2(j)$	
2	6879.928	6	14,531.035 <i>a</i>	6879.041	12	14,532.907 <i>a</i>
4	77.637	12	35.874 <i>a</i>	76.715	13	37.824 <i>a</i>
6	75.590	13	40.202 <i>a</i>	74.653	13	42.183 <i>a</i>
8	73.798	12	43.992 <i>a</i>	72.843	12	46.013 <i>a</i>
10	72.247	11	47.266 <i>a</i>	71.285	10	49.311 <i>a</i>
12	70.946	8	50.029 <i>a</i>	69.942	7	52.16 <i>b</i>
14	69.942	7	52.16 <i>b</i>	68.915	7	54.33 <i>b</i>
16	69.093	6	53.953 <i>a</i>	68.106	6	56.05
18	68.553	3	55.10 <i>b</i>	67.554	5	57.22
20	68.237	6 <i>d</i>	55.77 <i>b</i>	67.247	6	57.87
22	68.237	6 <i>d</i>	55.77 <i>b</i>	67.209		57.95
24	68.429	1	55.36	67.403		1
26	68.915	7	54.33 <i>b</i>	67.865	0	56.56
28	69.626	00	52.83(<i>S</i>)	68.553	3	55.10 <i>b</i>

TABLE 1—Continued

α BAND						
j	λ	I $P_1(j)$	$\nu_{\text{vac.}}$	λ	I $P_2(j)$	$\nu_{\text{vac.}}$
0	6287.747	1	15,899.56a
2	6289.397	1	15,893.30a	90.222	2	95.39a
4	92.162	2	86.41a	92.957	3	88.40a
6	95.178	3	78.81a	95.961	3	80.79a
8	98.456	2	70.58	99.229	3	72.53
10	6302.001	2	61.78a	6302.764	2	63.60
12	05.810	2	52.12a	06.566	2	54.02
14	09.885	2	41.89	10.638	1	43.78
16	14.234	0	31.00	14.977	0	32.86
18	18.851	00	19.45	19.587	00	21.30
		$R_1(j)$			$R_2(j)$	
2	6284.537	0	15,907.68	6283.795	1	15,909.56a
4	82.725	2	12.27	81.956	2	14.22a
6	81.178	1	16.19a	80.393	2	18.18a
8	79.896	2	19.44a	79.100	3	21.46a
10	78.878	2	22.02a	78.078	2	24.05
12	78.126	2	23.93	77.311	2	25.99
14	77.643	1	25.15	76.818	1	27.24a
16	77.425	0	25.70	76.609	2d	27.77a,b
18	77.533	000	25.43	76.609	2d	27.77b
α' BAND						
j	λ	I $P_1(j)$	$\nu_{\text{vac.}}$	λ	I $P_2(j)$	$\nu_{\text{vac.}}$
0	5796.088	0	17,248.24S
2	5798.182	4	17,242.01S	97.499	00	44.05
4	5800.628	0	34.74(S)	99.969	00	36.70
6	03.333	0	26.71	5802.669	0	28.69
8	06.294	0	17.92	05.624	0	19.91
10	09.525	00	08.35	08.869	00	10.30
12	13.054	00	17,197.90(S)	12.400	00	99.84(S)
14	16.841	00	86.71(S)	16.265	00	17,188.41(S)
16	20.894	000	74.74	20.294	000	76.51
18	25.295	000	61.77(S)	24.642	000	63.69
20	30.089	000	47.66(S)	29.317	0000N	49.93(S)
22	34.854	0000N	33.65(S)	34.224	0000	35.50(S)
		$R_1(j)$			$R_2(j)$	
2	5793.394	000	17,256.27(S)	5792.768	00	17,258.13
4	91.924	00	60.64	91.269	00	62.60
6	90.769	00	64.09	90.097	0	66.09
8	89.855	0	66.81	89.202	0d	68.76b
10	89.202	0d	68.76b	88.539	0	70.74
12	88.879	00	69.72b	88.182	00	71.80b
14	88.879	00	69.72b	88.089	000	72.08
16	88.994	000	69.38	88.182	00	71.80b
18	89.484	000	67.92	88.774	00	70.04

