AN ISOTOPE OF OXYGEN, MASS 17, IN THE EARTH'S ATMOSPHERE

BY W. F. GIAUQUE AND H. L. JOHNSTON

Recently[1,2] the presence of an oxygen isotope, mass 18, in the earth's atmosphere, was reported. In this paper it will be shown that an additional isotope of oxygen with mass 17 is also present. As in the previous case, the conclusion is based on a study of atmospheric absorption spectra obtained by H. D. Babcock of Mount Wilson Observatory. Since our interpretation of the weak A' band in the atmospheric absorption of sunlight as originating from the 18–16 oxygen molecule, Babcock has carried out further measurements which have supplied additional support by extending the various branches of the bands. He has also found a new series of very weak lines. Babcock has kindly permitted us to make use of his manuscript in advance of publication.[3] He suggests that this new series is due to the forbidden alternate rotation levels of the 16–16 oxygen molecule, although, as he states, they do not occupy the correct positions by many times the experimental error.

We have found that these lines originate from an oxygen molecule consisting of an atom of mass 17 in combination with one of mass 16. In agreement with the predictions of the theory of wave mechanics the normal state of this molecule has one-half unit of vibration and both odd and even rotation levels exist.

The method of calculation of the isotopic separation of the lines makes use of the equations given for this purpose by Loomis.[4] In calculating the vibrational isotope effect we have previously made use of the equation given by Birge[5] for the normal oxygen molecule, namely

$$\nu^n = 1565.37n - 11.37n^2$$

and that given by Dieke and Babcock[6] for the 1.6 volt level as

$$\nu^n = 1415.017\,n - 11.91\,n^2 - 0.3525\,n^3$$

Birge[7] has recently found that the latter equation is incorrect due to an error in computation and should be

$$\nu^n = 1418.69\,n - 13.925\,n^2 - 0\,02\,n^3$$

where $n = 0, 1, 2, \ldots$

[1] Giauque and Johnston, Nature, 123, 318 (1929).
[2] Giauque and Johnston, THIS JOURNAL, 51, 1436 (1929).
[3] Babcock, Proc. Nat. Acad. Sci., 15, 471 (1929).
[4] Loomis, Bull. Natl. Research Council, 11, Chap. V (1926).
[5] Birge, ibid., 11, Chap. V (1926).
[6] Dieke and Babcock, Proc. Nat. Acad. Sci., 13, 670 (1927).
[7] Birge, Nature, in press.

As a result of this observation Birge shows that the systematic difference of observed and calculated isotopic effects which occurred in our calculations on the 18–16 molecule is practically eliminated, and demonstrates the remarkable accuracy of the measurements of Dieke and Babcock.[6]

On the basis of the two vibration equations given by Birge, the data for the 18–16 molecule have been recalculated.

The above vibrational formulas should be transposed so that the state given as zero corresponds to $n = {}^1/_2$ as required by the theory of wave mechanics.

The formulas for the separation of the P and R branches of the 18–16 and 16–16 molecules are as follows

$$\Delta\nu_P = 2.07 + 0.0556\ [B''m^2 - \beta''m^4 - B'(m - 1)^2 + \beta'(m - 1)^4]$$
$$\Delta\nu_R = 2.07 + 0.0556\ [B''m^2 - \beta''m^4 - B'(m + 1)^2 + \beta'(m + 1)^4]$$
$$m = 1/2,\ 3/2,\ 5/2,\ \ldots$$

For the separations of the lines due to the 17–16 and 16–16 molecules

$$\Delta\nu_P = 1.09 + 0.0294\ [B''m^6 - \beta''m^4 - B'(m - 1)^2 + \beta'(m - 1)^4]$$
$$\Delta\nu_R = 1.09 + 0.0294\ [B''m^2 - \beta''m^4 - B'(m + 1)^2 + \beta'(m + 1)^4]$$

The constants as given by Dieke and Babcock[6] are

$$B'' = 1.438 \qquad \beta'' = 6.31 \times 10^{-6}$$
$$B' = 1.390 \qquad \beta' = 5.75 \times 10^{-2}$$

The lines calculated for the 16–18 and 16–17 molecules are given beside the observed data in Table I. In order to clear up any doubt concerning

