NEW TERMS IN THE OXYGEN ARC SPECTRUM

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Abstract

Methods have been developed for the powerful excitation of the oxygen arc spectrum in the absence of bands, in large diameter heavy current discharge tubes and in narrow capillary quartz discharge tubes. In both tubes the green auroral line appears strongly. The oxygen arc spectrum has been photographed with these discharge tubes with large dispersion and many new lines have been observed. Fifty new lines have been classified in the oxygen arc spectrum involving six new triplet terms and one new singlet term based on the $2s^22p^3(^2D)$ and $2s^22p^3(^2P)$ configurations of the ion.

Apparatus and Procedure

The strong excitation of the oxygen arc spectrum in discharge tubes is often rendered difficult by the appearance of numerous bands of the neutral and ionized molecule. These bands may be easily eliminated in two ways. One method is similar to the well-known experiments of Wood[1] on the excitation of the Balmer spectrum in absence of hydrogen bands. The atoms formed in the oxygen discharge show a strong tendency to recombine under the influence of any catalytically acting substance. With current densities of as little as 50 milliamperes/cm^2 the walls of the tube are strongly heated, the sodium of the glass vaporizes and accelerates catalytically the recombination of the atom with the emission of the oxygen band spectrum. The recombination may be prevented by water-cooling the glass walls and part of the measures here described were made with such water-cooled discharge tubes. The tubes had a length of about 60 centimeters and diameters of 30 to 50 millimeters. Large double-walled brass electrodes, cooled by flowing water, were set in side-tubes so that the discharge could be observed end-on. A constant current of 5 amperes from a 10 kw 2000 volt generator was sent through the tubes, and regulated by suitable ballast resistances. Oxygen either electrolytic or obtained by heating potassium permanganate was purified by liquefaction, dried, and drawn constantly through the discharge tube by an oil pump. At a pressure of a few millimeters the discharge formed a rosy core along the axis of the tube and under these conditions the oxygen arc spectrum is very brilliant and the green aurora line 5577.350A appears strongly. Slight impurities on the glass tube wall greatly diminish the intensity of the arc lines. Dust or sealing wax particles have a catalytic action on the recombination of the atoms into molecules. Dusting the walls with salts like alkali chlorides, which have no affinity for

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[1] R. W. Wood, Proc. Roy. Soc. London **A97**, 455 (1920).

oxygen, however suppresses the recombination strongly. With such discharge tubes, the oxygen arc spectrum was photographed with large glass and quartz spectrographs built in this laboratory.

The oxygen arc spectrum may also be brilliantly excited by the use of high current densities in narrow capillaries. Oval quartz capillaries of 1×2 milli-

TABLE I.

