NOVEMBER 1, 1933 PHYSICAL REVIEW VOLUME 44

The Arc Spectrum of Sulfur in the Ultraviolet

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(Received August 2, 1933)

A Schüler tube with a water-cooled aluminum cathode, with He gas for maintaining the discharge, was attached to a vacuum spectrograph employing a 1.5 meter grating of 15,000 lines per inch. The sulfur spectrum was excited by vaporizing some sulfur in the tube while the discharge was in operation. The wave-length range photographed was from 0–2600A, and in the region 1050–2400A many new lines were observed and classified. It was thus possible to establish the low singlet terms of the arc spectrum and some of the higher terms built on the doublet *P* and *D* states of the ion as well as some higher members of series built on the quartet *S* state of the ion.

As a continuation of the work on the arc spectra of the elements of the oxygen group, it seemed desirable next to obtain more complete data for the vacuum region. The analyses of oxygen by Frerichs[1] and Hopfield[2] being the chief guide as to the nature of all these spectra, the next succeeding element, sulfur, was chosen as the first to be studied. The discharge tube used was, however, designed with the intention that it should be equally suitable for selenium and tellurium.

The essential features of the tube, which was of the Schüler type, are shown in Fig. 1. It was attached to a vacuum spectrograph employing a 1.5 meter grating, which gave a dispersion of about 11A per mm. Suitable provision was made for the circulation and purification of the helium used in maintaining the discharge. The power was supplied by an a.c. rectifier set which would deliver currents up to 2 amperes at potentials not exceeding 2000 volts.

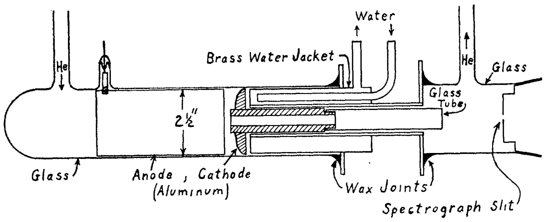

FIG. 1. Discharge tube.

The tube was first run at a high current density and the helium circulated until impurities had been removed as much as possible, after which it was taken apart and several grams of sulfur were placed in the anode end and then put back on the spectrograph. An oven was placed around the anode end, and while the discharge was in operation, the temperature was raised till the sulfur began to vaporize and its lines appeared in the visible spectrum.

A number of photographs were taken in the vacuum region with various densities of sulfur vapor and lengths of exposure up to 4 hours. As the current through the tube was increased some difficulty was experienced in making the bright glow remain in the hollow cathode and, for this reason, the maximum current employed for any length of time was limited to 1.8 amperes. When the vapor density was high, the sulfur lines became broad and in many cases showed strong reversal. Both the arc and first spark spectra were excited at all times and no distinguishing characteristics were observed but this caused no great difficulty, as there is little overlapping of the two in the region being examined.

Selenium was then used in place of sulfur in the same kind of tube and under the same conditions and several photographs were taken which served to identify many impurity lines in the sulfur pictures. A pure helium discharge did not show nearly as many such lines as did the helium and selenium combination.

Of the total wave-length range covered by these photographs (0–2600A), only that from 1050–2400A should contain arc lines and accurate

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[1] R. Frerichs, Phys. Rev. **34**, 1239 (1929); Phys. Rev. **36**, 398 (1930).

[2] J. J. Hopfield, Phys. Rev. **37**, 160 (1931).