TABLE I

CALCULATED AND OBSERVED LINES IN THE A BANDS OF THE 16–18 AND 16–17 OXYGEN MOLECULES

P₁ Branch

j'	Cm.$^{-1}$ 16–16 Calcd.	Obs.	Cm.$^{-1}$ 16–18 Calcd.	Obs.	Cm.$^{-1}$ 16–17 Calcd.	Obs.
0	13,118.06	13,118.04	13,120.29	13,120.29	13,119.24	
1	*115.04*	*115.45*	117.44	117.50	116.31	13,116.28
2	111.99	112.02	114.56	114.59	113.35	
3	*108.85*	*109.14*	111.59		110.30	110.38
4	105.58	105.64	108.50	108.55	107.13	
5	*102.28*	*102.54*	105.39		103.93	103.97
6	098.83	098.87	102.13	102.16	100.58	
7	*095.35*	*095.61*	098.84		097.20	097.36b
8	091.73	091.72	095.43	095.42	093.70	
9	*088.03*	*088.32d*	091.94		090.11	090.07
10	084.23	084.22	088.35	088.32b,d	086.43	
11	*080.33*	*080.67*	084.67	084.60b	082.63	082.60
12	076.34	076.34	080.90	080.89	078.77	078.92b
13	*072.28*	*072.70*	077.06	077.02	074.83	074.78
14	068.13	068.10	073.14	073.11	070.81	070.94b
15	*063.84*	*064.22*	069.09	069.02	066.64	066.80b,d
16	059.45	059.47	064.96	064.97	062.40	
17	*055.02*		060.78	060.71	058.10	

TABLE I (*Continued*)

j'	Cm.⁻¹ 16-16 Calcd.	Obs.	Cm.⁻¹ 16-18 Calcd.	Obs.	Cm.⁻¹ 16-17 Calcd.	Obs.
18	050.49	050.48	056.50	056.48	053.70	
19	*045.86*		052.12		049.21	
20	041.12	041.13	047.65	047.67		
21	*036.32*		043.12			
22	031.40	031.40	038.47	038.46		
23	*026.39*		033.74	033.65		
24	021.29	021.29	028.93	028.88		

P_2 Branch

j'	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
0	*13,120.15*	Excluded	*13,122.38*	Excluded	*13,121.33*	Excluded
1	*117.13*	*13,116.28*	119.53	13,119.64	118.40	
2	114.07	114.11	116.64	116.62	115.43	13,115.45
3	*110.93*	*110.38*	113.67	113.56	112.38	
4	107.68	107.63	110.60	110.56	109.23	
5	*104.32*	*103.97*	107.43		105.97	
6	100.89	100.81	104.19	104.13	102.64	
7	*097.36*	*096.82*	100.85		099.21	
8	093.72	093.64	097.42	097.36b	095.69	095.61
9	*090.00*	*090.07*	093.91		092.08	
10	086.18	086.12	090.30	090.25	088.38	088.32b,d
11	*082.27*	*082.60*	086.61	086.57	084.57	084.60b
12	078.26	078.22	082.82	082.79	080.69	080.67
13	*074.18*	*074.78*	078.96	078.92b	076.73	
14	069.99	069.96	075.00	074.97	072.67	072.70
15	*065.71*	*066.80*	070.96	070.94b	068.51	
16	061.32	061.34	066.83	066.80b,d	064.27	064.22
17	*056.85*	*056.48*	062.61	062.60	059.93	
18	052.30	052.34	058.31	058.35	055.51	
19	*047.64*	*047.67*	053.91	053.94	050.99	
20	042.92	042.95	049.45	049.45	046.37	
21	*038.09*		044.89	044.91		
22	033.20	033.21	040.27	040.20		
23	*028.16*		035.51	035.55		
24	023.09	023.09	030.73	030.74		

R_1 Branch

j'	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
1	*13,123.77*	*13,123.95*	13,125.69		13,124.78	13,124.78
2	126.37	126.40	128.14		127.30	127.42
3	*128.99*	*129.14*	130.59	13,130.49	129.83	
4	131.48	131.51	132.96		132.25	
5	*133.90*	*134.18*	135.25	135.26	134.60	
6	136.24	136.21	137.46	137.49	136.87	
7	*138.47*		139.56	139.49b,d	139.03	
8	140.59	140.60	141.57	141.55b	141.09	
9	*142.63*		143.49	143.54b,d	143.07	143.0
10	144.57	144.54	145.33	145.29	144.95	
11	*146.44*		147.09	147.01b	146.76	
12	148.17	148.13	148.73	148.72b,d	148.45	148.60d
13	*149.51*		150.28		150.04	

TABLE I   (Concluded)

j'	Cm.⁻¹ 16–16		Cm.⁻¹ 16–18		Cm.⁻¹ 16–17	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
14	151.38	151.35	151.77		151.57	
15	*152.83*		153.14		152.97	
16	154.17	154.12	154.41		154.27	
17	*155.44*		155.61	155.64b	155.53	155.64b
18	156.63	156.43	156.76			
19	*157.72*		157.79	157.75b		
20	158.72	158.72	158.74			
21	*159.61*		159.59	159.53		
22	160.39	160.38	160.33			
23	*161.06*		160.97			
24	161.61	161.62	161.48			
25	*162.08*		161.92	161.93		
26	162.51	162.51	162.32			
27	*162.92*		162.71			