Intensity	Wave-lengths	Wave-numbers (vacuum)	Classification	Wave-numbers (calculated)
5	8819.60	11335.27		
2	8586.00	11643.67		
1	8575.32	11658.18		
1	8508.66	11749.51		
1	8429.128	11860.37	$3s(^2P):{}^3P_0-4p(^2D):{}^3D_1$	11860.27
2	8428.342	11861.47	$3s(^2P):{}^3P_1-4p(^2D):{}^3D_2$	11861.49
4	8426.326	11864.46	$3s(^2P):{}^3P_2-4p(^2D):{}^3D_3$	11864.46
1	8424.780	11866.49	$3s(^2P):{}^3P_1-4p(^2D):{}^3D_1$	11866.58
1	8420.968	11871.87	$3s(^2P):{}^3P_2-4p(^2D):{}^3D_2$	11871.85
4	8235.408	12139.38	$3s(^2D):{}^3D_1-3p(^2D):{}^3P_2$	12139.45
15	8233.085	12142.80	$3s(^2D):{}^3D_1-3p(^2D):{}^3P_{1,0}$	12142.85
10	8230.016	12147.32	$3s(^2D):{}^3D_2-3p(^2D):{}^3P_2$	12147.32
10	8227.680	12150.77	$3s(^2D):{}^3D_2-3p(^2D):{}^3P_{1,0}$	12150.72
20	8221.829	12159.40	$3s(^2D):{}^3D_3-3p(^2D):{}^3P_2$	12159.34
4	7995.086	12504.25	$3p(^4S):{}^3P_2-3s(^2D):{}^3D_3$	12504.25
1	7987.404	12516.26	$3p(^4S):{}^3P_2-3s(^2D):{}^3D_2$	12516.27
2	7987.036	12516.84	$3p(^4S):{}^3P_{1,0}-3s(^2D):{}^3D_2$	12516.83
1	7982.408	12524.10	$3p(^4S):{}^3P_2-3s(^2D):{}^3D_1$	12524.14
1	7981.990	12424.75	$3p(^4S):{}^3P_{1,0}-3s(^2D):{}^3D_1$	12524.70
4	7952.182	12571.72	$3s(^2D):{}^3D_1-3p(^2D):{}^3F_2$	12571.72
6	7950.824	12573.87	$3s(^2D):{}^3D_2-3p(^2D):{}^3F_3$	12573.91
10	7947.566	12579.00	$3s(^2D):{}^3D_3-3p(^2D):{}^3F_4$	12579.00
3	7947.204	12579.59	$3s(^2D):{}^3D_2-3p(^2D):{}^3F_2$	12579.59
3	7943.178	12585.96	$3s(^2D):{}^3D_3-3p(^2D):{}^3F_3$	12585.96
3	7480.652	13364.15	$3s(^2P):{}^3P_0-3p(^2P):{}^3D_1$	13364.05
3	7479.148	13366.84	$3s(^2P):{}^3P_1-3p(^2P):{}^3D_2$	13366.95
2	7477.264	13370.22	$3s(^2P):{}^3P_1-3p(^2P):{}^3D_1$	13370.36
5	7476.473	13371.65	$3s(^2P):{}^3P_2-3p(^2P):{}^3D_3$	13371.65
2	7473.226	13377.47	$3s(^2P):{}^3P_2-3p(^2P):{}^3D_2$	13377.31
2	7471.374	13380.75	$3s(^2P):{}^3P_2-3p(^2P):{}^3D_1$	13380.72
5	7157.360	13967.80	$3d(^4S):{}^3D_{1,2}-3p(^2D):{}^1P_1$	13970.2
1	6727.138	14861.06	$3s(^4S):{}^5S_2-3p(^4S):{}^3P_{0,1}$	14861.28
5	6727.866	14861.68	$3s(^4S):{}^5S_2-3p(^4S):{}^3P_2$	14861.84
4	6654.121	15024.14		
5	6374.292	15683.64		
4	6366.282	15703.42		
3	6324.682	15806.71	$3d(^4S):{}^3D_{1,2,3}-3p(^2D):{}^3P_2$	15806.43
1	6323.283	15810.21	$3d(^4S):{}^3D_{1,2}-3p(^2D):{}^3P_{1,0}$	15809.83
1	6266.692	15952.98		
2	6264.346	15958.95	} 7.73	
5	6261.314	15966.68		
1	6258.965	15972.67	} 11.99	
3	6256.616	15978.67		
3	6106.398	16371.76		
3	5995.198	16675.43		
1	5993.102	16681.24		
2	5991.852	16684.72		
1	5991.255	16686.39		
5	5750.424	17385.22	} 58.61	
3	5731.103	17443.83	} 31.98	
1	5720.613	17475.81		
3	5410.76	18476.6	} 7.4	(wave-lengths by
4	5408.59	18484.0	} 12.7	Fowler: Report
3	5404.87	18496.7		on line spectra)

TABLE I. (*Continued*)

