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THE ARC SPECTRUM OF COPPER*

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Abstract

The arc spectrum of coppper is partly an ordinary doublet spectrum with lowest term $^2S=62308.0$; and partly a complicated spectrum with lowest term $m^2D_3=51105.5$ and $m^2D_2=49062.6$. The next lowest terms of the complicated spectrum are ^4P, ^4F, ^4D,' ^2F, ^2P, $^2D'$ in the order given extending from $^4P_3=23289.4$ to $^2D'_3=15709.7$. They combine with ^2S and m^2D. The quartets are all inverted, while the doublets are not. There are eleven higher terms which include amongst others a second set ^2F, ^2P, $^2D'$. This is all as predicted by the Heisenburg-Hund theory. Most of the lines of the arc spectrum are due to the combinations of the above quartets and doublets with a set of terms having negative wave-numbers extending from -95.2 to -14772.4. In particular, the lowest four negative terms are a complete ^4D and form by combination with ^4P, ^4F, $^4D'$ multiplets of great intensity in the visible. The other negative terms include a set ^4S, $^4P'$, ^4D, $^4F'$, ^4G, which also combine with considerable intensity with the first mentioned quartets. The limit of the negative quartet terms can be calculated to be at roughly $-22,000$. This should be the lowest spark ^3D term.

The nature of the quartet spectrum was partly determined from Zeeman effects in the ultra-violet below 2500. The g-values of many of the terms are irregular but the g-sums are correct. Line intensities were used mainly as criteria for the designation of terms. Unresolved Zeeman effects give confirmation in many cases.

The two types of spectra are connected by combinations of the lowest terms of each with higher terms of the other. Other theoretically possible combinations do not occur.

THE spectrum of copper has long been known to contain term sequences of ordinary doublet type.[1] The lowest term is a ^2S term 62308.0, and there are known, in addition, a number of P, D, and F terms. This spectrum is discussed below.

There exist also two ^2D terms whose abnormally low values prevent their inclusion in the ordinary D-sequence. They have wave numbers $m^2D_2=49062.6$ and $m^2D_3=51105.5$ and are thus inverted. The combinations of all of the above terms account for only about 45 lines of the 500 or more known to be due to the copper atom. In a recent paper[2] the

* After this paper had been written, there was received a paper by C. S. Beals "Quartet terms in the arc spectrum of copper" (Proc. Roy. Soc. A **111**, 1926). By the aid of Zeeman effects Beals has discovered the main set of quartet terms comprising the low ^4P,$^4D'$,^4F and the higher ^4D with which they combine. The two papers are in complete agreement on this most important point, except that Beals has observed the one line λ 4069 which is missing in the tables. Beals' evidence for the classification of the quartet terms is probably more conclusive than the author's.

[1] A. Fowler, "Report on Series in Line Spectra."

[2] A. G. Shenstone, Phil. Mag. **49**, 952 (1925).

author has shown that this complex part of the spectrum is intimately connected with the terms m^2D.

A large part of the spectrum has now been analysed, and a comparison is made below between that analysis and the results predicted by the very successful theory developed by Pauli,[3] Heisenberg,[4] and Hund,[5] on the basis of the conclusions of Russell and Saunders[6] from the calcium spectrum.

The copper ion in its lowest state should consist of an electron configuration which can be represented as d^{10}, where the index indicates the number of electrons in orbits whose k-values are given by the letters s, p, d, etc. The inner closed shells of electrons are omitted for convenience. This state is a ^1S term, on which would be built by the addition of one electron the ordinary doublet spectrum of the atom. Another possible condition of the ion is d^9s. The composition of the quantum vectors of the separate electrons in such a configuration can be shown to result in any one of the four terms included under the notation ^3D and ^1D. The addition of a further s-electron yields terms of the atom ^4D, ^2D, ^2D, which, due to Pauli's equivalent electron principle, merge, in the lowest state (d^9s^2) into a ^2D alone. This term should be inverted and very low and is, undoubtedly, m^2D referred to above. It should be the leading member of two series of ^2D terms, one of which should converge to the spark ^1D and the other to two components of the spark ^3D term. The ^4D terms should have as limit the ^3D spark term.

The next lowest terms of the atom should be given by the addition of a p-electron to d^9s, namely d^9sp. This configuration can be shown to give terms ^4P, $^4D'$, ^4F, ^2P, $^2D'$, ^2F, based on the spark ^3D, and ^2P, $^2D'$, ^2F, based on the spark ^1D. From empirical rules deduced from other spectra, the quartets should be the lowest terms. All the above terms should combine with m^2D and ^2S where the j-selection principle permits. Some of these terms have already been found from the absorption experiments of Zumstein,[7] the author (loc. cit.), and McLennan and McLay.[8] The remainder of the quartets and lower doublets have now been identified from their combinations, as well as a further eleven terms which probably include the second set of doublets originating from the spark ^1D, as well as terms which belong to the electron configuration d^8s^2p.

[3] W. Pauli, Jr. Zeits. f. Physik **31,** 765 (1925).
[4] W. Heisenberg, Zeits. f. Physik **32,** 841 (1925).
[5] F. Hund, Zeits. f. Physik **33,** 345 (1925).
[6] H. N. Russell and F.A. Saunders, Astrophys. J. **61,** 38 (1925).
[7] R. V. Zumstein, Phys. Rev. **25,** 523 (1925).
[8] J. C. McLennan and A. B. McLay, Trans. R. S. Can. **19,** 89 (1925).