R₂ Branch

j'	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
1	*13,125.68*	*13,124.78*	*13,127.60*	Excluded	*13,126.69*	Excluded
2	128.31	128.28	130.08	13,130.09	129.24	13,129.14
3	*130.94*	*130.49*	132.54	132.55	131.78	
4	133.43	133.45	134.91	134.94	134.20	134.18
5	*135.87*	*135.26*	137.22	137.26	136.57	
6	138.20	138.22	139.42	139.49b,d	138.83	
7	*140.46*	*139.49*	141.55	141.55b	141.02	
8	142.60	142.61	143.58	143.54b,d	143.10	
9	*144.64*		145.50	145.50	145.08	
10	146.62	146.61	147.38	147.35	147.00	147.01b
11	*148.48*	*148.60*	149.13	149.10	148.80	148.72b,d
12	150.21	150.22	150.77	150.77	150.49	
13	*151.87*	*151.95*	152.34	152.34	152.10	151.95
14	153.43	153.50	153.82		153.62	
15	*154.91*		155.22	155.23b	155.05	155.23b
16	156.28	156.43	156.52		156.38	
17	*157.56*		157.73	157.75b,b	157.63	157.75b,b
18	158.75	158.72	158.87			
19	*159.86*		159.93	159.91		
20	160.86	160.85	160.88			
21	*161.74*		161.72	161.62		
22	162.52	162.51b	162.46			
23	*163.20*		163.11	162.99		
24	163.79	163.81	163.66			
25	*164.30*		164.14	164.18		
26	164.71	164.70	164.53			
27	*165.10*		164.89	164.95		

the possibility that the new very weak lines might be due to the forbidden alternate rotation levels of the 16–16 molecule, the positions of the forbidden lines are calculated and given in italics along with the assignments of Babcock, also in italics, in Table I.

$$j'(P) = m - 1/2 \qquad j'(R) = m + 1/2$$

where j' refers to the rotation levels of the upper electronic state. In addition to the change made in the 16–18 calculated values introduced by the use of the corrected vibrational wave number referred to above, several of the values at the bottom of the R branches have been changed slightly to conform with smooth values of the 16–16 molecule.

Excluding all lines that have been used in more than one place, the algebraic sum of the residuals has been calculated and divided by the number of lines to show the smallness of any systematic deviation. For the 16–18 band we obtain from 54 lines the value -0.012 cm.$^{-1}$ with a maximum deviation of -0.11 cm.$^{-1}$. For the 16–17 band, which is fainter and therefore harder to measure, a consideration of 20 lines leads to -0.018 cm.$^{-1}$ with maximum deviations of -0.15 cm.$^{-1}$ and $+0.15$ cm.$^{-1}$.

As was shown by Mulliken,[8] to whom the interpretation of the 16–16 band is due, the line corresponding to $j' = 0$ of the P_2 branch is excluded. This line is also experimentally absent for the 16–16 and 16–17 molecules. Professor Mulliken has called our attention to a paper by Kramers[9] in which it is shown that for the oxygen molecule the wave mechanics leads to a single level for the state where j''_K (rotational quantum number) $= 0$, although the higher levels are triplet in character. As Mulliken points out, this excludes the line corresponding to $j' = 1$ for the R_2 branches of the 16–18 and 16–17 molecules. In the previous treatment[2] of the 16–18 band we placed the line 13,127.42 in one of these positions with the notation that the poor agreement was possibly due to a beginning state anomaly. However, it now appears probable that the above exclusion is correct. The corresponding line for the 16–17 molecule is absent. The line 13,127.42 is in fair agreement with the $j' = 2$ line of the R_1 branch for the 16–17 molecule but there is doubt as to whether this entirely explains its presence since the intensity is much greater than that of the other 16–17 lines. There is, of course, always the possibility that, like a number of other lines intermixed with the oxygen bands, it has some origin other than the oxygen molecule.

Babcock[3,10] has carried out some very accurate intensity measurements to make an estimation of the relative amount of Isotope 18. We are somewhat doubtful regarding the assumption that relative absorption can be used as an exact measure of amount, for, as previously pointed out,[2] the isotopic molecules may be slightly polar due to zero point vibration of the unsymmetrical masses. Such polarity may increase the absorption coefficients of the 18–16 and 17–16 molecules. The values obtained from intensity measurements should be maximum amounts.

It should be possible to obtain information on the question of the effect of unsymmetrical masses on the absorption coefficient in the following

[8] Mulliken, *Phys. Rev.*, **32**, 880 (1928).

[9] Kramers, *Z. Physik*, **53**, 422 (1929).