Intensity	Wave-lengths	Wave-numbers (vacuum)	Classification	Wave-numbers (calculated)
5	4233.32	23615.5	} 58.9	wave-lengths by
3	4222.78	23674.4	}	Fowler: Report
2	4217.09	23706.4	} 32.0	on line spectra
10	3954.387	25279.36	$3p(^4S):{}^3P_2-3s(^2P):{}^3P_2$	25279.34
5	3954.596	25279.87	$3p(^4S):{}^3P_{1,0}-3s(^2P):{}^3P_2$	25279.87
2	3953.056	25289.73	$3p(^4S):{}^3P_2-3s(^2P):{}^3P_1$	25289.70
1	3952.982	25290.24	$3p(^4S):{}^3P_{1,0}-3s(^2P):{}^3P_1$	25290.26
3	3951.987	25296.57	$3p(^4S):{}^3P_{1,0}-3s(^2P):{}^3P_0$	25296.57
1	3825.530	26132.78	$3s(^2D):{}^3D_1-3p(^2P):{}^3D_2$	26132.51
4	3825.249	26134.70	$3s(^2D):{}^3D_2-3p(^2P):{}^3D_3$	26134.72
3	3825.090	26135.65	$3s(^2D):{}^3D_2-3p(^2P):{}^3D_1$	26135.92
3	3824.425	26140.33	$3s(^2D):{}^3D_1-3p(^2P):{}^3D_2$	26140.38
—	—	—	$3s(^2D):{}^3D_2-3p(^2P):{}^3D_1$	26143.79
10	3823.469	26146.85	$3s(^2D):{}^3D_3-3p(^2P):{}^3D_3$	26146.74
—	—	—	$3s(^2D):{}^3D_3-3p(^2P):{}^3D_2$	26152.40
—	2883.82	34666.3	$3s(^4S):{}^3S_1-3p(^2D):{}^1P_1$	34663.5
				(wave-lengths by Hopfield l.c. (λvac.!))
—	1217.6	82128.78	$2p:{}^1S_0-3s(^2P):{}^1P_1$?	—
—	1152.0	86805.86	$2p:{}^1D_2-3s(^2P):{}^1P_2$?	
—	999.47	100053.0	$2p:{}^1D_2-3s(^2P):{}^1P_1$?	
—	990.73[2]	100935.7	$2p:{}^3P_0-3s(^2D):{}^3D_1$	100922
—	990.11	100998.9	$2p:{}^3P_1-3s(^2D):{}^3D_{1,2}$	{100981, 100989}
—	988.67	101146.0	$2p:{}^3P_2-3s(^2D):{}^3D_{1,2,3}$	{101128, 101140, 101148}

meters cross-section were used, with heavy iron electrodes in side tubes, externally water-cooled. These tubes carried steady currents of 1.2 to 1.5 amperes. Spectrograms were made with the 6.5 meter grating in Paschen mounting in the third basement of the laboratory. The temperature was so constant here that exposures of 72 hours showed no broadening of the lines. As an indication of the intensity of the light source it may be said that the strong infra-red doublet λ8446A of oxygen was strongly recorded in the first order of the grating on neocyanin plates in 10 seconds. Spectrograms were made on Eastman neocyanin and kryptocyanin plates, Ilford panchromatic plates and Cramer contrast plates. The iron arc lines were used as standards. Part of the exposures were made with commercial oxygen and showed weakly the strongest nitrogen lines as well as argon lines which were also used as standards.

In contrast to other observers[3] who found the auroral line 5577.350A only in wide tubes, it appeared likewise strongly in the narrow capillaries and was photographed with the grating. It is possible that the slight argon content of the oxygen used may have strengthened the line. Such powerful

[2] Unpublished classification of S. B. Ingram, privately communicated.

[3] J. C. McLennan, J. H. McLeod and W. C. McQuarrie, Proc. Roy. Soc. London **A114,** 1 (1927).

excitation of the auroral line in narrow capillaries would greatly simplify investigations of the Zeeman effect of this line in comparison with the methods hitherto[4] used.

Table I contains the lines measured on the spectrograms taken with the big grating. It is noteworthy that none of the oxygen spark lines in the visible or near ultra-violet appear in direct current discharges in oxygen. The lines 2883 and 3954 previously given as spark lines[5] belong to the arc spectrum. The latter is not identical with a spark-line of the same wave-length, since this line belongs to a spark doublet whose other component does not appear in the oxygen arc spectrum.

In Table I there are, among other lines, all the unclassified lines observed by Runge and Paschen.[6] Our exposures with the grating extend only to 3800A and we have not observed the region of the short wave-length lines measured by Schniederjost[7] and Jevons.[8] Jevons has however shown that all

TABLE II.