TABLE I

Term	Type	Intervals.	$^2S_1$ 62308.0	m^2D_2 49062.6	m^2D_3 51105.5	No. of Comb.
23289.4	a^4P_3			————	27816.1 (2)	15
		1095.4				
22194.0	a^4P_2		40114.0 (8)	26868.5 (2)	28911.4 (3)	16
		829.7				
21364.3	a^4P_1		40943.9 (6)	27698.3 (2)		7
21398.9	a^4F_5					5
		244.3				
21154.6	a^4F_4				29950.8 (6)	17
		409.4				
20745.2	a^4F_3			28317.4 (6)	30360.5 (2)*	18
		739.7				
20005.6	a^4F_2		42302.6 (1*u*)	29057.1 (3)	————	13
18794.1	a^4D_4'				32311.3 (6)	19
		892.3				
17901.8	a^4D_3'			31160.8 (4)	33203.7 (5)	19
		137.9				
17763.9	a^4D_2'		44544.3 (2)	31298.7 (6)	33341.6 (2)	18
		371.6				
17392.3	a^4D_1'		44915.9 (2*R*)	31670.3 (3)		9
18581.9	a^2F_3			30480.7 (3)?	32523.6 (4)	18
		1237.1				
17344.8	a^2F_4				33760.5 (6)	13
16487.2	a^2P_1		45821.2 (1*u*)	32575.4 (4*u*)		8
		58.4				
16428.8	a^2P_2		45879.3 (1*u*)	32633.8 (6)	34676.7 (4)	15
16135.2	a^2D_2'		46172.7 (1*u*)	32927.4 (6)	34970.2 (2)	14
		425.5				
15709.7	a^2D_3'			33353.0 (4)	35395.7 (8)	15
12925.0	3^2P_2		49383.0 (Calc)	36137.6 (8)	38180.2 (10*r*)	3
			2^2S_1 (combs.)			
7523.9	e_3'			41538.7 (6)	43581.4 (8*R*)	2
7280.3	d_2'			41782.3 (8*r*)	43825.1 (2)†	4
6278.3	b^2F_4				44827.1 (6*R*)	9
5964.7	c_2'	621.6	13206.3 (5)	43098.1 (4)	45141.0 (6*R*)	8
5656.7	b^2F_3			43405.7 (6)	45448.6 (2)‡	10
5027.3	b_4'				46078.4 (2*u*)	3
4889.4	a_1'		14281.7 (1*u*)	44173.3 (6*R*)		3
4358.8	b^2P_2	414.5	14812.3 (2*u*)	44704.0 (1*u*)	46747.0 (1*u*)	4
4188.7	b^2D_3'	571.5		44874.0 (6*R*)	46916.7 (1)	6
3944.3	b^2P_1		15226.8 (3*u*)	45118.8 (4*R*)	47157.7 (0)†	4
3617.2	b^2D_2'		15553.7 (1)	45445.3 (2)‡	47488.1 (0)‡	10

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All of these terms are given in Table I together with their combinations with ^2S and m^2D. Small letters have been prefixed to the term designations in order to distinguish between terms of the same type. The wave lengths are mainly Hasbach's, but in the region below λ2300 they have been corrected by the use of Mitra's[9] standards, omitting his determination of λ2148 which is almost certainly incorrect.

The nature of several of the terms of Table I was determined by observations of Zeeman effects in the ultra-violet, using for the purpose a Hilger E1 quartz spectrograph. With this instrument simple patterns such as are given by terms of $j=1$ or 2 combining with ^2S are resolvable if the source produces sufficiently fine lines. Most of the copper arc lines are known to be diffuse; and, in the ultra-violet, most of them, being ^2S and m^2D combinations, are wide reversed lines. This difficulty was surmounted without the trouble of a vacuum source by using an iron or zinc anode and copper cathode. Zinc was found to be particularly efficient in reducing the width of the copper lines, even the resonance lines λ3247 and λ3274 appearing in fine emission. In the early work the iron lines served as standards of Zeeman separations. Hilger Schumann plates were used, and with them, exposures rarely exceeded five minutes. A quartz double image prism was made use of to obtain both polarisations on the plate simultaneously. The magnetic field obtained was about 25,000 gauss.

The results obtained for the 1^2S_1 combinations are given in Table II.

TABLE II

λ	Designation	Zeeman Pattern	g (calc)	g (Landé)
2492.142	$1^2S_1-a^4P_2$	$\pm(0)\ 1.69a$	1.7 ?	$\frac{26}{15}$
2441.625	$1^2S_1-a^4P_1$	$(0)\ 2.34a$	2.68	$\frac{8}{3}$
2244.24	$1^2S_1-a^4D_2'$	$(.45)\ .\overline{66}-a$	1.10	$\frac{6}{5}$
2225.665	$1^2S_1-a^4D_1'$	$(.91)\ 1.11a$	.20	0
2181.71	$1^2S_1-a^2P_1$	$(.77)\ 1.21a$	.44	$\frac{2}{3}$
2178.95	$1^2S_1-a^2P_2$	$(.43)\ .\overline{70}\ 1.5a$	1.14	$\frac{4}{3}$
2165.10	$1^2S_1-a^2D_2'$	$(.45)\ .\overline{66}-a$	1.10	$\frac{4}{5}$

The Zeeman patterns obtained for the two lines λ2492 and λ2442 leave little doubt that they are $^2S-{}^4P_2$ and $^2S-{}^4P_1$. The terms $\nu=22194.0$ and 21364.3 have, therefore, been designated a^4P_2 and a^4P_1. The designation of the term $\nu=23289.4$ as a^4P_3 is based on the evidence of other combinations which are given below. The failure to observe the line $m^2D_2-a^4P_3$ is due to two facts. It is theoretically a very faint line; and its position at λ3878.9 is in the midst of very strong nitrogen bands which it has been found impossible to eliminate. An arc in 99% argon gave these bands in great strength as did also an arc in carbon dioxide. A very small amount of nitrogen is evidently sufficient for the appearance of these bands.

[9] Mitra, Ann. d. Physique **19**, 315 (1923).

There is evidence for the identification of the four terms given as ^4F from three sources; unresolved Zeeman effects, some complete patterns communicated to me by Mr. Loring of Harvard University, and intensities of combinations. The line λ2363.20, $^2S-a^4F_2$, is extremely faint and has never appeared on plates of the Zeeman effect. The combination line $mD^2{}_3-a^4F_2$, theoretically a very faint line, is missing from the tables. A line in the correct position has been measured by the author, but there is a possibility that this is a band line. There is a difficulty in the line $m^2D_3-a^4F_3$. Hasbach's wavelength 3292.903* gives a wave-number in error by +.7 and Kaiser's value gives an error of −.2. There is good evidence, however, that this is really a double line with a wave number difference of about 1.2, the other member of the pair being a a^4F_5 combination.

