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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

AN ISOTOPE OF OXYGEN, MASS 18. INTERPRETATION OF THE ATMOSPHERIC ABSORPTION BANDS

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In connection with our study of the entropies of gases we have recently considered the available spectroscopic data for oxygen. The atmospheric absorption bands of oxygen contain the necessary information concerning the rotation levels of the oxygen molecule but we found that no completely satisfactory interpretation of these bands has been given, although Mulliken[1] has recently arrived at a partial solution. However, he expresses the opinion that a revised interpretation will probably be necessary in order to include a weak band for which no explanation has been offered by any previous worker.

We can have little confidence in an entropy calculation based on uncertain interpretation since a misunderstood multiplicity would introduce a serious error in our result. We were thus led to a further study of the data.

We may say at once that, in view of our result, no revision of Mulliken's interpretation is necessary.

The most accurate data are those of Dieke and Babcock[2] so they alone have been considered.

The absorption bands are due to a 1.6-volt excitation from the various rotation levels of the normal oxygen molecule, to the various rotation levels of several vibration states of the 1.6-volt level. Only the alternate rotation levels are present, as would be expected for a non-polar molecule with two non-spinning nuclei. All of the lines of the bands, which are of the P and R types, appear as doublets and in addition a weak band is present, the "A′ band," which appears to be an exact duplication of the A band except that the rotation lines have a different spacing.

Our principal problem was to decide whether the A and the A′ bands originated from a common source or not. We tried many ways of combining the lines both within the strong A and the weak A′ bands, respectively, and also combining weak with strong but could find no scheme that would account for the bands arising from a single molecular form. Mulliken considers that the normal oxygen molecule must be a triplet

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

[2] Dieke and Babcock, *Proc. Nat. Acad. Sci.*, **13**, 670 (1927).

S state and mentions the previous workers who have concluded this from the various spectroscopic observations and magnetic susceptibility data. The upper state of the atmospheric bands is a singlet S state. A triplet S state results from two unbalanced spinning electrons coupled together and having three possible orientations. One of these, called the F_1 state, has the spin momentum with the molecular rotation; in the F_3 state the spin is against the molecular rotation and the F_2 state has the spin approximately at right angles to the axis of the molecular rotation. With the above scheme Mulliken fully explains all of the observed lines of the A band and also the absence of the first line of the P_2 series. It is noteworthy that the energies accompanying the extremely loose couplings of the spin with the weak magnetic field, caused by the thermal rotation of the molecule, are of a reasonable amount, decreasing for F_1 states and increasing for F_3 states as the molecular rotation increases, as would be expected. This behavior is completely duplicated by the A′ band except for the previously mentioned different spacing of the lines.

It occurred to us that the A′ band might result from an isotope of oxygen and we have found that it is fully explained as originating from an oxygen molecule consisting of an atom of mass 16 combined with an atom of mass 18. Such an isotope has not previously been observed but its existence in small amount has certainly not been disproved. Since it is of practically the same mass as water, it might easily be misinterpreted in a mass spectrograph.

The necessary equations for this calculation have been given by Loomis.[3] The electron excitation is assumed to be identical, within the limit of error, for both the heavier and lighter molecules. Only the $^1/_2 \longrightarrow {}^1/_2$ vibration change was observed in the weak system. The vibrational isotope effect is given by the formula

$$\nu_2^{n={}^1/_2} - \nu_1^{n={}^1/_2} = (\rho - 1)\nu_1^{n={}^1/_2}$$

where $\rho = \sqrt{(M_1 + M_2)/2M_2}$ and M_1 and M_2 are the masses of the respective atoms. The rotational isotope effect is given by

$$\nu_2^m - \nu_1^m = (\rho^2 - 1)\nu^m$$

where m is the rotational quantum number. The symbol ν refers to the energy change divided by h for the various states concerned. The total isotope effect is the sum of the two.

Using the above formulas we obtain the following expressions for the isotopic doublets.

$$\begin{aligned}\Delta\nu_P &= 2.12 + 0.0556\ [B''m^2 - \beta''m^4 - B'(m-1)^2 + \beta'(m-1)^4]\\ \Delta\nu_R &= 2.12 + 0.0556\ [B''m^2 - \beta''m^4 - B'(m+1)^2 + \beta'(m+1)^4]\\ m &= \frac{3}{2}, \frac{7}{2}, \frac{11}{2}, \ldots\end{aligned}$$

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[3] Loomis, *Bull. Nat. Res. Council,* **11**, Chap. V (1926).

The constants as given by Dieke and Babcock are $B'' = 1.438$, $\beta'' = 6.31 \times 10^{-6}$, $B' = 1.390$ and $\beta' = 5.75 \times 10^{-6}$.

The rotation quantum number m is retained for convenience in using the equation of Dieke and Babcock instead of using the formulation in terms of j_k as indicated by wave mechanics. $m = j_k + {}^1/_2$, where j_k is the number of units of angular momentum due to the rotation of the molecule.

