SOME NEW FEATURES OF THE ATMOSPHERIC OXYGEN BANDS, AND THE RELATIVE ABUNDANCE OF THE ISOTOPES O^{16}, O^{18}

BY HAROLD D. BABCOCK

MOUNT WILSON OBSERVATORY, CARNEGIE INSTITUTION OF WASHINGTON

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Accurate values of certain constants associated with the atmospheric oxygen bands and with the oxygen molecule were derived from improved data in a preceding joint paper.[1] A new band, named A', was described and attributed to oxygen but no explanation was offered for it. In a recent paper Mulliken[2] has discussed the interpretation of the atmospheric bands, showing that they may be attributed to a transition from the normal ^3S state to a metastable ^1S excited state of the molecule, but he did not account for the A' band. Giauque and Johnston,[3] however, have pointed out that the A' band as described by Dieke and Babcock,[4] corresponds to one which would be expected if oxygen consists of two isotopes, one of mass 16 and another, much less abundant, of mass 18. Aston[5] finds with the mass spectrograph no evidence for O^{18} and concludes that if it exists its proportion can hardly exceed 1:1000 of O^{16}.

Further data confirming the existence of O^{18} are now presented and the proportions of O^{16} and O^{18} are found to be consistent with Aston's conclusion. In addition, some other new features of the band spectrum of oxygen are described, one of which indicates the existence in the ordinary molecule of something equivalent to a minute dissymmetry.

Table 1 gives a revised description of the A' band, following the notation of Dieke and Babcock. The band is now considerably extended in all branches and a few inadvertent errors in the previous description are corrected. An important change is the inclusion of the odd-numbered doublets with intensities similar to those of even number formerly given alone. Some of the added material was measured by us but omitted from our paper because we failed to recognize its connection with the band. On account of the dissymmetry of the molecule O^{16}–O^{18} the odd-numbered doublets should appear, and interpolation between the even-numbered doublets shows that the new lines do in fact coincide with their expected positions. The data of table 1 confirm the existence of O^{18}. Excepting the zero line of the P branch, which is a forbidden line, the vacant spaces in table 1 are due to obscuration by strong lines of the A band.

A comparison of the observed positions of the even-numbered doublets in the A' band with those calculated from the theory of the isotope effect in band spectra is summarized in table 2. The equations used are those stated by Giauque and Johnston as follows:

$$\Delta\nu(P) = 2.12 + 0.0556[B''m^2 - \beta''m^4 - B'(m-1)^2 + \beta'(m-1)^4]$$
$$\Delta\nu(R) = 2.12 + 0.0556[B''m^2 - \beta''m^4 - B'(m+1)^2 + \beta'(m+1)^4]$$

where $m = {}^3/_2, {}^7/_2, {}^{11}/_2$ .... The constants are as found by Dieke and Babcock:

$$B'' = 1.438;\ B' = 1.390;\ \beta'' = 6.31 \times 10^{-6};\ \beta' = 5.75 \times 10^{-6}.$$

Only the residuals, observed *minus* computed wave number, are given in table 2, and those lines which occur in more than one place in the band are omitted, since their positions are less accurately determined. The average residual is -0.05 cm.$^{-1}$, and, as the signs are practically all negative, it is evident that there is a small systematic discrepancy between the observed and computed positions of the A' lines. This difference appears slightly greater than the estimated errors of observation, although it must be remembered that we are comparing positions of lines whose intensities are widely different and, in spite of numerous precautions, some unsuspected instrumental error may have entered. The residuals show no relation to the amount of rotational energy, and, if real, the systematic difference would appear to be associated with the vibrational