The remainder of the resolved patterns yield g-values for the terms involved which are in disagreement with Landé's values. This is, undoubtedly, due to the fact that the spectrum is of the "second rank," i.e. it is produced by atoms in which two electrons are neither in s-orbits nor in closed groups, the lack of one electron from the M-shell in this case being equivalent spectroscopically to the presence of one d-electron.

The magnetic splitting of the line λ2225 allows the calculation of $g=.20$ for the term $\nu=17392.3$. This is closer to the theoretical value zero for $^4D'_1$ than to the g of any other term with $j=1$. There is little doubt of the designation $^4D'_2$ for $\nu=17763.9$ but there is a real difficulty involved in the choice between 17901.8 or 18581.9 for $^4D'_3$. The unresolved patterns of the lines λ3010 and λ3073 are practically identical; as are also those of the lines λ3208 and λ3279. An examination of the m^2D combinations shows, however, that the listed intensities are in error, and that in reality λ3279 is considerably stronger than λ3073, indicating that $\nu=18581.9$ is an F_3 term and not a D_3. The term $\nu=17901.8$ has, therefore, been placed as $^4D'_3$. The line λ3093 shows in the magnetic field as a triplet with separation $(0\pm1.7a)$ and can hardly be other than $m^2D_3-a^4D'_4$.

From the evidence just given, the term $\nu=18581.9$ is very probably a^2F_3 and it has been so designated. Its companion a^2F_4 must then be $\nu=17344.8$, the only remaining term with $j=4$. The doublet separation is 1237.1.

The remaining four terms of the lower term group of Table I should be $^2P_1$ $^2P_2$ $^2D'_2$ $^2D'_3$. The g-value .44 for $\nu=16487.2$ indicates that it can reasonably be called a^2P_1. The Zeeman patterns of λ2824 $(0\pm1.2a)$ and λ2998 $(0\pm1.7a)$ (shaded inwards) agree very well with those calcu-

* Incorrectly given in Kayser and Konen, vol. VII, p. 342 as λ 3293. 903.

lated for $^2D_3 - ^2D'_3$ and $^2D_2 - ^2D'_3$ from Landé's table, i.e. $(0 \pm \frac{6}{5}a)$ and $\frac{(\pm(13)\,357\bar{9}a)}{5}$. This term 15709.7 has, therefore, been designated $a^2D'_3$.

There remain the two terms $\nu = 16428.8$ and $\nu = 16135.2$ which should be a^2P_2 and $a^2D'_2$. Their g-values are practically identical, and they both combine with m^2D_2 more strongly than with m^2D_3 which is, of course, incorrect for $^2P_2$. It may be that, the spectrum being of the second rank, the identities of these two terms have become confused. With that reservation the term $\nu = 16428.8$ has been chosen as a^2P_2 since its combinations with m^2D depart least from the theoretical expectation.

It has been shown that the terms of Table I are in agreement with the predictions of the Hund theory; but that the g-values, as expected, do not agree with those of an ordinary set of quartet and doublet terms. The g-sums should, however, be correct. That is, the sum of the g's of all terms with the same j should equal the sum of the Landé g's for the equivalent quartet and doublet terms. This is correct within the experimental error. The experimental g's are each subject to an error of about .02 for $j = 1$ and .04 for $j = 2$.

Terms. $j = 1$.

$$\begin{cases} g\text{-sum (exp)} & 2.68 + .44 + .20 = 3.32 \pm .06. \\ g\text{-sum (theor)} & \frac{8}{3} + \frac{2}{3} + 0 = \frac{10}{3} = 3.33. \end{cases}$$

Terms. $j = 2$.

$$\begin{cases} g\text{-sum (exp)} & 1.10 + 1.14 + 1.10 + 1.70 + .44 = 5.48 \pm .20 \\ g\text{-sum (theor)} & \frac{4}{3} + \frac{4}{5} + \frac{6}{5} + \frac{26}{15} + \frac{2}{5} = 5.46 \end{cases}$$

The experimental g-value for a^4F_2 (.44) is from the results of A.R. Loring, who has kindly communicated to me some of his Zeeman effects obtained on the large grating of the Jefferson Laboratory at Harvard University. The value 1.7 for $^4P_2$ is taken from the unresolved pattern given in Table II and may be slightly in error.

Of the remaining terms of Table I, $\nu = 12925.0$ is either 3^2P_2 or the pair 3^2P_2 and 3^2P_1 of the ordinary spectrum together. This has been discussed in my previous paper (loc. cit.). The difficulty has not been eliminated by the present investigation.

The eleven terms of Table I which have not yet been considered should include the set of $^2P, D', F$, which arise from the addition of a p-electron to the ^1D of the spark. A consideration of intensities of combinations both with m^2D and with the higher terms identifies $b^2F_3 = 5656.7$ and $b^2F_4 = 6278.3$ with some certainty. In particular with $c^2G_4 = -8819.7$ and $c^2G_5 = -8551.3$, they form the intense triplet λ6905 (6), λ6741 (7), λ6621 (4).

Anything approaching a positive identification of the ^2P and $^2D'$ terms is not possible because of the paucity of combination lines. Four terms which may reasonably represent them have been tentatively chosen. The remaining five terms, which should include some members of the quartets arising from the configuration d^8s^2p, have been allotted small letters for identification purposes. The nature of all of these terms could be determined by observations of Zeeman effects in the long wave-length end of the spectrum.

The combinations of 1^2S and m^2D, with the terms of Table I account for almost all of the important lines of the spectrum below λ3100. A large majority of the remaining lines can also be accounted for by the combinations of these terms with a new set of terms, all of which are negative. The starting point for the discovery of these negative terms was given by the constant frequency differences of Rydberg.[10] Two of these differences occur as $a^4D'_4 - a^2F_3 = 212.2$ and $a^2F_3 - a^4D'_3 = 680.1$. The other two 50.4 and 129.7 are differences of negative terms.

