ground is subtracted from the curve, only a small activity remains in the region 30°–45°; this activity is of about the same intensity as that previously ascribed to scattering and it is probably due to the same cause. In short, the distribution found for oxygen would be nearly the same as that for carbon if the carbon curve were shifted about 15° toward smaller angles. The maximum angle of projection may, then, be taken as approximately 30° and from Eq. (6) $Q=-1.3$ MV. The agreement with the value $Q=-1.8$ MV as obtained with the excitation curve is as good as could be expected in an experiment of such low resolving power.

In conclusion, the author wishes to express his thanks to Professor Lawrence and to other workers in the laboratory for their assistance and advice in this work. The financial support of the Research Corporation and the Chemical Foundation is gratefully acknowledged.

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Rotational Structure of the Schumann-Runge Bands of Oxygen in the Vacuum Region

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Absorption bands of the Schumann-Runge system of oxygen have been photographed with a 3-meter vacuum spectrograph in the region λ1760−λ1925. A rotational analysis yields constants for the upper states which are new in the range $v'=8$ to 15 inclusive. Origins of the bands in this progression are represented within the limits of accuracy of the observations by the following equation:

$$\nu_{(v',\,0)}=49{,}014.93+700.360(v+\tfrac{1}{2})-8.0023(v+\tfrac{1}{2})^2-0.37535(v+\tfrac{1}{2})^3.$$

The energy of dissociation, D_0'', is 5.05 volts.

INTRODUCTION

A ROTATIONAL analysis of absorption bands of the Schumann-Runge system of O_2 obtainable in air at atmospheric pressure has been made by Curry and Herzberg,[1] who obtained data on the upper vibrational levels $v'=1$ to 7 inclusive. In the course of some experiments on absorption in the vacuum region of diatomic gases at low pressures, we obtained clearly resolved rotational structure of further members of the system, and have been able to extend the analysis to $v'=15$. The emission bands of this system all lie on the long wave-length side of the origin of the system and involve no upper levels with v' greater than 2; hence the absorption bands furnish the only available information about the higher levels of the upper electronic state, and we are reporting briefly the results of our analysis.

EXPERIMENTAL

The spectrograph used was designed by Professor H. E. White and built in the shops of the Physics Department. The design is similar to that of the 2-meter instrument described by Jeppesen,[2] except for the enlarged dimensions required to accommodate the 3-meter grating. The grating was ruled with about 14,000 lines per inch, at the National Physical Laboratory, in England. Light from the slit falls on the grating at a grazing angle of about 7 degrees, and the plateholder covers the range 0–3100A in the first order. Two oil diffusion pumps in series, backed by a Megavac pump, exhaust the 180-liter receiver to 10^{-5} mm in about one hour. During the absorption experiments, tank oxygen was admitted directly to the receiver at pressures ranging from 0.02 to 20 mm. At higher pressures in the receiver, the flow of gas through the slit to the discharge tube was too rapid to be balanced

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[1] Curry and Herzberg, Ann. d. Physik **19**, 800 (1934).

[2] C. R. Jeppesen, Phys. Rev. **44**, 165 (1933).