	$2p$	$^3P_2$:109831 $^3P_1$:109672 $^3P_0$:109605	$^1D_2$, $^1S_0$		
		$2s^22p^3$:^4S	$2s^22p^3$:^2D	$2s^22p^3$:^2P	$2s2p^4$:^4P
	$3s$	$^5S_2$:36069.0 $^3S_1$:33043.3	$^3D_3$: 8702.91 $^3D_2$: 8690.89 $^3D_1$: 8683.02 $^1D_2$	$^3P_2$: − 4072.10 $^3P_1$: − 4082.54 $^3P_0$: − 4088.85 $^1P_1$	
$2s^22p^3$	$3p$	$^5P_1$:23211.9 $^5P_2$:23209.2 $^5P_3$:23205.8 $^3P_{0,1}$:21207.72 $^3P_2$:21207.16	$^3F_4$: −3876.09 $^3F_3$: −3883.02 $^3F_2$: −3888.70 $^3P_2$: −3456.43 $^3P_1$: −3459.83 $^1P_1$: −1620.2 $^3D_{1,2,3}$, $^1F_3$, $^1D_2$	$^3D_3$: −17443.83 $^3D_2$: −17449.49 $^3D_1$: −17452.90 $^3P_{0,1,2}$, $^3S_1$ $^1D_2$, $^1P_1$, $^1S_0$	
	$3d$	$^5D_{0,1,2,3,4}$:12417.3 $^3D_{1,2,3}$:12350.0	$^3G_{3,4,5}$, $^3F_{2,3,4}$, $^3D_{1,2,3}$, $^3P_{0,1,2}$ $^3S_1$ $^1G_4$, $^1F_3$, $^1D_2$, $^1P_1$ $^1S_0$	$^3F_{2,3,4}$, $^3D_{1,2,3}$, $^3P_{0,1,2}$ $^1F_3$, $^1D_2$, $^1P_1$	
$2s2p^4$	$2p$				$^3P_{0,1,2}$ $^1P_1$

the lines ascribed by Schniederjost to the oxygen arc spectrum are,—with the exception of λλ2895.37, 2883.93, 2858.81, 2708.18,—bands heads due to carbon compounds.

[4] J. C. McLennan, Proc. Roy. Soc. London **A120**, 327 (1928).

[5] W. Jevons, Phil. Mag. VI, **47**, 586 (1924); F. Paschen, Ann. d. Physik **23**, 261 (1907).

[6] C. Runge und F. Paschen, Ann. d. Physik **61**, 641 (1897).

[7] W. Schniederjost, Zeits. f. wiss. Phot. **2**, 283 (1904).

[8] W. Jevons, reference 4.

Since the intensity of the lines in the infra-red depends to so great an extent on the sensitizing of the plates, the intensities given are only comparable within the individual line groups.

Discussion

Table II and Fig. 1 give a summary of the terms to be expected on the Hund theory and those found. The diagram also shows the newly observed combinations. The term $2s^2\ 2p^3\ (^2D)\ 4p^3$: $D_{1,\ 2,\ 3}$ ($^3D_1 = 15949.12$, $^3D_2 = 15944.03$, $^3D_3 = 15936.64$) is not included in Table II.

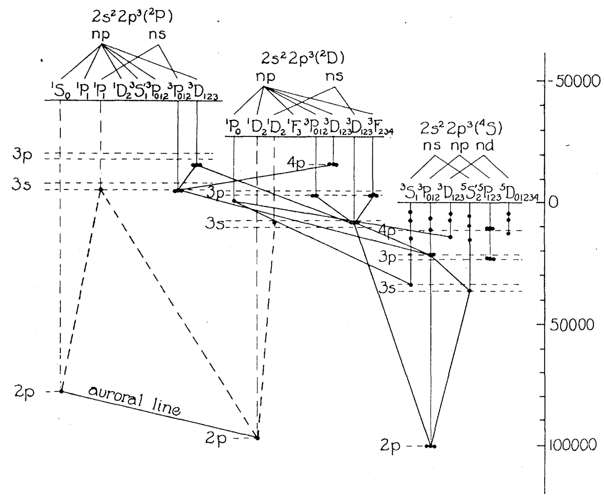

Fig. 1.

The oxygen arc spectrum is based on the deepest terms of the ion: $2s^22p^3:{}^4S$, $2s^22p^3:{}^2D$, $2s^22p^3:{}^2P$ and perhaps also $2s2p^4:{}^4P$ must be considered. The Runge-Paschen series as well as Hopfield's ultra-violet series are built on the deepest term of the ion: $2s^22p^3:{}^4S$. The deepest term ^3P is common to all three systems belonging to the configuration $2s^22p^3$.