TABLE I. *Lines of S I. R = reversed; d = diffuse.*

Int.	λ (vac)	ν (vac)	Transition	Int.	λ (vac)	ν (vac)	Transition
15*R*	1914.68	52228.0	$3p\,{}^3P_1-4s({}^4S)\,{}^5S_2$	4	1318.97	75817.0	
20*R*	1900.27	52624.1	${}^3P_2-4s({}^4S)\,{}^5S_2$	8*R*	1316.59	75954.0	$3p\,{}^3P_2-4d({}^4S)\,{}^3D$
25*R*	1826.25	54757.0	${}^3P_0-4s({}^4S)\,{}^3S_1$	4	1313.25	76146.7	${}^3P_0-6s({}^4S)\,{}^3S_1$
25*R*	1820.37	54934.0	${}^3P_1-4s({}^4S)\,{}^3S_1$	5	1310.21	76323.4	${}^3P_1-6s({}^4S)\,{}^3S_1$
25*R*	1807.31	55331.0	${}^3P_2-4s({}^4S)\,{}^3S_1$	9*R*	1305.89	76576.1	${}^3P_0-4s({}^2P)\,{}^3P_1$
12*R*	1782.25	56109.0		4	1303.42	76721.4	${}^3P_2-6s({}^4S)\,{}^3S_1$
1	1713.54	58358.8		7*R*	1303.12	76738.9	${}^3P_1-4s({}^2P)\,{}^3P_0$
8	1707.13	58578.0	${}^1D_2-4s({}^2D)\,{}^3D_1$	6*R*	1302.86	76754.2	${}^3P_1-4s({}^2P)\,{}^3P_1$
8	1706.38	58603.5	${}^1D_2-4s({}^2D)\,{}^3D_3$	9*R*	1302.32	76786.2	${}^3P_1-4s({}^2P)\,{}^3P_2$
5	1704.99	58651.5	${}^1D_2-3d({}^4S)\,{}^5D$	5	1296.18	77150.0	${}^3P_2-4s({}^2P)\,{}^3P_1$
20*R*	1687.54	59258.0	${}^1S_0-4s({}^2P)\,{}^1P_1$	6	1295.62	77183.1	${}^3P_2-4s({}^2P)\,{}^3P_2$
25*R*	1666.68	59999.7	${}^1D_2-4s({}^2D)\,{}^1D_2$	0	1283.11	77935.6	
6	1641.30	60927.3	${}^1D_2-3d({}^4S)\,{}^3D$	4	1280.13	78117.3	${}^3P_0-5d({}^4S)\,{}^3D$
2	1592.72	62785.7	${}^1D_2-3s3p^5\,{}^3P_2$	5*d*	1277.24	78294.0	$\left\{\begin{array}{l}{}^3P_1-5d({}^4S)\,{}^3D\\{}^3P_2-4s({}^2P)\,{}^1P_1\end{array}\right.$
15*R*	1487.12	67243.9	${}^3P_0-4s({}^2D)\,{}^3D_1$				
12	1485.61	67312.6	${}^3P_0-3d({}^4S)\,{}^5D$	1	1272.07	78612.0	${}^3P_0-7s({}^4S)\,{}^3S_1$
12*R*	1483.24	67420.0	${}^3P_1-4s({}^2D)\,{}^3D_1$	4	1270.78	78692.0	${}^3P_2-5d({}^4S)\,{}^3D$
15*R*	1483.05	67428.6	${}^3P_1-4s({}^2D)\,{}^3D_2$	2	1269.20	78789.5	${}^3P_1-7s({}^4S)\,{}^3S_1$
15*R*	1481.65	67492.2	${}^3P_1-3d({}^4S)\,{}^5D$	2	1262.83	79187.0	${}^3P_2-7s({}^4S)\,{}^3S_1$
6*R*	1474.54	67817.6	${}^3P_2-4s({}^2D)\,{}^3D_1$	2	1247.17	80181.5	
12*R*	1474.37	67825.6	${}^3P_2-4s({}^2D)\,{}^3D_2$	2	1241.95	80518.8	
15*R*	1473.98	67843.3	${}^3P_2-4s({}^2D)\,{}^3D_3$	15*R*	1204.30	83035.6	
15*R*	1472.97	67890.0	${}^3P_2-3d({}^4S)\,{}^5D$	2	1191.80	83906.7	
4	1471.82	67943.0	${}^1D_2-4s({}^2P)\,{}^3P_2$	2	1190.11	84025.5	
12*R*	1448.20	69051.4	${}^1D_2-4s({}^2P)\,{}^1P_1$	2	1171.91	85330.8	
6	1444.27	69239.3	${}^3P_2-4s({}^2D)\,{}^1D_2$	1	1157.37	86402.8	
12*R*	1436.94	69592.3	${}^3P_0-3d({}^4S)\,{}^3D$	2	1152.11	86796.9	
15*R*	1433.28	69770.0	${}^3P_1-3d({}^4S)\,{}^3D$	2*d*	1056.79	94626	
15*R*	1425.10	70170.7	${}^3P_2-3d({}^4S)\,{}^3D$	1	1055.15	94773	
12*R*	1412.85	70779.0	${}^3P_0-5s({}^4S)\,{}^3S_1$	1	1053.21	94948	
12*R*	1409.32	70956.2	${}^3P_1-5s({}^4S)\,{}^3S_1$	1	1052.60	95003	
10*R*	1401.50	71351.9	${}^3P_2-5s({}^4S)\,{}^3S_1$	2	1052.25	95215	
15*R*	1396.10	71628.1	${}^3P_1-3s3p^5\,{}^3P_2$	1	1049.77	95259	
12*R*	1392.59	71808.5	${}^3P_0-3s3p^5\,{}^3P_1$	1	1049.06	95323	
5*R*	1389.16	71986.1	${}^3P_1-3s3p^5\,{}^3P_1$	1	1048.43	95381	
12*R*	1388.39	72026.0	${}^3P_2-3s3p^5\,{}^3P_2$	1	1047.86	95433	
12*R*	1385.51	72175.6	${}^3P_1-3s3p^5\,{}^3P_0$	1	1047.56	95460	
15*R*	1381.55	72382.6	${}^3P_2-3s3p^5\,{}^3P_1$	2	1045.74	95626	
3	1363.04	73365.2		0	1036.41	96487	
1	1353.47	73883.9		1	1006.95	99310	
9*R*	1326.64	75378.4	${}^3P_0-4d({}^4S)\,{}^3D$	8	1006.15	99389	
10*R*	1323.52	75556.1	${}^3P_1-4d({}^4S)\,{}^3D$	2	1000.75	99925	