The origin of the negative terms must be sought in electron configurations from which transitions can take place to the structure d^9sp. Such a one is d^9ss mentioned above, which can be responsible for $^4D_1$ ^2D and ^2D. From analogy with the spectra of the preceding elements iron, cobalt and nickel, the ^4D term should be the lowest and should produce strong multiplets in combination with a^4P, a^4D' and a^4F of the Table I. Such a quartet term is found in the following three multiplets (Table III).

TABLE III
Multiplets

		c^4D_4 −95.2	c^4D_3 −640.2	c^4D_2 −1276.4	c^4D_1 −2164.2
a^4P_3	23289.4	(6) 23384.5	(4u) 23929.6	24565.8 (calc)	
a^4P_2	22194.0		(6u) 22834.0	(2u) 23470.7	(2) 24358.2
a^4P_1	21364.3			(3u) 22640.6	(4) 23528.5
a^4F_5	21398.9..	(8) 21494.2			
a^4F_4	21154.6	(6) 21249.9	(6u) 21794.8		
a^4F_3	20745.2	(2) 20840.4	(6u) 21385.5	(4u) 22021.7	
a^4F_2	20005.6		(1u) 20646.0	(4u) 21282.0	(4) 22169.8

[10] Rydberg, Astrophys. J. **6**, 239 (1897).

TABLE III (continued)

		c^4D_4 −95.2	c^4D_3 =640.2	c^4D_2 −1276.4	c^4D_1 −2164.2
a^4D_4'	18794.1	(4) 18889.3	(1u) 19434.3		
a^4D_3'	17901.8	(3) 17997.0	(2u) 18542.0	(1u) 19177.9	
a^4D_2'	17763.9		(2u) 18404.2	(1u) 19040.5	(3) 19928.1
a^4D_1'	17392.3			(1u) 18669.0	(2) 19556.6

The identities of the terms designated c^4D_1 and c^4D_2 in these multiplets are fixed beyond doubt by the results of Loring at Harvard University. The g's of these two terms are 0 and $\frac{10}{7}$ the theoretical values given by Landé. The two other terms have the distinct peculiarity that all their lines are diffuse lines. Moreover, the sharp lines due to c^4D_1 and c^4D_4 are much more sensitive to low voltage discharge. In spite of such differences in behaviour, however, there can be little doubt that the four terms do form a complete ^4D term; and in all probability it is the one mentioned above arising from d^9ss. Confirmation of the identity of c^4D_2 is obtained from Loring's unresolved Zeeman pattern for λ4587, $a^4F_4-c^4D_3$. In the magnetic field the line shows as a triplet (0).97a. The theoretically strongest component would be the innermost at .9a. None of the other lines arising from c^4D_2 or c^4D_3 appear as anything but a wide haze.

It has not, as yet, been found possible to designate all of the negative terms. This arises from several causes. First, there are so many possibilities involved in the structures in which these terms have their origin. The possible terms originating in d^9ss mentioned above are probably mingled not only with d^9sd but also with d^8s^2d. Such configurations produce a multitude of quartet and doublet terms of all types from S to H. Moreover, term separations will certainly be large, and will not necessarily decrease as we proceed to higher series members since the limits may be different components of the spark ^3D and ^1D. The intensities given in the table are not sufficiently accurate nor on a large enough scale to be of much value. A thorough investigation of relative intensities is, perhaps, the best method of attack on these negative terms.

Table IV contains all of the negative terms. Where no notation has been assigned, the terms are given in small letters using as subscript the most probable j value. The last column contains the number of combinations made with the terms of Table I.

TABLE IV

Term	j	Intervals	Designation.	No. of Comb.
−95.2	4		c^4D_4	9
		545.0		
−640.2	3		c^4D_3	10
		636.2		
−1276.4	2		c^4D_2	8
		887.8		
−2164.2	1		c^4D_1	7
−2349.5	3		c^2D_3	9
−4834.3	3		a_3	5
−5663.9	2		b_2	6
−8545.3	2		d^4S_2	11
−8551.5	5		c^2G_5	5
−8690.0	3 or 4	268.2	c_3	6
−8790.2	3		d_3	12
−8819.7	4		c^2G_4	10
−8822.6	6	848.1	d^4G_6	1
−8870.1	3		d^4P_3'	13
−8960.1	4		d^4D_4	8
		749.0		
−8982.4	5		d^4F_5'	6
−9574.9	1		d^4P_1'	6
		−44.2		
−9619.1	2	798.8	d^4P_2'	10
		802.6		
−9670.7	5		d^4G_5	5
		37.9		
−9708.6	4		d^4G_4	8
−9758.9	3		d^4D_3	13
		134.5		
−9785.0	4		d^4F_4'	11
−9843.1	2 or 3		d^4G_3	
−10794.6	3 or 4		g_4	4
		1211.5		9
−10796.8	1		c^2S_1	8
−10890.7	2 or 3		h_2	9
−10996.5	2 or 3		d^4F_3'	10
		11.9		
−11008.4	2		d^4F_2'	8
−11687.0	4		e^4D_4	4
		317.6		
−12004.6	3		e^4D_3	5
−12801.3 ?	1	970.9	1_1	3
−12955.4	2	780.9	c^2P_2'	5
−12975.5	2		e^4D_2	3
−13264.8 ?	3 or 4		n_4	3
−13756.4	1		e^4D_1	4
−14722.0 ?	3 or 4		o_4	3
−14760.1 ?	3 or 4		p_4	3
−14772.4 ?	3 or 4		q_4	3

Fig. 1 gives the intensities of all the lines produced by combination of the positive and negative terms. The intensity of a line appears opposite the two terms whose difference is the frequency of the line.