TABLE 1

A′ BAND

j	λ	INT. $P_1(j)$	VAC.	λ	INT. $P_2(j)$	VAC.
0	7619.691	00	13120.29	.....	...	.....
1	21.312	00	17.50	7620.064	00	13119.64
2	22.998	00	14.59	21.818	00	16.62
3	.....	...	.....	23.540	00	13.56
4	26.513	0	08.55	25.345	0	10.56
5	.....	...	.....	.....	...	.....
6	30.232	0	02.16	29.084	0	04.13
7	.....	...	.....	.....	...	.....
8	34.161	0	13095.42	33.028	0	13097.36
9	.....	...	.....	.....	...	.....
10	38.298	0	88.32	37.172	0	90.25
11	40.47	0	84.60	39.32	0	86.57
12	42.639	0	80.89	41.53	0	82.79
13	44.90	0	77.02	43.79	0	78.92
14	47.188	0	73.11	46.10	0	74.97
15	49.581	0	69.02	48.46	0	70.94
16	51.95	00	64.97	50.88	00	66.80
17	54.45	00	60.71	53.34	00	62.60
18	56.925	00+	56.48[b]	55.83	00	58.35
19	59.90	$\begin{Bmatrix} 00 \\ 00 \end{Bmatrix}$	51.42[d]	58.42	00	53.94
20	62.10	000	47.67	61.05	0000	49.45
21	.....	...	.....	63.72	000	44.91
22	67.51	0000	38.46	66.49	0000	40.20
23	70.34	0000	33.65	69.22	0000	35.55
24	73.15	0000	28.88	72.05	0000	30.74

j	λ	INT. $R_1(j)$	VAC.	λ	INT. $R_2(j)$	VAC.
1	.....	...	.....	7615.55	0	13127.44[b]
2	7615.55	0	13127.42[b]	14.00	00	30.09
3	13.71	00	30.60[b]	12.57	0	32.55[b]
4	12.57	0	32.55[b]	11.188	0	34.94
5	11.002	0	35.26	09.84	00	37.26
6	09.71	00	37.49	08.55	0 0	39.49[b,d]
7	08.55	0 0	39.49[b,d]	07.358	1	41.55[b]
8	07.358	1	41.55[b]	06.211	0 0	43.54[b,d]
9	06.211	0 0	43.54[b,d]	05.07	0	45.50
10	05.194	0	45.29	04.004	0	47.35
11	04.2	0?	47.01	02.996	0	49.10
12	03.212	0	48.72[d]	02.028	00	50.77
13	.....	...	.....	01.12	0	52.34
14	01.38	0000	51.9	.....	...	.....
15	.....	...	.....	7599.45	0	55.23
16	.....	...	.....	.....	...	.....
17	7599.215	0	55.64	97.995	1	57.75[b]
18	.....	...	.....	.....	...	.....
19	97.995	1	57.75[b]	96.75	000	59.91
20	.....	...	.....	.....	...	.....
21	96.97	0000	59.53	95.58	00	61.93
22	.....	...	.....	94.28	0	64.18
23	.....	...	.....	.....	...	.....
24	.....	...	.....	93.84	0	64.95

[b] = used in more than one position in the bands.

[d] = double

part of the isotopic displacement. Since it amounts to less than 4 parts in a million, it can hardly be taken as a refutation or even a serious weakening of the arguments in favor of the existence of O^{18}. No other hypothetical isotopes of oxygen correspond to the observations.

An examination of the *B* band was made under favorable conditions in the hope of finding further evidence, although the isotopic band would be expected to appear less strongly here than in the case of the *A* band. The photographs show many new faint lines intermingled with the *B* band and some of these have the appearance of a new band with nearly the same displacement from *B* as that of *A′* with respect to *A*. But the isotopic displacement calculated for O^{16}—O^{18} is in this case very different, and no correspondence has yet been found between these new lines and those to be expected in a band truly analogous to *A′*. Further study of this material is in progress. It is clearly of atmospheric origin and probably arises from oxygen, but more accurate measurements are needed before it can profitably be discussed.

A summary of the evidence for the existence of O^{18} would include: (1) as shown by Dieke and Babcock, the *A′* band has the same origin as the *A* band; (2) the odd-numbered doublets are present in *A′* as required by the theory; (3) the observed positions of the *A′* lines closely correspond to those calculated from the theory when coefficients for the molecule O^{16}–O^{18} are used; (4) the theory is well confirmed in the case of other elements whose isotopes have been discovered and studied with the mass spectrograph.

TABLE 2

RESIDUALS, OBSERVED *minus* COMPUTED ISOTOPIC DISPLACEMENT OF A′ BAND FROM A. (UNIT, CM.$^{-1}$)

P_1	P_2	P_1	P_2	R_1	R_2
−0.03	....	−0.06	−0.06	....	−0.01
−0.05	−0.11	−0.06	−0.10	....	−0.04
−0.06	−0.04	−0.05	−0.04	+0.01	±0.00
−0.06	−0.03	−0.04	−0.08	−0.06	−0.07
−0.05	−0.03	−0.03	−0.10	−0.02	−0.06
−0.07	−0.04	−0.10	−0.04	....	....
−0.06	−0.04	....	....	....	....