[10] Babcock, *Nature*, **123**, 761 (1929).

manner. Since electrical dissymmetry results from the vibration of the molecule, a greater effect would be expected for greater amounts of vibration. If intensity measurements on bands resulting from a higher state of vibration were carried out, it is possible that the absence of the above effect might be demonstrated or, if it proved to be real, the data might permit a correction.

Babcock estimates that the 18–16 molecules are present to the extent of one part in 1250 and therefore that oxygen contains one part of Isotope 18 in 2500. However, as previously mentioned,[2] a factor of 2 enters into this calculation, due to the fact that the 18–16 molecules have twice as many states in which to exist as have the 16–16 molecules, thus leading to a corresponding reduction in line intensity. When this factor is considered Babcock's results lead to one part in 625 for the 18–16 molecules and the Oxygen 18 atoms are present to the extent of one part in 1250, as a maximum.

From Babcock's estimate of the relative intensity of the lines due to the 17–16 molecules, we estimate the abundance of Oxygen 17 as about one part in 10,000 as a maximum.

Oxygen of mass 17 has been reported by Kirsch and Pettersson,[11] by Blackett,[12] and by Harkins and Shadduck[13] from data obtained on collisions between alpha particles and nitrogen nuclei. One or two collisions per hundred thousand result in combination of the alpha particle with the nitrogen, forming an unstable isotope of fluorine which immediately ejects a proton and becomes Oxygen 17. Blackett assigned a life of less than 10^{-10} sec. to Fluorine 18. Blackett also showed from the time factor in his fog track experiments that Oxygen 17 had a life of at least one-thousandth of a second.

We wish to thank Professor R. T. Birge for his friendly interest in the work and for calling attention to the collision experiments leading to Oxygen 17.

Summary

A new weak band recently discovered in the atmospheric absorption of oxygen by Mr. H. D. Babcock of Mount Wilson Observatory has been explained and shows that an isotope of oxygen of mass 17, as well as the previously discovered Oxygen 18, is present in the earth's atmosphere. On the basis of accurate intensity measurements by Babcock, 18–16 molecules are present to the extent of one part in 625 and 17–16 molecules to the extent of about one part in 5000. Thus Oxygen 18 has an abun-

[11] Kirsch and Pettersson, *Arkiv. Mat. Astron. Fysik*, **19**, 15, 1–16 (1925); *Physik. Z.*, **26**, 457 (1925).

[12] Blackett, *Proc. Roy. Soc. (London)*, **107A**, 349 (1925).

[13] Harkins and Shadduck, *Nature*, **118**, 876 (1926); *Proc. Nat. Acad. Sci.*, **12**, 707 (1926).

dance of one part in 1250 and Oxygen 17 about one part in 10,000.   All of
the above figures are maximum estimates.

BERKELEY, CALIFORNIA

FURTHER EXPERIMENTAL TESTS OF THE GIBBS ADSORPTION THEOREM.   THE STRUCTURE OF THE SURFACE OF ORDINARY SOLUTIONS

BY JAMES W. McBAIN AND ROBERT DuBOIS

The present investigation was undertaken to determine by direct meas-
urement the absolute amounts of various solutes adsorbed, or concen-
trated, at the air–solution interface.   The experimental results throw
further light on the structure of surface layers of solutions and in addi-
tion furnish data for the test of the validity of the Gibbs adsorption equa-
tions both in their strict form and in the approximate form commonly
used.   They fully substantiate the experimental findings of McBain and
Davies[1] for the large amounts of solute transported on a moving bubble.
It is now undeniable that a bubble moving through a solution actually
transports far more solute than can be close packed into a monomolecular
layer on its surface, and several fold greater than the amounts predicted
from the classical theorem of Gibbs.

The Gibbs adsorption theorem may be expressed in the equivalent form

$$\Gamma = -\frac{d\sigma}{RT\,d\ln a} = -\frac{a}{RT} \times \frac{d\sigma}{da}$$

or, approximately

$$\Gamma = -\frac{d\sigma}{RT\,d\ln c} = -\frac{c}{RT} \times \frac{d\sigma}{dc}$$

where a is the activity of the solute and c its concentration, R is the gas
constant, and T is the absolute temperature (Γ, R and a or c being expressed,
of course, in consistent units); $d\sigma/dc$ is the slope of the surface tension/-
concentration curve at the concentration c.

These equations, particularly the last, have been used by numerous
writers to calculate the surface concentrations of many substances.   The
results so obtained have generally been accepted with singular confidence
in lieu of actual measurement and are still used as the basis of extensive
deductions as to the structure of interfacial adsorption layers and of solu-
tion surfaces.   It was and is of importance, therefore, that the validity
of the equations should be tested experimentally.   So far the evidence
has been decidedly adverse.   Agreement in one case cannot obscure dis-
agreement in all others.

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[1] J. W. McBain and G. P. Davies, THIS JOURNAL, **49**, 2230 (1927).