The first term, 2.12 cm.$^{-1}$, in the doublet formulas is the vibrational isotope effect for the zero point state of one-half unit of vibration. Its calculation makes use of the formula given by Birge[4] for the vibration of the normal oxygen molecule

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

and of that given by Dieke and Babcock[2] for the 1.6-volt level

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

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

In accordance with wave mechanics both of these formulas should be transposed so that the state given as zero by the formulas corresponds to $n = {}^1/_2$.

Dieke and Babcock's j numbering of the lines is correct if it is taken as $j (= j_k)$ of the molecule in the upper state.

The calculated and observed values are given in Table I.

TABLE I

ROTATIONAL–VIBRATIONAL ISOTOPE DOUBLETS FOR OXYGEN

j_k, normal state	Calcd. separation in cm.$^{-1}$	$P_1' - P_1$	$P_2' - P_2$	j_k, normal state	Calcd. separation in cm.$^{-1}$	$R_1' - R_1$	$R_2' - R_2$
1	2.28	2.25	Excl. transition	1	1.82	..	..
				3	1.53	..	1.49
3	2.62	2.57	2.52	5	1.27	1.28	1.27
5	2.97	2.91	2.93	7	1.03	0.95	0.93
7	3.35	3.29	3.32	9	0.81	.75	.74
9	3.75	3.70	3.72	11	.61	.59	.55
11	4.17	4.10	4.13				
13	4.61	4.55	4.57				
15	5.07	5.01	5.01				
17	5.56	5.50	5.46				

The average deviation of observed minus calculated separations is -0.05 cm.$^{-1}$. The maximum deviation is -0.13 cm.$^{-1}$. This is well within the limit of accuracy of the data and is certainly better than we had expected in view of Dieke and Babcock's remarks about the accuracy.

We would obtain about the same ρ from a 17–17 molecule but calculation shows a poorer agreement with the data and the chance of formation of such molecules rather than 16–17 molecules seems definitely to eliminate it as a possibility. No other possibility would give even rough agree-

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[4] Birge, *Bull. Nat. Res. Council*, **11**, Chap. V (1926).

ment. We are thus forced to conclude that an isotope of oxygen, mass 18, exists in the earth's atmosphere. From the relative intensities of the bands the amount must be very small and would thus be difficult to detect in a mass spectrograph. It seems possible that the 16–18 molecule might be a more efficient absorber of radiation than the 16–16 molecule due to the slight polarity introduced by the zero point vibration; thus relative intensities may be taken as an upper limit to the amount of 16–18 oxygen present.

Our conclusions are supported by the absence of the excluded line in the A′ band which would correspond to the $j'' = 0 \longrightarrow j' = 0$ transition, as was pointed out by Mulliken. It may also be noted that the vibrational and rotational isotope effects considered independently are in agreement. For example, $I_{18-16}/I_{16-16} = 1.059$ is the theoretical ratio of the two moments of inertia, while Dieke and Babcock's constants give 1.062 for the ratio in the normal state and 1.060 for the 1.6-volt level.

Addendum

Since the above paper was written, we have communicated with Mr. H. D. Babcock, of Mount Wilson Observatory, who has kindly placed some additional material in our hands. This consists of thirty-four weak lines and we have found that twenty-seven of these are due to the 16–18 oxygen molecule, being the alternate lines in the P_1', P_2', R_1' and R_2' series referred to above. This is in accordance with the predictions of wave mechanics since when the two ends of a molecule are different, all the rotation levels should be present. Since the lines corresponding to these new members of the above series do not occur in the 16–16 band, isotopic doublets are not observed in this case We have, therefore, made use of the equations given by Dieke and Babcock for the 16–16 molecule combined with the isotope effect to calculate the wave numbers to be expected for the new lines. In making this calculation we found that the equations of Dieke and Babcock did not reproduce their published data with sufficient accuracy for our purpose so we made use of a linear deviation plot in calculating the positions of the new lines.

The observed and calculated values are given below in Table II. The designations are in accordance with those used by Dieke and Babcock.[2] The quantum number j refers to the rotation state in the upper electronic level. The symbol *b* indicates that an observed line has been used in two places and *bb* indicates use in three places. The symbol *d* is used where the line is known to be double. A number of the missing lines have undoubtedly been obscured by near coincidence with strong lines of the A band.

The seven unexplained lines which do not necessarily belong to oxygen are given in Table III.