On the basis of the somewhat unreliable available data, a number of negative terms may be identified with reasonable certainty. The combinations of the pair of terms b^2G mentioned above agree very well with

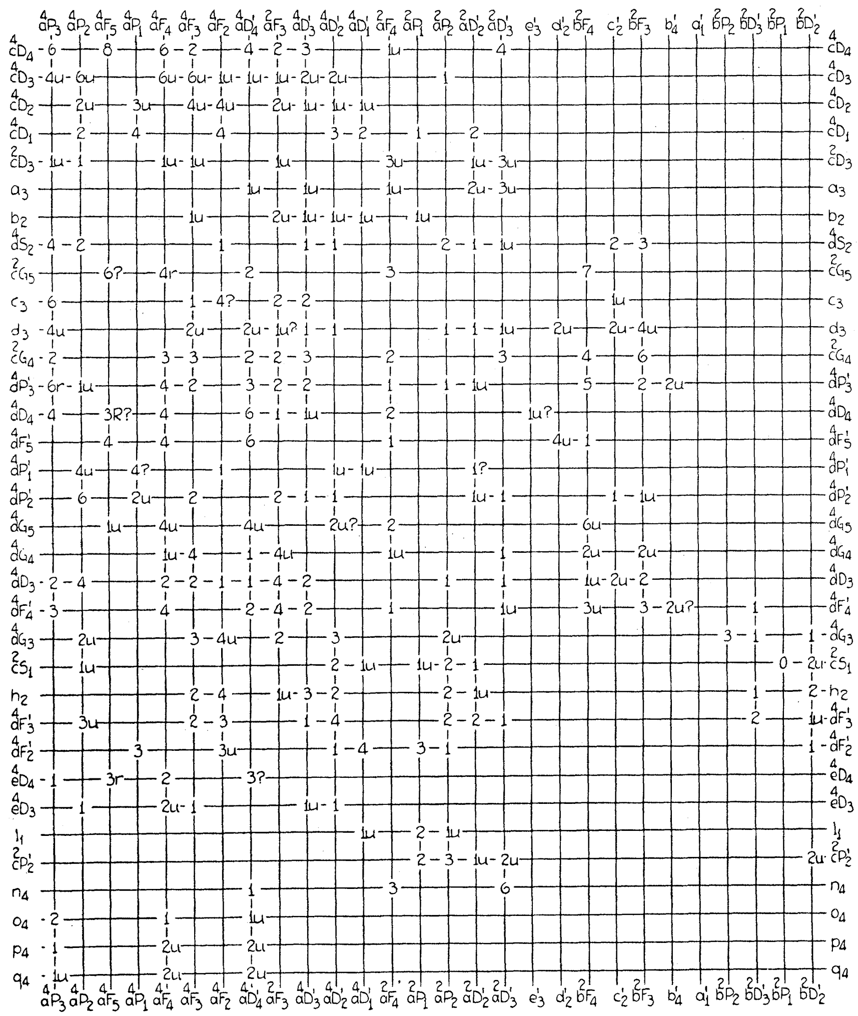

Fig. 1. Diagram giving the intensities of all the lines produced by combination of the positive and negative terms.*

those that would be expected theoretically. The identification of the four terms of Table IV listed as a complete $^4F'$ term is based on the following incomplete multiplets. Intensities only are given.

* The terms d^4G_6, g_4, e^4D_2, e^4D_1 of Table IV are omitted in Fig. 1, having been found after the plate had been made.

		$^4D'$				^4F				^4P		
		4	3	2	1	5	4	3	2	3 .	2	1
$^4F'$	5	(6)				(4)	(4)					
	4	(2)	(2)				(4)			(3)		
	3		(1)	(4)				(2)	(3)		(3u)	
	2			(1)	(4)				(3u)			(3)

The term separations are 11.9 : 1211.5 : 802.6. These are not unreasonable when the proximity of the limit is considered as well as the probability that the $^4F_2$ and $^4F_3$ terms converge to a single member of the spark ^3D, whereas $^4F_4$ and $^4F_5$ will converge to the other two members whose separations should be large.

A partially inverted $^4P'$ term is listed in Table IV. The combinations with the $^4D'$, ^4F and ^4P of Table I are as follows:—

		$^4D'$				^4F				^4P		
		4	3	2	1	5	4	3	2	3	2	1
$^4P'$	3	(3)	(2)				(4)	(2)		(6r)	(1u)	
	2		(1)	(1)				(2)			(6)	(2u)
	1			(1u)	(1u)				(1)		(4u)	(4)?

In addition to the above $^4F'$ and ^4P terms, a $^4S_2$ and parts of a ^4G and ^4D term have been identified. If the strong line λ3307.952 (8) is taken as a $^4F_5 - d^4G_6$, the term $d^4G_6 = -8822.6$; and the F G and D G multiplets are:—

		a^4F				a^4D'			
		5	4	3	2	4	3	2	1
d^4G	6	(8)							
848.1									
	5	(1u)	(4u)			(4u)			
37.9									
	4		(1u)	(4)	(3)	(1)	(4u)		
134.5									
	3				(4u)			(3)	

The intensities of combinations given by the terms g_4 and h_2 of Table IV would allow them also to be classified as $^4G_4$ and $^4G_3$. Moreover, the intervals would then be more in agreement with those of the term ^4F. The choice between these alternatives must be left for decision on the basis of more certain evidence.

The set of terms ^4S, P', D, F' G which have just been considered are probably those which theoretically result from the addition of a d-electron to the positive ion configuration d^9s; such terms would be expected, as is observed, to combine strongly with the configuration d^9sp, the terms of Table I. A part of another ^4D term is also given in Table IV. It is dealt with below in connection with limits.

Confirmation of the nature of a number of the terms just considered is given by the following unresolved Zeeman patterns. Of the calculated Zeeman patterns, only the theoretically strongest components are given.

λ	Z.E. (obs)	Z.E. (calc)	Comb.
3290.55	(0)1.31	(0)1.33	$a^4F_5—d^4F_5'$
3231.17	(0)1.24	(0)1.24	$a^4F_4—d^4F_4'$
3224.65	(0)1.94	(−)−1.98	$a^4F_2—d^4F_3'$
3223.43	(0)0+	(0) .4	$a^4F_2—d^4F_2'$
3099.92	(0)1.03	(−) .97−	$a^4P_3—d^4D_4$
3128.69	(0) .95	(−) .84−	$a^4P_2—d^4D_3$
3108.60	(0)1.52	(0)1.6	$a^4P_3—d^4P_3'$
3243.16	(0) .96	(−) .97−	$a^4F_4—d^4G_5$
3335.24	(0)1.16	(−)−1.06	$a^4F_4—c^2G_4$
3307.95	(0)1.11	(−)1.0−	$a^4F_5—d^4G_6$

(The last line is from Loring's results).