2. *The Empirical Structure of the Bands.*—We number the lines (table 1) in such a way that the first complete doublet on both sides of the zero

line has the number two. The other lines will then have the successive even numbers, as the doublets belonging to the odd numbers are missing. We designate the longer wave-length component by a subscript one and the other component by a subscript two. Table 2 shows that the differences, $R_i(j) - P_i(j)$ are identical for the four bands under consideration,* ($i = 1, 2$), which means that $R_i(j)$ and $P_i(j)$ have the same initial† state.

TABLE 2
 $R_i(j) - P_i(j)$

	A	B	α	α'	A'
2	{ 14.38 14.17	14.379 14.167	14.38 14.17	*14.26 14.08	
4	{ 25.87 25.82	25.877 25.816	25.86 25.82	25.90 25.90	24.38
6	{ 37.34 37.41	37.374 37.379	37.38 37.39	37.38 37.40	35.33 35.36
8	{ 48.88 48.97	48.852 48.924	48.86 48.93	48.89 *48.85	46.13 46.18
10	{ 60.32 60.49	60.325 60.451	60.24 60.45	*60.41 60.44	56.97 57.10
12	{ 71.79 72.00	71.805 *72.04	71.81 71.97	*71.82 *71.96	67.83 67.98
14	{ 83.25 83.54	*83.17 *83.46	83.26 83.46	*83.01 83.67	
16	{ 94.65 *95.09	94.718 94.95	94.70 *94.91	94.64 *95.29	
18	{ *105.95 *106.38	*106.03 106.41	105.98 *106.47	*106.15 106.35	
20	{ *117.59 *117.90	*117.59 117.87			
22	{ 128.98 *129.30	*128.89 129.26			
24	{ 140.33 140.72	140.31 140.70			
26	{ *151.69 152.11	*151.63 152.10			
28	{ *163.02 *163.48	163.02 *163.56			

We can, therefore, write

$$\left. \begin{aligned} P_i(j) &= F'_i(j) - F''_i(j + 1) \\ R_i(j) &= F'_i(j) - F''_i(j - 1) \end{aligned} \right\} \quad (1)$$

The dependence on the final state cannot be tested by the combination principle, as we have no two bands with the same initial vibrational state. But the form (1) is the simplest assumption and makes the structure of the bands analogous to that of other well-known bands.

The lines can be represented approximately by a quadratic formula, though there are small but distinctive deviations in the P_2 and R_2 branch for small values of j . If we neglect these at first, we may write

$$F(j) = A + Bm^2 - \beta m^4 \quad (2)$$

in which A represents that part of the energy (divided by h) which is not dependent on the rotational quantum number; β is a small correction term which is due to the non-rigidity of the molecule. We want to calculate the constants which are involved in forming the bands. On account of (1) and (2), the differences tabulated in table 2 are equal to

$$R_i(j) - P_i(j) = F''_i(j + 1) - F''_i(j - 1) = 4B''_i m_i - (8m_i^2 + 8m_i^3)\beta''_i$$

and can be used to calculate the values for B''_i , β''_i and m_i for the final state. In the same way, the constants for the initial state can be obtained from

$$R_i(j + 1) - P_i(j - 1) = F'_i(j + 1) - F'_i(j - 1) = 4B'_i m_i - (8m_i^2 + 8m_i^3)\beta'_i$$