TABLE II

OBSERVED LINES DUE TO 16–18 OXYGEN MOLECULE COMPARED WITH VALUES CALCULATED FROM 16–16 MOLECULE DATA

P_1' (*j*)	λ	$\nu_{\text{vac.}}$	$\nu_{\text{calcd.}}$
1	7,621.312	13,117.50	13,117.49
3	......	......	111.64
5	.....	......	105.44
7	32.150	13,098.87*b*	13,098.89
9	.....	......	91.99
11	40.47	84.60	84.72
13	44.90	77.02	77.11
15	49.581	69.02	69.14
P_2' (*j*)			
1	7,620.064	13,119.64	13,119.58
3	23.540	113.56	113.72
5	.....	......	107.48
7	31.021	100.81*b*	100.90
9	.....	......	13,093.96
11	39.32	13,086.57	86.66
13	43.79	78.92	79.01
15	48.46	70.94	71.01
17	53.34	62.60	62.66
R_1' (*j*)			
1	.....	......	13,125.74
3	7,613.569	13,130.83	130.64
5	11.002	135.26	135.30
7	08.552*d*	139.49*b*	139.61
9	06.211*d*	143.54*b*	143.54
R_1' (*j*)	λ	$\nu_{\text{vac.}}$	$\nu_{\text{calcd.}}$
11	04.2	147.0	147.14
13	02.346	150.22*b*	150.33
15	.....	......	153.19
17	7,599.215	155.64	155.66
19	.....	......	157.77
21	96.965	159.54	159.51
23	96.208d	160.85*bb*	160.92
25	95.579	161.94	161.94
27	95.245	162.51*bb*	162.60
R_2' (*j*)			
1	7,615.553	13,127.42[a]	13,127.65
3	12.574	132.55	132.59
5	09.840	137.26	137.27
7	07.358	141.55*b*	141.60
9	05.068	145.50	145.55
11	02.996	149.10	149.18
13	01.118	152.34	152.39
15	7,599.449	155.23	155.27
17	97.995	157.75	157.75
19	96.750	159.91	159.89
21	95.759	161.62*b*	161.66
23	94.970	162.99*bb*	163.08
25	94.284	164.18	164.14
27	93.848	164.94	164.82

[a] Possibly beginning state anomaly.

TABLE III

UNEXPLAINED LINES

λ	7,641.53*d*[a]	40.25	37.172*d*[a]	35.9	20.507	13.246	60.5
$\nu_{\text{vac.}}$	13,082.79	84.98	90.25	92.44	118.88	131.39	143.0

[a] Close double used once in description of A′ band.

Babcock has also estimated the relative intensities of A′ and A lines as roughly 1% and that the odd and even members of the A′ band are of about equal intensity. As we have pointed out in the above paper this probably cannot be taken as a measure of the relative amounts since the absorption coefficients may be quite different. Assuming that the two sorts of molecules did exist in the above proportions, the lighter isotope of oxygen would have an atomic weight of about 15.98. This is obtained due to the existence of twice as many levels in the 16–18 molecule, thus making the total absorption 2% of that due to 16–16 oxygen. The mass spectrograph results obtained by Aston in terms of the lighter isotope seem to fall too close to the atomic weight values based on other methods to permit a value of 15.98 for the light isotope of oxygen. The situation is complicated by the possibility of isotopes of all the light elements but the general agreement seems significant. Aston has pointed out that it is very difficult to prove the non-existence of other isotopes of oxygen with the mass spectrograph. However, this appears to be the most promising possibility for the estimation of the relative amount of O^{18}.

The presence of isotopes of oxygen will, of course, not affect chemical atomic weights except in the remote possibility of non-uniform distribution but before we can know the relationship between ordinary atomic weights and the results of the mass spectrograph, the amount of O^{18} must be known.

Another point of interest in connection with the new lines is as follows. If P, Q and R branches resulted from each of the triplet states of the oxygen molecule, we would have nine branches. Only four branches have been observed. This seems to indicate that the rotational momentum is required to change by an amount of plus or minus one that is, $\Delta j_k = \pm 1$ in addition to the usual requirement $\Delta j = \pm 1$ or 0. Professor R. S. Mulliken of the University of Chicago has called our attention to the similarity of the above selection rule to that in the atomic case where for line spectra $\Delta l = \pm 1$ and $\Delta j = \pm 1$ or 0.

Summary

The weak band in the atmospheric absorption of oxygen has been explained and demonstrates the existence of an isotope of oxygen, mass 18, present in small amount.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY OF HYDROGEN IODIDE FROM 15°K. TO ITS BOILING POINT AND ITS HEAT OF VAPORIZATION. THE ENTROPY FROM SPECTROSCOPIC DATA

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We have previously shown[1] that for hydrogen chloride and for hydrogen bromide the entropies as calculated for the gaseous state with the assistance of spectroscopic data are in agreement with those obtained from our calorimetric measurements and the third law of thermodynamics. This paper contains similar calorimetric data for hydrogen iodide, again leading to agreement between the two methods of obtaining the entropy.

Preparation of Hydrogen Iodide.—Hydrogen iodide was prepared directly from the elements in a manner very similar to that used for the preparation of hydrogen bromide. Iodine was sublimed into a large tube which was attached to a reaction tube containing a platinum spiral wound on quartz. The whole apparatus was then immersed in a water-bath which was kept at the boiling point by electrical heating of the platinum

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[1] Giauque and Wiebe, THIS JOURNAL, (a) **50**, 101 (1928); (b) **50**, 2193 (1928).