The remaining terms of Table IV should in the main belong to the doublet system but three only have been designated with any certainty. These are a $^2P_2$, a ^2S, and a $^2D_3$. The line intensities are low and the combinations few. A number of the terms given are calculated from only three combinations and are, therefore, perhaps doubtful. The three highest terms o_4, p_4 and q_4 are peculiar in the simularity of their combinations and in the fact that they include three lines which appear in the low voltage arc. The difference o_4-q_4 is 50.4, one of Rydberg's[11] differences. It occurs also in two other places as the difference of two negative terms.

It has been mentioned above that the terms m^2D should be the leading members of two series, one of which should converge to the spark ^1D (d^9s). The other should have as its two limits two of the three ^3D spark terms. It is of the greatest importance to find the higher members of these two series. O. Laporte has kindly communicated to me a conclusion to which he has come from the consideration of other complicated spectra; namely, that the following inequality of terms should be true.

$$\left\{(d^{z-2}\,s^2)-(d^{z-1}\,s)\right\}\text{ arc} > \left\{(d^{z-2}\,s)-(d^{z-1})\right\}\text{ spark}$$

In the case of the copper spectrum this means that the total length of the series headed by m^2D should be greater than the length of the ^2S series. Since $1^2S-m^2D=11202.5$, the limit of the ^2D series must be higher than -11202.5. The second member of the ^2D series (d^9ss) should be looked

[11] Rydberg, Astrophys. J. 6, 239 (1897).

for in the neighborhood of c^4D which is also presumably due to d^9ss. A term which gives combinations of the correct relative intensities is found at -2349.5. Taking this as the second member, the series limit is calculated to be about -24000. Confirmation* of such a value for the limit is obtained by considering the terms c^4D and e^4D as successive members of the series of quartet terms which are also due to d^9ss. The calculated limits fall at about -22300, in sufficient agreement with the limit calculated above from the ^2D terms. This means that the difference between the ^1S and ^3D of the spark spectrum is about 22300 cm^{-1}, the ^1S being the lower. The justification for the calculation of even approximate series limits from only two terms is contained in the fact, communicated to me by Laporte, that, in complicated spectra, series of terms which are due to the change in total quantum number of an s-electron only, are very closely "Rydbergian."

The behaviour of the spectrum lines in various sources is peculiar. The author made, some time ago, a large number of observations on the spectrum emitted by a low voltage arc in copper vapour. Excitation by six to seven volt electrons produces only the lines involving ^2S and m^2D and 2^2P. An arc at about eight volts and low current brings out a number of other lines, but by no means in the order in which the ordinary arc intensities would lead one to expect. Instead, the lines emitted practically all belong to four of the negative terms: namely, $c^4D_4 = -95.2$, $c^4D_1 = -2164.2$, and the terms $c^2G_4 = -8819.7$, $d^4D_4 = -8960.1$. Each of three other terms include in their combinations two low voltage arc lines, namely, $c^2G_5 = -8551.5$, $e^4D_4 = -11687.0$ and $q_4 = -14772.4$. The lines in question remain the only arc lines emitted even when the potential in the arc is sufficient to excite many of the ultra-violet spark lines. This peculiar behaviour is paralleled by the observations of R. S. Mulliken[12] on the excitation of copper lines by the action of active nitrogen on the copper halides. The same lines were observed in that experiment together with a number of new lines which are considered in connection with the regular doublet spectrum.

Ordinary Series

Since it has been found possible to add several terms to the ordinary doublet series of copper, it seems useful to restate the details of that part of the spectrum. The values of $1^2S = 62308.0$, and of the other known terms, are taken from Fowler's[1] calculations of the diffuse and sharp

* The discovery by the author since this paper was written that the extreme interval of the lowest spark ^3D (d^9s) is almost exactly equal to $c^4D_4 - c^4D_1$ and $e^4D_4 - e^4D_1$ is excellent confirmation of the correctness of the assignation of these terms to the structure d^9ss.

[12] R. S. Mulliken, Phys. Rev. **26,** 1 (1925).

TABLE V

Principal Series. $1^2S_1 - n^2P$.

$1^2S_1 = 62308.0$

λ		ν	Δν	n	$n^2P_{1,2}$.
3273.967	(10*r*)	30535.2	248.4	2	31772.8
3247.550	(10*r*)	30783.6			31524.4
2024.33	(*R*)	49383.0	0 ?	3	12925.0

series. The terms added agree so well with those calculated that no alteration in the limit is necessary. The principal series (Table V) is represented by the resonance lines and by one strong reversed line in the proper position for $1^2S - 3^2P_2$. As mentioned above this term 3^2P_2 is apparently single.

It has been found possible to extend the sharp series (Table VI) to the term 6^2S by including the pairs λ3598.01(2*u*), λ3566.14 (1*u*) and λ3463.5 (1*u*), λ3433.98 (1) Ex. The terms $5^2S = 3739.2$ and $6^2S = 2660.3$ fit very well into the series as given by Fowler.