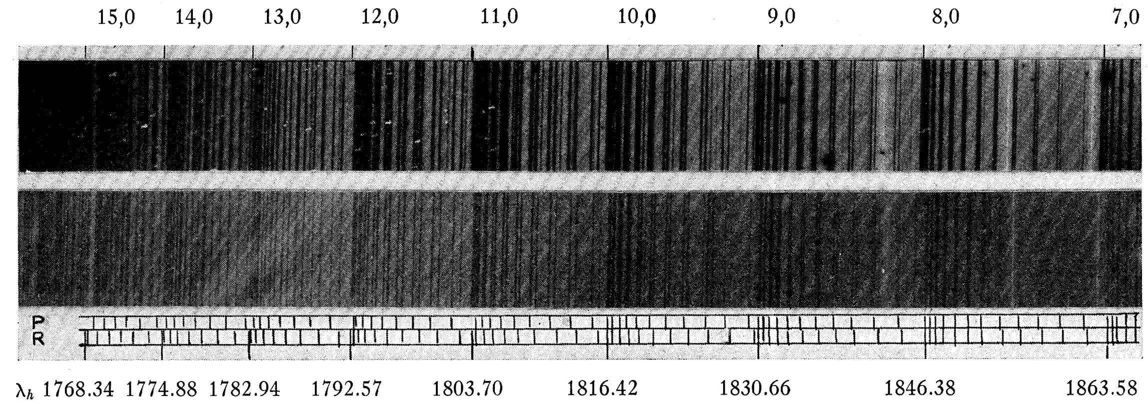

FIG. 1. Absorption bands of the Schumann-Runge system of O_2, showing rotational structure. Absorption lines are black in the reproduction. Pressure of O_2 in receiver, upper strip 15 mm, lower strip, 5 mm.

by the pumping system attached to the latter.

The source of light was a condenser discharge through a glass capillary tube, the arrangement being patterned after that of Rathenau.[3] The capillary, 30 cm long and 1 mm in inside diameter, was sealed on the end of a tapered glass tube which had a ground surface fitting into the tubular grounded electrode, and another ground surface into which the high potential electrode support was placed. Both electrodes were water cooled, so that stopcock grease could be used for assembling the tube. The capillary had to be replaced after each exposure because the interior was eroded to double the diameter by the discharge. The condenser had a capacity of 2 mf and it was charged by means of a transformer and two kenotrons to the voltage at which the discharge occurred through the capillary. It was found advisable to have a protective gap in parallel with the discharge tube to avoid shattering the glass by excessive voltages built up when the pressure in the tube became too low to conduct the discharge. The parallel gap was set to break down at about 20,000 volts, and the tube was pumped so as to operate at slightly less than that voltage. An exposure of 15 minutes comprising about 2000 sparks was required to produce strong blackening of the plates.

Wave-lengths were determined with the aid of a graph of deviations from linear dispersion prepared for each plate. A few emission lines as well as absorption lines appeared on our plates, but not enough were present to provide satisfactory standards. On one of our plates emission bands of the fourth-positive system of CO were present together with the Schumann-Runge absorption bands, the former having appeared during a prolonged warming up of the capillary by means of an ordinary 60-cycle high voltage transformer discharge. The wave-lengths of the CO heads as given by Read[4] served to establish a correction curve for the plate which was used to obtain satisfactory values for selected Schumann-Runge band lines on the same plate. The latter, in turn, were then available for plotting the corrections on other plates on which direct standards were lacking. A few of the lines recently remeasured by Boyce and Rieke[5] appeared on some of the plates, and indicated that the absolute error probably is less than 0.05A. The relative error in any band appears to be less than 0.02A. Lines 0.12A apart were clearly resolved.

RESULTS

The bands reproduced in Fig. 1 illustrate the extent of the resolution of the band structure. In bands near the origin of the system, the lines $P(K)$ and $R(K+2)$ are closer together, and cannot be resolved near the heads of the bands. Observed lines as assigned are listed in Table I, the letter P or R being used to call attention to a line which is assigned in both branches. No Q branch is expected or observed in these bands.

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[3] G. Rathenau, Zeits. f. Physik **87**, 32 (1933).

[4] D. N. Read, Phys. Rev. **46**, 571 (1934).

[5] Boyce and Rieke, Phys. Rev. **47**, 653 (1935).