Only the first ten lines (to R (18) and P (16) incl.) were used for the calculation of the constants in order to be sure that no higher terms have an appreciable influence, and because the wave-lengths of overlapping lines in the head, especially of the A band, cannot be determined with great accuracy. The values for the constants are given in table 3: n means the vibrational quantum number; the value for the zero line ν_{01} of each band is given in the row of its initial state. Not much significance can be attached to the values for the correction term β . The values of m calculated in this way are, for the first few terms:

final state

m_1 :	2.500	4.500	6.500	8.499
m_2 :	2.448	4.462	6.472	8.459

initial state (B band)

m_1 :	1.502	3.501	5.504	7.502
m_2 :		3.448	5.454	7.452

It is seen from this that the m -values for the F'_1 and F''_1 state are very nearly half integers, whereas the values for the F'_2 and F''_2 state are considerably lower. On the whole, the F_2 terms cannot be so well represented

by a formula of the type (1), and there are distinct deviations for small values of the rotational quantum number. The significance of this will be discussed later on. The zero line for the P_2 and R_2 branch is approximately 1.9 cm.^{-1} higher than that of the P_1 and R_1 branch.

TABLE 3

	B_1	B_2	β_1	β_2	ν_{01}
Initial state					
$A, n = 0$	1.390	1.402	} $5.75 \cdot 10^{-6}$	$10.63 \cdot 10^{-6}$	13,122.97
$B, n = 1$	1.372	1.384			14,525.72
$\alpha, n = 2$	1.354	1.364			15,902.50
$\alpha', n = 3$	1.336	1.346			17,251.19
$A', n = 1$	1.311	1.318	_____	_____	13,123.00
Final state					
$n = 0$	1.438	1.447	$6.31 \cdot 10^{-5}$	$7.92 \cdot 10^{-6}$	
$A', n = 0$	1.354	1.361	_____	_____	

The observed doublet separation, which is the same for all bands, can be accounted for with the above terms. If we express the deviation of m from half integer values in F_2 by a linear term αm , the doublet separation becomes

$$\begin{aligned} \Delta P(m) &= \nu_{02} - \nu_{01} - B_2'' + B_1'' - \alpha'' - 2(B_2'' - B_1'')m + (\alpha' - \alpha'')m + (C_2 - C_1)m^2 \\ \Delta R(m) &= \nu_{02} - \nu_{01} - B_2'' + B_1'' + \alpha'' + 2(B_2'' - B_1'')m + (\alpha' - \alpha'')m + (C_2 - C_1)m^2 \\ (C &= B' - B''). \end{aligned}$$

These formulæ give all the properties of the observed doublet separation, although an *exact* quantitative test cannot be obtained, because the small differences $B_2 - B_1$, $\alpha' - \alpha''$, etc., are not known with sufficient accuracy. The value for the doublet separation of the zero lines is found to be 1.93. The zero lines follow the formula

$$\nu_{01} = 13122.965 + 1415.017n - 11.911n^2 - 0.3525n^3 \quad (n = 0, 1, 2, 3, \dots)$$

in which the constants differ only slightly from those calculated by Kratzer⁵ from the old data. It is also seen from table 3 that the constants B' have the linear dependence on the vibrational quantum number postulated by Kratzer's theory.

The A band includes a number of *weak lines*, and those in the tail are at once seen to form doublets of the same kind as the strong lines. In the head also doublets can be picked out, and then the constants can be calculated in the same way as for the strong branches. These are also given in table 3. The weak lines have been called A' . It appears that the weak branches have exactly the same structure as the strong ones. The only difference is the value for the constant B . The zero lines for the strong and weak branches are the same within the limits of experimental error. The weak branches are too faint to be observed in the other bands. There is still a small number of unclassified faint lines of atmos-

pheric origin, but it is not certain whether they belong to these bands. They may be partly due to water vapor.

The significance of the empirical structure of the bands for the structure of the oxygen molecule is not yet satisfactorily cleared up in all points. Approximately we have $B = h/8\pi^2cJ$, and from this it follows that the moment of inertia J for the O_2 -molecule in its normal state is $19.27 \cdot 10^{-40}$, and in the excited state, $19.93 \cdot 10^{-40}$, which gives for the distance between the nuclei $1.205 \cdot 10^{-8}$ and $1.225 \cdot 10^{-8}$ cm., respectively.