measurements were not made outside of these limits. After eliminating the lines indicated as impurities, it was possible to identify nearly all of the remaining ones in the selected region as definitely belonging to either S I or S II. Table I gives a list of all those lines which might belong to S I with their transition designations where known. No attempt was made to classify any new lines in S II and only those given by Ingram,[3] nearly all of which were found, were regarded as belonging to that spectrum.

While this work was being done, a paper by Frerichs[4] appeared extending the analysis of the S I spectrum in the long wave-length region and since he used a grating of high dispersion, his data are the most accurate yet reported for that region. His table of terms includes several established by the ultraviolet measurements of Hopfield,[5] although the present work indicates these should be slightly changed numerically, and yields a number of additional terms. All the term values given in Table II of this article constitute an addition to the term table given in Frerichs' paper. One correction should be made to the table as given in his paper; namely, the reduction by one of the total quantum numbers of all the *d* electrons, to which change he has expressed his agreement in a personal communication.

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[3] S. B. Ingram, Phys. Rev. **32**, 172 (1928).

[4] R. Frerichs, Zeits. f. Physik **80**, 150 (1933).

[5] J. J. Hopfield, Phys. Rev. **22**, 523 (1923); Nature **112**, 790 (1923); Phys. Rev. **27**, 638 (1926).