TABLE I. *Observed band lines, in cm^{-1}.*

K	$R(K)$	$P(K)$
	(4,0) $\nu_0=51{,}969.6$	
1		51,972.3 R
3	51,972.3 P	960.7 R
5	960.7 P	945.9 R
7	945.9 P	922.7 R
9	922.7 P	900. R
11	900. P	868. R
13	868. P	830. R
15	830. P	
	(5,0) $\nu_0=52{,}562.6$	
1		52,560.2 R
3	52,560.2 P	550.0 R
5	550.0 P	534.5 R
7	534.5 P	513.8 R
9	513.8 P	487.4 R
11	487.4 P	454.9 R
13	454.9 P	417.5 R
15	417.5 P	374.1 R
17	374.1 P	325.3 R
19	325.3 P	271.2 R
21	271.2 P	211.1 R
23	211.1 P	
	(6,0) $\nu_0=53{,}124.3$	
1	53,125.4	53,122.0 R
3	122.0 P	111.5 R
5	111.5 P	095.7 R
7	095.7 P	074.1 R
9	074.1 P	046.5 R
11	046.5 P	53,013.3 R
13	53,013.3 P	52,974.5 R
15	52,974.5 P	930.2 R
17	930.2 P	879.6 R
19	879.6 P	823.7 R
21	823.7 P	762.1 R
23	762.1 P	694.3 R
25	694.3 P	620.5 R
27	620.5 P	
	(7,0) $\nu_0=53{,}658.5$	
1	53,660.1	53,656.1 R
3	656.1 P	645.2 R
5	645.2 P	629.8 R
7	628.8 P	606.9 R
9	606.9 P	579.1 R
11	579.1 P	545.0 R
13	545.0 P	506.8
15	504.0	461.1
17	457.1	408.6
19	405.2	351.1
21	348.0	287.9
23	283.9	218.4
25	213.6	142.3
	(8,0) $\nu_0=54{,}158.9$	
1	54,160.0	54,154.7 R
3	154.7 P	146.2
5	143.0	130.7
7	126.6	107.3
9	102.0	079.2
11	073.5	044.1
13	54,037.7	54,003.2
15	53,997.7	53,956.3
17	950.2	903.1
19	895.5	844.5
21	836.9	779.3
23	770.6	707.7
25	699.0	
	(9,0) $\nu_0=54{,}624.4$	
1	54,625.1	54,619.4 R
3	619.4 P	610.5
5	607.5	594.1
7	590.2	571.2
9	565.8	541.7
11	536.3	506.0
13	499.5	464.8
15	456.1	416.4
17	407.3	362.0
19	351.7	301.2
21	289.7	233.7
23	221.7	
	(10,0) $\nu_0=55{,}053.3$	
1	55,053.4	55,048.5 R
3	048.5 P	55,040.3
5	036.1	55,021.5
7	55,017.3	54,998.2
9	54,992.2	968.6
11	960.5	932.1
13	922.7	889.0
15	878.1	839.3
17	826.6	782.8
19	769.9	720.5
21	704.3	649.8
23	632.9	
	(11,0) $\nu_0=55{,}441.5$	
1	55,441.6	55,436.4 R
3	436.4 P	428.1
5	423.2	409.9
7	403.8	385.7
9	377.4	355.4
11	344.3	316.5
13	304.5	271.3
15	257.8	220.9
17	204.1	163.3
19	144.1	097.6
21	076.7	
	(12,0) $\nu_0=55{,}786.9$	
1	55,785.8	55,780.5 R
3	780.5 P	773.1
5	767.5	754.7
7	746.6	729.6
9	719.0	697.6
11	684.2	658.8
13	642.7	612.4
15	593.6	559.0
17	537.3	499.4
19	474.8	—
	(13,0) $\nu_0=56{,}087.6$	
1	56,086.5	—
3	080.2	56,073.3
5	066.1	055.1
7	044.7	56,029.0
9	56,015.5	55,996.1
11	55,979.5	955.3
13	935.6	907.5
15	884.7	852.2
17	825.7	—
	(14,0) $\nu_0=56{,}342.6$	
1	56,341.9	—
3	334.9	56,327.6
5	320.0	308.9
7	297.*	282.2
9	266.4	247.4
11	228.1	206.7
13	183.6	155.5
15	128.1	099.1
	(15,0) $\nu_0=56{,}551.0$	
1	56,550.2	
3	542.9	56,534.9
5	527.5	519.5*
		515.4*
7	505.2	494.0
	501.6	483.8
9	471.6	457.9
	468.1	451.9
11	431.8	412.4
	427.7	407.6
13	383.8	360.3
	378.7	355.2

* blend
P, *R* indicate lines assigned in both branches.