3. Mulliken⁶ has developed a systematic analysis of band spectra to which Hund⁷ gave a theoretical background. According to this theory the type of an electronic molecular term is determined by quantum numbers which are analogous to those used for the classification of line spectra. The resultant spin of the electrons, s , determines the multiplicity of the terms.

The components of the electronic angular momentum are σ_k and σ_s , and the spin along the nuclear axis is $\sigma = \sigma_k + \sigma_s$. If $\sigma_k = 0, 1, 2, \dots$, we have S, P, D, \dots terms. For all particulars it is necessary to consult the above-mentioned papers.

The fact that both initial and final state of the atmospheric absorption bands are not single for zero rotation shows that neither can be a singlet nor an S state. It seems very probable that we have here a ${}^3D^3P$ transition. For a 3P state $s = 1$, $\sigma_k = 1$, $\sigma = 0, 1, 2$; for a 3D state $s = 1$, $\sigma_k = 2$, $\sigma = 1, 2, 3$. Hund derives a selection rule $\Delta\sigma = 0$, if $\sigma_k > 0$, which is fulfilled, e.g., in the second positive nitrogen group. On account of this rule, only the levels with $\sigma = 1$ and 2 can combine with each other. The fact that alternate rotational levels are suppressed because we have a symmetrical molecule eliminates the Q branches. There are, however, some difficulties in accounting for the missing lines. We confine ourselves to these few remarks about the electronic structure, as this will be discussed more fully, together with the electronic structure of the Runge bands, in a subsequent paper.

We are indebted to Dr. St. John for unpublished data on the revision of Rowland's Table of Solar Spectrum Wave-Lengths, to Mr. W. P. Hoge for assistance in some of the measurements, and to Dr. Pettit and Miss Ware for operating the microphotometer for us.

REMARKS ON THE TABLES

Intensities in A band from Meggers; in B , α , α' , from Rowland.

S indicates a line influenced by a solar line.

(S) is used where such influence is possible, but doubtful.

a indicates lines for which wave-lengths have highest weight.

b indicates lines occurring in more than one place.

* in table 2 means that one of the lines involved is a b or an S line.

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* j means here only the ordinal number of the lines.

† The expressions initial and final state are always used from the point of *emission*.

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REVISION OF ROWLAND'S PRELIMINARY TABLES OF SOLAR SPECTRUM WAVE-LENGTHS

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The first extensive list of wave-lengths in the solar spectrum was made by A. J. Ångström in 1868.¹ In recognition of this work his name has been given to the unit of wave-length in the international system.² In 1893 Rowland published "A New Table of Standard Wave-Lengths" containing several hundred lines in the solar spectrum.³ This represented the results of some ten or more years of investigation, during which period he constructed the ruling engine and produced the first concave grating. This table of wave-lengths so surpassed in accuracy all previous work that it received world-wide acceptance and was made the basis of his "Preliminary Table of Solar Spectrum Wave-Lengths,"⁴ which for a generation has been the world's standard and the vade-mecum of astronomers and physicists.

The starting point of the Rowland system was the mean wave-length of the D_1 line of sodium as referred to the standard meter by five investigators:

	λ	wgt.
Ångström	5895.81	1
Müller and Kempf	5896.25	2
Kurlbaum	5895.90	2
Peirce	5896.20	5
Bell	5896.20	10

Mean 5896.156 in air at 20°C. and 760 mm. pressure

From the sodium line about 15 lines in the visual region were determined by the method of coincidences between spectra of different orders. The list was increased by interpolation, extended into the ultra-violet by photography, and during a period of eight or nine years the thousand lines, more or less, of the "New Table of Standards" were intertwined with each other in an immense number of ways. Rowland says, in a note, that the