TABLE II. *Multiplets and term values of S I.*

$3p^4$	$^3P_2$ 83560.7	(397.2)	$^3P_1$ 83136.5	(177.5)	$^3P_0$ 82986.0	(8665.1)	$^1D_2$ 74320.9	(9793.4)	$^1S_0$ 64527.5
$3p^34s(^4S)^5S_2$ 30936.9	52624.1 (20*R*)	(396.1)	52228.0 (15*R*)						
$3p^34s(^4S)^3S_1$ 28229.0	55331.0 (25*R*)	(397.0)	54934.0 (25*R*)	(177.0)	54757.0 (25*R*)				
$3p^34s(^2D)^3D_1$ 15743.3	67817.6 (6*R*)	(397.6)	67420.0 (12*R*)	(176.1)	67243.9 (15*R*)	(8664.9)	58578.0 (8)		
$3p^34s(^2D)^3D_2$ 15734.4	67825.6 (12*R*)	(397.0)	67428.6 (15*R*)						
$3p^34s(^2D)^3D_3$ 15716.7	67843.3 (15*R*)	(397.2)		(177.5)		(8665.1)	58603.5 (8)		
$3p^33d(^4S)^5D$ 15670.7	67890.0 (15*R*)	(397.7)	67492.2 (15*R*)	(179.6)	67312.6 (12*R*)	(8661.1)	58651.5 (5)		
$3p^34s(^2D)^1D_2$ 14321.3	69239.3 (6)	(397.2)		(177.5)		(8664.9)	59999.7 (25*R*)		
$3p^33d(^4S)^3D$ 13392.7	70170.7 (15*R*)*d*	(400.7)	69770.0 (15*R*)	(177.7)	69592.3 (12*R*)	(8665.0)	60927.3 (6)		
$3p^35s(^4S)^3S_1$ 12207.3	71351.9 (10*R*)	(395.7)	70956.2 (12*R*)	(177.2)	70779.0 (12*R*)				
$3s3p^5\ ^3P_2$ 11535.1	72026.0 (12*R*)	(397.7)	71628.1 (15*R*)	(177.5)		(8664.9)	62785.7 (2)		
$3s3p^5\ ^3P_1$ 11177.7	72382.6 (15*R*)	(397.5)	71986.1 (5*R*)	(177.6)	71808.5 (12*R*)				
$3s3p^5\ ^3P_0$ 10987.9			72175.6 (12*R*)						
$3p^34d(^4S)^3D$ 7606.7	75954.0 (8*R*)	(397.9)	75556.1 (10*R*)	(177.7)	75378.4 (9*R*)				
$3p^36s(^4S)^3S_1$ 6839.3	76721.4 (4)	(398.0)	76323.4 (5)	(176.7)	76146.7 (4)				
$3p^34s(^2P)^3P_0$ 6424.6			76738.9 (7)						
$3p^34s(^2P)^3P_1$ 6410.7	77150.0 (5)	(395.8)	76754.2 (6)	(178.1)	76576.1 (9)				
$3p^34s(^2P)^3P_2$ 6377.6	77183.1 (6)	(396.9)	76786.2 (9)	(177.5)		(8665.7)	67943.0 (4)		
$3p^34s(^2P)^1P_1$ 5269.5	78294.0 (5)*d*	(400.0)		(177.5)		(8665.1)	69051.4 (12*R*)	(9793.4)	59258.0 (20*R*)
$3p^35d(^4S)^3D$ 4868.7	78692.0 (4)	(398.0)	78294.0 (5)*d*	(176.7)	78117.3 (4)				
$3p^37s(^4S)^3S_1$ 4374.4	79187.0 (2)	(397.5)	78789.5 (2)	(177.5)	78612.0 (1)				

The only previous measurement and classification of ultraviolet lines of S I has been reported by Hopfield[5] but these results include none of the terms built on the ^2D and ^2P states of the ion. The location of such terms was the chief aim of this investigation. The terms built on the ^4S state of the ion were fairly completely identified. In some of the series only one or two members had been observed but they were all definitely fixed with respect to the limit by some combination with series containing more terms. From the present data, however, it was possible to identify immediately a number of these higher series members and also, by triplet intercombinations which were relatively weak, to locate the low ^1D term.