TABLE VI

Sharp Series. $^2P_{2,1} - nS$

$^2P_1 = 31772.8$ $^2P_2 = 31524.4$

λ		ν	Δν	n	n^2S
8092.74	(10)	12353.4	248.4	2	19171.1
7933.20	(10)	12601.8			
4530.843	(6*r*)	22064.8	248.5	3	9459.5
4480.376	(6*r*)	22313.3			
3861.755	(3*u*)	25887.7	248.4	4	5636.7
3825.05	(3)	26136.1			
3598.01	(2*u*)	27785.3	248.3	5	3739.2
3566.14	(1*u*)	28033.6			
3463.5	(1*u*)	28864.3	248.1	6	2660.3
3433.98	(1) Ex.	29112.4			

Three new members and a possible fourth have been added to the diffuse series. The lines λ3512.122 (4*u*) and λ3481.9 (1*u*) are $2^2P_2 - 6^2D_3$ and $2^2P_1 - 6^2D_2$. The disparity between the intensities is accounted for by the fact that λ3512 is, undoubtedly, at least one other combination. It may in reality be three lines, since $^2P_2-6^2F$ also falls in this position. The further extension of this series is made possible by Mulliken's experiments mentioned above. In his experiments a number of new lines were measured and attributed to copper. Several of them have also been observed by the author in the low-voltage arc. It now appears that these lines are mainly, at least, members of the diffuse series. The wave-length measurements are at best accurate to .1°A, but they agree very reasonably with the calculated positions of the higher series members. In Table VII the values of the terms 7, 8, 9*D* have been obtained by extrapolation from the known terms and not from the observed lines.

TABLE VII

Diffuse Series. $2^2P_{2,1}-n^2D_{2,3}$.
$2^2P_1 = 31772.8$ $2^2P_2 = 31524.4$

λ		ν	$\Delta\nu$	n	$n^2D_{2,3}$.
5220.041	(6)	19151.6		3	12372.8
			6.9		
5218.170	(10)	19158.5	248.3		12365.9
5153.226	(8*u*)	19399.9			
4063.296	(4*u*)	24603.6		4	6920.8
			3.7		
4062.694	(6*u*)	24607.3	248.5		6917.1
4022.667	(6*u*)	24852.1			
3687.5	(3*u*)	27111.0		5	4415.5
3654.3	(2*u*)	27357.3			4413.4
3512.122	(4*u*)	28464.7		6	3059.7
3481.9	(1*u*)	28711.8			3061.0
					Calc. from series.
3414.2	(Mul)	29281.1		7	2245.0
3385.4	(Shen)	29530.2			
3353.8	(Mul)	29808.4		8	1718.
3326.2	(Mul)	30055.7			
3313.2	(Mul)	30174.0		9	1357. ?

The first pair of lines only of the fundamental series is known (Table VIII), but the *F* terms may be calculated from combinations with m^2D and 2^2P (Table IX). If these combinations are assumed correct, it appears

TABLE VIII

F—series. $3^2D_2 = 12372.8$; $3^2D_3 = 12365.9$.

λ	ν	n	$nF_{3,4}$.
18229.5	5484.1	4	6880.0
18194.7	94.6	5	4400.0
		6	3059.0

that the approximate values of the 4^2F term are $4^2F_3=6879.1$ and $4^2F_4=6881.6$. The term would, therefore, be inverted, which would be strange

TABLE IX

Combinations

λ	Int.	ν (obs.)	ν (calc.)	Comb.
16008.5		6245.0	6246.1	$2^2S—3^2P_2$
16653.4		6003.2	6004.2	$3^2P_2—4^2D_3$
5782.158	(8)	17289.8	17289.8	$m^2D_2—2^2P_1$
5700.249	(6)	17538.2	17538.2	$m^2D_2—2^2P_2$
5105.55	(8*u*)	19581.1	19581.1	$m^2D_3—2^2P_2$
2766.39	(8)	36137.6	36137.6	$m^2D_2—3^2P_2$
2618.38	(10*r*)	38180.2	38180.5	$m^2D_3—3^2P_2$
2369.89	(6)[x]	42183.1	42182.6	$m^2D_2—4^2F$
2260.51	(4)	44224.1	44225.5	$m^2D_3—4^2F$
2238.45	(2*u*)	44659.9	44662.6	$m^2D_2—5^2F$
4056.7	(2*Rv*)	24643.6	24644.4	$2^2P_2—4^2F$
4015.8	(1*u*)	24894.6	24892.8	$2^2P_1—4^2F$?
3652.40	(1*u*)	27371.5	27372.8	$2^2P_1—5^2F$?

[x]Also a spark line.

in a spectrum of this type. The peculiar *PF* combinations have been included although they involve violations of both the *k* and *j* selection principles. The theoretical and experimental frequencies do not agree very closely.

It is of importance to note that none of the terms of this normal spectrum, except ^2S, combine with any of the terms of the complicated spectrum, although this could not be predicted from the assumed atomic structures. For instance, there is nothing theoretically to prevent a transition from $d^{10}d$ to d^9sp, but it apparently does not occur.

The present analysis of the copper arc spectrum is in almost total disagreement with that given by H. Stücklen[13] in a recent paper. The analysis given in that paper is based on experiments with the under-water spark between copper electrodes. A number of lines are arranged in groups according to their appearance in absorption as the self-induction of the circuit is changed. The lines obtained by this method are arranged in six groups and are presumed to be all arc lines. The last three groups, however, contain spark lines. From the conditions of excitation, there cannot be much doubt that these spark lines are from low terms of the spark system. The lines in question are λ2192.24, 2246.98, 2242.60, 2218.08. 2210.24, 2189.60. In the analysis they are considered as arc lines

[13] H. Stücklen, Zeits. f. Physik. **34,** 562 (1925).

and some of them are included in two multiplets together with lines which are certainly arc. There can be no doubt that the arrangement in the form of multiplets is merely fortuitous. Amongst other constant frequency differences given in Stücklen's paper is 1497.9. This difference actually occurs no less than eight times and always between spark lines. The Zeeman effect of one of the pairs of lines is as follows:—

	Z.E. (obs.)	(calc.)	Desig.
2356.623	$\pm$ (0,.9)1.45, $\overline{2.49}$	$\dfrac{\pm(0\ 2)1,3,5}{2}$	${}^3D_1-{}^3P_2$
2276.261	$\pm$ (1.0) .48, 1.52	$\dfrac{\pm(2)1,\ 3}{2}$	${}^3D_1-{}^3P_1$

It seems probable that the ${}^3D_1$ term involved is the low spark ${}^3D$ which is due to the configuration d^9s. A considerable number of other regularities in the spark spectrum have been found and an analysis is being attempted.* It is important to find the ${}^1S$ term (d^{10}) but it seems likely from the calculation of arc limits that its value is so low that the lines due to its combinations will be found to lie well outside of the quartz region.