Another feature of both the *A* and *B* bands consisting of a series of exceedingly weak doublets, which are recorded only with powerful spectrographs when the sun is near the horizon, has been brought out during the progress of this work. These are found symmetrically placed between the intense doublets of both the *P* and *R* branches. The new doublets are listed in table 3 along with the ordinary lines of these bands which are repeated from the paper of Dieke and Babcock. The intensities given for the strong lines are only qualitative. The weak lines here considered are estimated to be about one-tenth as strong as the adjacent lines in the isotopic band and, as will be seen from what follows, this would correspond to about one ten-thousandth the intensity of the adjacent strong lines of the ordinary band. Comparison with the positions calculated for the missing doublets by means of the isotopic displacement and also by graphical interpolation between the strong doublets shows that the observed positions agree approximately but not exactly. The mean difference is -0.11 cm.$^{-1}$ with a range from $+0.58$ to -0.70 cm.$^{-1}$. The errors of observation, although considerably larger for these difficult lines, are not great enough to account for such differences. These doublets cannot be ascribed to a third isotope of oxygen[6] and there is no place for them in any of the bands already described except the one chosen. They cannot be explained as accidental coincidences, since there are too many of them in view of the fact that practically no other lines of similar character occur in this region. It seems probable that they are in fact the missing doublets, affected by some slight perturbation. The existence

TABLE 3

A BAND

j	λ	INT. $P_1(j)$	ν VAC.	λ	INT. $P_2(j)$	ν VAC.
0	7620.996	15	13118.04	.....	...	.....
1	22.50	0000	15.45	7622.02	0000	13116.28
2	24.493	23	12.02	23.289	22	14.11
3	26.17	0000	09.14	25.45	0000	10.38
4	28.203	25	05.64	27.050	24	07.63
5	30.01	000	02.54	29.19	000	03.97
6	32.150	25	13098.87	31.021	24	00.81
7	34.05	000	95.61	33.34	000	13096.82
8	36.317	25	91.72	35.196	24	93.64
9	38.298	0	88.32[d]	37.28	0000	90.07
10	40.694	23	84.22	39.583	22	86.12
11	42.77	0000	80.67	41.64	0000	82.60
12	45.297	19	76.34	44.197	18	78.22
13	47.43	0000	72.70	46.21	0000	74.78
14	50.120	16	68.10	49.032	15	69.96
15	52.39	0000	64.22	50.88	000	66.80[d]
16	55.172	13	59.47	54.078	12	61.34
17	.....	...	.....	56.925	00	56.48[b]
18	60.447	10	50.48	59.359	9	52.34
19	.....	...	.....	62.10	000	47.67[b]
20	65.938	6	41.13	64.873	6	42.95
		R_1			R_2	
1	7617.56	0000	13123.95	7617.08	0000	13124.78
2	16.143	10	26.40	15.048	17	28.28
3	14.55	00	29.14	13.77	0	30.49
4	13.180	19	31.51	12.054	23	33.45
5	11.63	000	34.18	11.002	0	35.26[b]
6	10.450	23	36.21	09.290	27	38.22
7	.....	...	.....	08.55	0	39.49[b,b]
8	07.911	24	40.60	06.748	27	42.61
9	.....	...	.....	.....	...	.....
10	05.628	24	44.54	04.431	24	46.61
11	.....	...	.....	03.28	0	48.60[b, b]
12	03.533	17	48.13	02.346	18	50.22
13	.....	...	.....	01.34	0000	51.95
	x	x	x	x	x	x
25	.....	...	....	7594.28	0	64.18

B BAND (NEW LINES ONLY)

		P_1			P_2	
3	6888.41	000	14513.14	6887.20	0000	14515.69
5	91.59	000	06.44	90.73	000	08.26
7	95.37	0000	14498.49	94.34	0000	00.66
9	98.92	000N	91.00	97.94	0000N	93.1[d]
11	6903.03	0000	82.40	.....	...	.....
13	06.98	000	74.12	.....	...	.....
15	11.91	000	63.80	.....	...	.....

of these doublets has hitherto been unrecognized, although Mulliken[7] says of them

> These might perhaps after all be expected in very low intensity, corresponding to some small interaction neglected in the ordinary theory, even in a homopolar molecule without nuclear spin.