On the basis of the very complete analysis of the O II spectrum by Fowler[9] and by Bowen[10] it is possible to predict the approximate position and separation of the arc terms. In the figure the approximate position of the terms $2s^22p^3(^1D)3s$, $2s^22p^3(^2D)3p$, $2s^22p^3(^2P)3s$ and $2s\,^22p\,^3(^2P)3p$ is indicated. They are located by displacing the Runge-Paschen terms $2s^22p^3(^4S)3s$, $(^5S, {}^3S)$ and $2s^22p^3\ (^4S)3p(^5P, {}^3P)$ by the distance from the limit ^4S to the limits ^2D and ^2P respectively. It will be seen from the figure that the terms fall near the positions so determined.

The triplet separations give another indication of the correctness of the arrangement. The series limit of the ordinary Runge-Paschen series, the low

[9] A. Fowler, Proc. of the Roy. Soc. London **A110**, 476 (1926).
[10] J. S. Bowen, Phys. Rev. **29**, 242 (1927).

term ^4S of the ion is single which accounts for the relatively small separations of the triplet and quintet terms. The separations of the inverted terms of the ion $2s^22p^3:{}^2D$ and $2s^22p^3:{}^2P$ are 20 and 4.5 respectively. The new arc terms are also inverted and have the expected separations. In the term $2s^22p^3(^2D)3s:{}^3D$ the separation of the outer components is exactly 20 frequency units, for the other terms it is at least of the same order; in any case significantly greater than the separations of the Runge-Paschen terms.

The assignment of inner quantum numbers could in every case be made unambiguously from the observed combination. In one combination $2s^2 2p^3(^2D)3s:{}^3D-2s^22p^3(^2P)3p:{}^3D$ two strong lines are missing. For the strongest line of this multiplet however there is an old Zeeman effect determination by Paschen and Back,[11] who observed a triplet of 4/3 normal separation. According to the table of anomalous Zeeman effect of Kiess and Meggers[12] this Zeeman effect is found only for the line $^3D_3-{}^3D_3'$.

One two-fold term, -3459.83 and 3456.43, has been assumed to be an incompletely resolved ^3P term, in which the two components $^3P_0$ an $^3P_1$ fall together. These two terms do not appear to be two singlet terms since the combination with a ^3D term is very strong and since the five lines comprising this group under the most varied conditions of discharge seem in intensity and appearance to belong to one group.

A similar case is the Runge-Paschen term $2s^22p^3(^4S)3p^3:{}^3P$. The strong combination of this term with the term $2s^22p^3(^4S)3s:{}^3S$, the infra-red line λ8446A has previously always been observed as a narrow doublet and also in this investigation with the dispersion of 6.5 meter grating it was not possible further to resolve the stronger component of this doublet. (With the present mounting of the grating this line could not be photographed in the second order since the second order lay on the Rowland circle too close to the grating. The structure of the combinations of this term with the terms $2s^22p^3(^2D)3s:{}^3D$ and $2s^22p^3(^2P)3s:{}^3P$ showed that the two components $^3P_0$ and $^3P_1$ must fall together and that this term is normal and not inverted. It would be desirable in this connection to investigate the fine structure of this as well as of the next higher ^3P terms.

A narrow doublet at 6727A is given in the Table I as the intercombination between this ^3P term and the deepest ^5S term analogous to the intercombination observed by Hopfield between the deepest ^3P term and this ^5S term.

The remaining terms to be expected could not be located in the data available. Noticeably absent are the low $^3P-$ and $^1P-$ terms arising from the addition of an additional $2p$ electron to the $2s2p^4$ configuration of the ion. Such terms are known in the analogous spectra O III, N II, C I and give rise there to strong combinations. They are to be expected at about $-10,000$ cm^{-1} in O I. The strong characteristic group $2s^22p^4\,{}^3P-2s2p^5\,{}^3P$ which should lie near 800A has never been observed in oxygen.

Among the unclassified lines in the table are the two inverted triplets at λ6260 and 5410A observed by Runge and Paschen. Although they show

[11] F. Paschen und E. Back, Ann. d. Physik **39**, 915 (1912).