As an aid in locating the terms built on the two doublet limits, it was assumed that the terms arising from the same electron configuration would be at approximately equal distances from their respective limits, as was found to be the case in oxygen. The separations of the low levels of S II had been determined by Ingram[3] (the quartet-doublet separation by means of series limits and hence not very exactly), and these were used in placing the limits in Fig. 2. The expected positions of the various terms, as indicated by the assumption just mentioned, are marked by the circles. Two groups of strong lines were found which located the $4s(^2D)^3D$ and the $4s(^2P)^3P$ levels at almost exactly the predicted positions (the transitions being into the low ^3P levels). Furthermore, the outer separation of each triplet was very nearly equal to the separation of the doublet limit to which each series of such terms would converge.

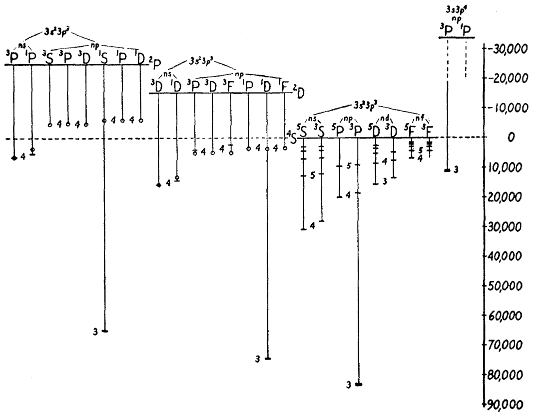

FIG. 2. Energy level of S I.

There were then remaining just three strong unclassified lines which lay anywhere near the positions expected for the corresponding singlet combinations. There was no doubt at all as to the identification of the transition $3p(^2D)^1D-4s(^2P)^1P$ and since the $3p^1D$ term had been located by intercombinations, the $4s^1P$ was also fixed. The other two lines differed in frequency by only about 750 cm^{-1} and it would not be unreasonable to call either one the transition $3p(^2P)^1S-4s(^2P)^1P$ or $3p(^2D)^1D-4s(^2D)^1D$. The choice made was based on two reasons, neither of which alone is absolutely conclusive but taken together are almost so, and especially when there is nothing which gives any positive indication the other way. The reasons are these. First, the transition $3p(^2D)^1D-4s(^2D)^1D$ should give a line of greater intensity than $3p(^2P)^1S-4s(^2P)^1P$, since the ^1P term lies considerably higher in the term scheme and the corresponding triplet transitions followed the usual intensity relations. Second, an intercombination line is observed, $3p(^4S)^3P_2-4s(^2D)^1D$, if the classification as given is correct, whereas no such line is found with the alternative level assignment.

Table II gives all the identified transitions into the normal S I configuration, with the term values referred to the ^4S limit written below each term, and the frequency differences indicated in parentheses. The numbers under the radiated wave numbers are the estimated intensities, *R* meaning reversed and *d* diffuse.

Recognition of the fainter lines of sulfur was rendered difficult and in certain regions impossible by the presence of many impurity lines; that is, lines which were common to both the sulfur and selenium plates. These were so numerous in places as to give the impression of bands, though close observation showed that they were not. No line was included in the list as sulfur if it apparently coincided with a line of comparable intensity on the selenium plate, even though it fitted in as a member of a series or had a correct frequency difference from another line.

All the remaining unidentified terms would lie near or above the ^4S limit and hence the transitions from them would be expected to be weak. This may account for the failure to observe transitions involving higher terms of series going to either of the doublet limits. The two strong lines at λ1782 and λ1204 still remain unidentified and there is no place for them in the classification of the S I spectrum here reported.

The author wishes to acknowledge his indebtedness to Professor R. C. Gibbs, under whose direction this research was carried on, for his interest and advice during the course of the work.