The intensities of the absorption lines in the oxygen bands show a remarkable range. During this investigation the most persistent features of the *A* band were photographed with an air path of 3 meters with a spectrograph whose photographic resolving power is about 20,000. If an instrument of higher power but shorter air path were available, it seems probable that 1 meter of air would suffice to show the strongest lines in this band. In contrast with such lines we have the last observable members of the regular sequence of doublets, at λ 7717–7718, barely recorded by a spectrograph of about 10 times as great resolving power with an air path 30,000 times as great, and also the strongest of the missing doublets, of comparable intensity. Between these extremes lie the strongest lines of the isotopic band, A', whose intensities relative to those of the *A* band should give an estimate of the relative abundance of O^{16} and O^{18}.

The ratio of these intensities is too great to be measured satisfactorily by direct comparison. Eye estimates are meaningless and even the microphotometer proves inadequate. Fortunately a null method of great simplicity is available. The two bands, *A* and A', are successively recorded on portions of the same photographic plate which are given the same development. For the *A* band an artificial source of light is used with a measured air path of a few meters, while for A' the solar spectrum is observed with identical instrumental adjustments but with a much greater equivalent air path, which may be readily calculated from the height of the barometer, known density of air under the conditions of observation, and zenith distance of the sun at the given time. By proper choice of circumstances homologous members of the two bands are made to appear alike and their actual relative intensities may then be taken as the ratio of the two air paths. The method may be refined by applying the microphotometer to test the equality of the two sets of lines, but this was hardly justified in the present case since eye estimates are quite reliable when the differences are small. Two determinations gave respectively 1:1175 and 1:1350 as the ratio of A' to *A*, which may therefore be put equal on the average to 1:1250, the actual ratio of O^{18} to O^{16} atoms.

The magnitude of this ratio explains the fact that the isotope of oxygen has not been discovered in the usual way with the mass spectrograph, and is in agreement with the conclusion of Aston to which reference has already been made. It is interesting to note that the spectroscopic method has once before led to the discovery of an isotope when Mulliken[8] showed the existence of Si^{30}, which was later confirmed by Aston[9] with the mass spectrograph. Other useful data on the relative intensities of lines in the atmospheric oxygen bands may be derived from photographs like those used in this investigation, but their discussion must be reserved for a future paper.

[1] Dieke and Babcock, these PROCEEDINGS, **13,** 1927 (670–678); *Mt. Wilson Comm.*, No. 101.

[2] Mulliken, *Phys. Rev.*, N. S., **32,** 1928 (880–887).

[3] Giauque and Johnston, *Nature,* **123,** 1929 (318).

[4] Dieke and Babcock, loc. cit.

[5] Aston, *Nature,* **123,** 1929 (488–489).

[6] *Note added in proof.*—In a letter soon to be published in *Nature,* Drs. Giauque and Johnston show that these weakest doublets in the *A* band correspond to a second isotopic molecule, O^{16}–O^{17}. I had examined the data with this point in view but an error in computation obscured the truth, and I was further misled by the approximate accordance noted in the text, as well as by the apparent repetition of the sequence of weak doublets in the *B* band, where the isotopic bands have not yet been shown to exist. Further study of my data has confirmed the conclusion of Giauque and Johnston.

[7] Mulliken, *Phys. Rev.*, N. S., **32,** 1928 (886).

[8] Mulliken, *Nature,* **113,** 1924 (423–424); **116,** 1925 (14); *Phys. Rev.*, N. S., **26,** 1925 (319–324).

[9] Aston, *Nature,* **114,** 1924 (273).

FOSSIL PLANTS AND MOUNTAIN UPLIFT IN THE PACIFIC STATES

BY EDWARD W. BERRY

DEPARTMENT OF GEOLOGY, JOHNS HOPKINS UNIVERSITY

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Through force of circumstances I have been compelled to devote considerable time during the past few years to extensive Miocene floras that have come to light, especially in eastern Washington and Idaho. The time spent has not been altogether unprofitable because of the bearing of these floras on the geologic history of the West—especially the time of uplift of the Sierra Nevada and Cascade ranges, on the distribution of terrestrial plants, and on the progressive provincialism of the North American flora, which last only reached its culmination in post-glacial times.

A preliminary statement of results has just been published as Professional Paper 154H by the U. S. Geological Survey. This deals with the fossil flora of a restricted area at or near Spokane, Washington. The present note is intended to call attention to some general conclusions