[12] C. C. Kiess and W. F. Meggers, Journ. Res. Bureau of Standards **1**, 641 (1928).

exactly the separation of the triplet term $2s^22p^3(^2D)3s:{}^3D$ they are apparently not combinations of this term with negative singlet terms. For in discharges in narrow capillaries both triplets as also observed by Runge and Paschen appear with the central line far exceeding the other two in intensity. On the contrary in discharges in a mixture of a small percentage of oxygen in helium the central component is weaker than the other two. It was impossible to resolve the central line and an explanation of this intensity variation does not appear. Among the lines in the Table I are also two wider triplets at 5730 and 4220A which both have the separations 58 and 32 cm^{-1}. No other combinations of the terms common to these triplets have been observed.

The two low terms $2s^22p^4:{}^1D$ and $2s^22p^4:{}^1S$ are of especial interest. According to McLennan[13] the green auroral line 5577.350 is the forbidden transition between these terms. Even the position of these terms is unknown. The classification is supported on one side by the analogous explanation of the nebular lines by Bowen [14] and on the other by the observation of the Zeeman effect of this line made by McLennan[13] and confirmed by Sommer.[15]

Various attempts have been made to fix the location of these terms. Hopfield[16] has shown that the ultra-violet lines λλ999.47 and 1217.62 have exactly for frequency difference the freqeuncy of the auroral line, and are thus combinations of these two terms with a third term. Cario[17] and also Kaplan[18] have given approximate values for the position of these two terms ^1D and ^1S on the basis that the distance of the deeper of the two terms from the lowest term ^3P cannot be greater than the difference between this lowest term and the frequency of the shorter of the Hopfield lines, in order that the two lines may fit in the term scheme of the oxygen arc spectrum. They overlook thus the fact, that this higher term may lie higher than the deepest ionizing limit and so be negative.

The green auroral line appears strongly in mixtures of helium, neon or argon with oxygen but fails to be excited according to Cario[17] in mixtures of krypton and oxygen. Although much has been learned in recent years of the excitation process in mixtures of the noble gases and other gases, it is still not possible on the basis of the above mentioned observations to make any precise assertions over the excitation potential of the green auroral line, since the energy required for dissociation preceding this excitation is not known.

A relatively plausible approximation of the location of the metastable terms may be made by comparison[15] with the similarly constructed O III spectrum. There also are found in it the same term configurations consisting of a ^3P term as lowest term and two slightly higher metastable singlet terms ^1D and ^1S. The "forbidden" combinations between these terms give according

[13] J. C. McLennan, Proc. Roy. Soc. London **A120**, 327 (1928).
[14] I. S. Bowen, Astrophys. J. **67**, 1 (1928).
[15] L. A. Sommer, Zeits. f. Physik **51**, 451 (1928).
[16] J. J. Hopfield, Phys. Rev. **29**, 923 (1927).
[17] G. Cario, Journal Franklin Institution **205**, 515 (1928).
[18] J. Kaplan, Proc. Nat. Acad. Amer. **14**, 882 (1928).

to Bowen[14] known nebular lines and the difference $^3P-{}^1D$ is less then $^1D-{}^1S$. If the location of the deepest terms in O I is analogous, the difference $^3P-{}^1D$ would be about 15,500 cm^{-1}.

We have as yet not investigated the extreme ultra-violet. Thus it is not possible to look for other combinations of these terms with higher terms. However by the determination of the terms $2s^22p^3(^2D)3s:{}^3D$ and $2s^22p^3(^2P)3s:{}^3P$ the approximate position of the singlet terms $2s^22p^3(^2D)3s:{}^1D$ and $2s^22p^3(^2P)3s:{}^1P$ is fixed. The two above mentioned lines found by Hopfield λλ999.47 and 1217.62 as well as a further strong unclassified oxygen arc lines at 1152.0 have therefore been included in the level figure as combinations between the metastable terms and these singlet terms. One obtains thus an estimate of the position of the metastable terms which agrees with that found by comparison with the O III spectrum. The definitive explanation of these terms is held in abeyance pending the conclusion of a projected investigation of the ultra-violet oxygen spectrum.

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