Both the upper and the lower electronic states are triplets, but the triplet separation is too small to be observed in these bands, as is clearly seen in Fig. 1. However, in the (14,0) band, the lines are slightly broadened, and in the (15,0) band they are clearly doubled. This splitting is much greater than that found in the emission bands as discussed by Lochte-Holtgreven and Dieke,[6] which appears with higher K values. In the (16,0) band, the structure is too complicated to be followed. No explanation is offered for these observed perturbations.

The rotational constants of the upper states have been deduced from the data of Table I by the following method, in order to avoid emphasis on values displaced by blending of lines. Making use of the relationship:

$$R(K)-P(K)=\Delta_2F'(K)$$
$$=4B'(K+\tfrac{1}{2})-8D'(K+\tfrac{1}{2})^3$$

the values of $\Delta_2F'(K)/(K+\frac{1}{2})$ were plotted against $(K+\frac{1}{2})^2$, and the best straight line was drawn through the points for each band. The intercept at $K=-\frac{1}{2}$ is $4B'$. The values of B' are expressible as a function of v' by the following equation, of which the coefficients were obtained by the method of least squares:[7]

$$B'=0.801-0.00651v'$$
$$-0.001079v'^2-0.0000056v'^3.$$

The calculated values are listed in Table II. Also listed are the constants for the lower state, based on the work of Mecke and Baumann[8] on the atmospheric absorption bands in which the frequency resolution is much greater than here.

The origin of each band was computed with the smoothed (calculated) values of B', and the B'' values just mentioned, for four selected lines

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[6] Lochte-Holtgreven and Dieke, Ann. d. Physik **3**, 937 (1929).

[7] Use was made of the abbreviated method of computing devised by Birge and Shea, U. Calif. Pub. Math. **2**, 67 (1927).

[8] Mecke and Baumann, Zeits. f. Physik **73**, 139 (1931).

TABLE II. *Rotational constants.*

v'	B'_v calc. (cm^{-1})	Obs.-Calc. (cm^{-1})
0	0.801	—
1	0.793	+0.005*
2	0.784	+1*
3	0.772	−2*
4	0.757	−3*
5	0.741	−6*
6	0.722	−3
7	0.701	+2
8	0.677	−6
9	0.651	±0
10	0.622	+11
11	0.591	+2
12	0.558	−4
13	0.522	+1
14	0.483	+9
15	0.442	−11

* Observed values from Curry and Herzberg,[1] also the following data: $D' = 4.38 \times 10^{-6}$ cm^{-1}; $B'' = 1.4377$ cm^{-1} and $D'' = 4.88 \times 10^{-6}$ cm^{-1}.

TABLE III. *Origins of absorption bands.*

v', v''	$\nu_{\text{calc.}}$ (cm^{-1})	Obs.-Calc. (cm^{-1})
0,0	49,363.1	—
1,0	50,046.2	−0.6*
2,0	50,710.0	+0.7*
3,0	51,352.4	−0.2*
4,0	51,970.3	−0.7
5,0	52,562.4	+0.2
6,0	53,126.1	−1.8
7,0	53,659.2	−0.7
8,0	54,159.3	−0.4
9,0	54,624.3	+0.1
10,0	55,051.9	+1.4
11,0	55,439.9	+1.6
12,0	55,786.0	+0.9
13,0	56,087.9	−0.3
14,0	56,343.4	−0.8
15,0	56,550.2	+0.8

* Observed values from Curry and Herzberg.[1]

in each band. The origins are represented with adequate accuracy by the equation[7]

$$\nu_{(v',\,0)} = 49{,}014.93 + 700.360(v+\tfrac{1}{2}) - 8.0023(v+\tfrac{1}{2})^2 - 0.37535(v+\tfrac{1}{2})^3.$$

In Table III the computed values are listed, together with residuals (obs.-calc.) based on Curry and Herzberg's values for $v' = 1$ to 3 and our values for the other origins. The extrapolated value for the origin of the (0,0) band is 49,363.1 cm^{-1}, which is 5.4 cm^{-1} greater than that obtained by the extrapolation of Curry and Herzberg.

DISCUSSION

On the basis of data available in 1929, Birge[9] found it necessary to use two parabolas to represent ω_v as a function of v for the "B" level of oxygen, whereas the present data are adequately represented by a single parabola. The earlier data were taken from the work of Leifson[10] and some unpublished work of Pulskamp.[11] In neither case was the fine structure completely resolved; in fact, Leifson observed only band heads. This lack of resolution, together with the scarcity of suitable standards, is quite enough to account for the complications encountered by Birge. The present data extend to an energy of vibration representing 96 percent of that required for dissociation. Extrapolation leads to a value of 7.01 electron volts, compared with 7.05 electron volts based on the earlier data. Assuming that the molecule dissociates from this state into one unexcited atom, and one ^1D atom with 1.96 electron volts energy, the value obtained for D_0'' is 5.05 electron volts.

ACKNOWLEDGMENTS

The authors have enjoyed discussions with Professor F. A. Jenkins throughout this work, and have been materially aided by his generous assistance. They acknowledge with thanks also the interest of Professor R. T. Birge in the analysis. The senior author is particularly thankful for the excellent research facilities provided for him by the Department of Physics at Berkeley during his vacation from the Ohio State University.

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[9] R. T. Birge, Trans. Faraday Soc. **25**, 707 (1929).

[10] S. W. Leifson, Astrophys. J. **63**, 73 (1926).

[11] C. A. Pulskamp, Ph.D. Thesis, U. of California (1929).

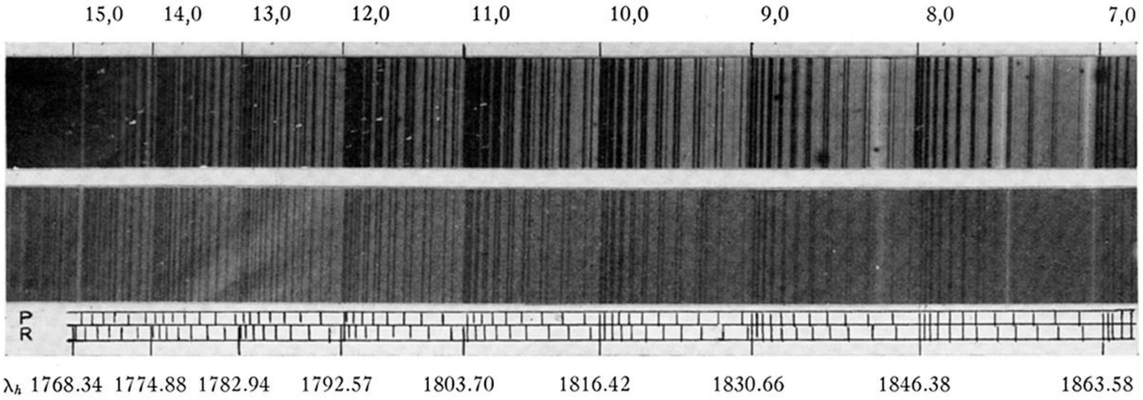

FIG. 1. Absorption bands of the Schumann-Runge system of O_2, showing rotational structure. Absorption lines are black in the reproduction. Pressure of O_2 in receiver, upper strip 15 mm, lower strip, 5 mm.