The copper arc spectrum has been shown to be in agreement with the Heisenburg-Hund theory. The structure may be represented by the diagram of Fig. 2. The negative energies in wave-numbers are given on the left hand side. The zero of energy is the ${}^1S$ spark term, the other spark terms then assuming negative values.

A few only of the terms of the ordinary arc series are given on the left of ${}^2S$, and heavy arrows are used to denote their inter-combinations. Dotted arrows indicate the limit of the particular series of terms when the total quantum number becomes large. On the right are the terms of the complicated spectrum founded on m^2D. They are grouped in the sets which arise from the particular electron configurations which are given in brackets. The few known terms which are probably due to the configurations d^8s^2p and d^8s^2d are omitted. They would have as limits the spark terms ${}^1S{}^1D{}^1G{}^3P{}^3F$, all of which will probably be higher than ${}^1D$.

The selection rule for the possible transitions from one configuration to another is, as given by Heisenberg,[4]

* The spark spectrum has now been analysed. The strong lines are almost all due to the combinations of a low ${}^3D$ and ${}^1D$ and a high ${}^3D$ and ${}^1D$ (d^9s) with an intermediate triad ${}^3P$, D', F, ${}^1P$, D', F (d^9p) The combinations of the last named terms with ${}^1S$ (d^{10}) would lie outside the observed region of the spectrum.

change in $k_1 = \pm 1$
change in $k_2 = 0, \pm 2$

where k_1 and k_2 are the azimuthal quantum numbers of the two electrons involved. No violations of this rule have been found within the second

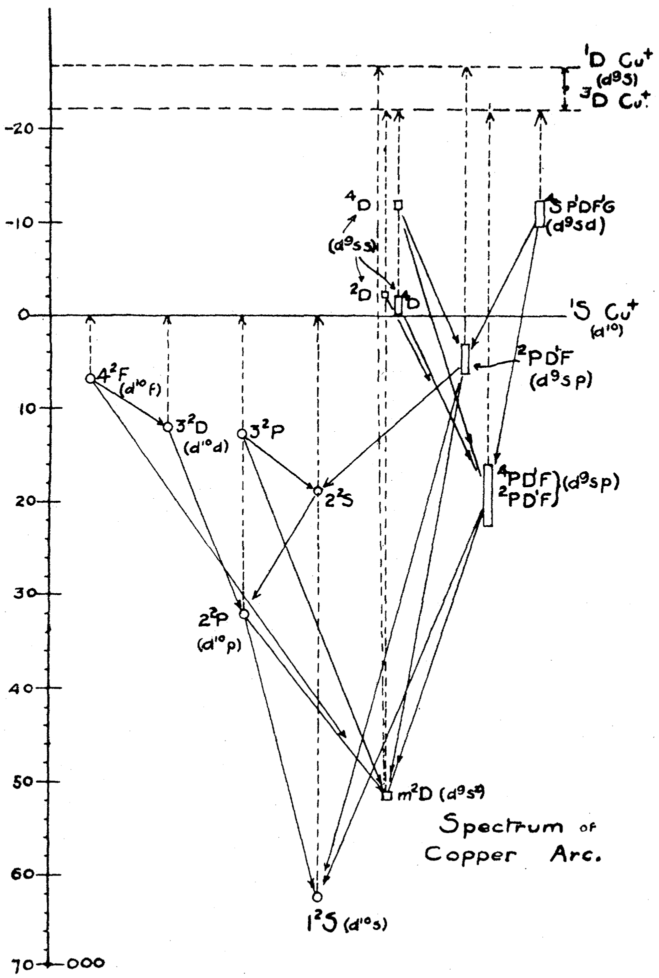

Fig. 2. Term diagram of the copper arc spectrum. Groups of terms, only, are indicated, and the electron configuration is given in brackets after each group. Dotted lines indicate limits and full lines, combinations.

rank part of the spectrum; but there are, apparently, violations in the combinations which occur between 2^2P $(d^{10}p)$ and ^2F $(d^{10}f)$ of the ordinary spectrum, and also in the combinations of m^2D (d^9s^2) with ^2F $(d^{10}f)$. In the latter case $\Delta k_1 = 3$ and $\Delta k_2 = 2$. There seems, however, to be another restricting influence which prevents transitions from the ordinary to the heavy metal types of electron configuration, except for the particular cases of $d^{10}s$ and d^9s^2. For instance, it might be expected that 2^2P $(d^{10}p)$ would produce strong lines in combination with members of the d^9ss and d^9sd sequences, but no such combination lines can be found. The lack of the transition $d^9ss \rightarrow d^{10}p$ is particularly strange when one considers the strength of the known triplet $m^2D - 2^2P$ $(d^{10}p \rightarrow d^9s^2)$. The relative intensity of these two combinations should be comparable to that of the first members of the principal and sharp series.

Table X contains the wave-lengths of all the lines of the copper arc spectrum which have been classified. The wave-lengths used are mainly those given by Meggers and by Hasbach. The gap between their observation is filled by the measurements of Aretz; and, over the whole spectrum, faint lines measured by other observers have been included. The allow-

TABLE X

Wave-lengths of all the classified lines of the copper arc spectrum.

λ	Authority	Intensity	ν	Designation.	ν(calc) $-$ ν(obs)
18229.	R	5	5484.1	3^2D_3—5^2F_4	1.8
194.	R	7	5494.6	3^2D_2—5^2F_3	−1.8
16653.	R	4	6003.2	3^2P_2—4^2D_2	1.0
008.	R	5	6245.0	2^2S—3^2P_2	1.1
8092.74	M	10	12353.4	2^2P_2—2^2S	
7933.20	M	10	12601.8	2^2P_1—2^2S	
7570.09	M	5	13206.3	2^2S_1—c_2'	
7427.26	M	1	13460.2	b^2D_2'—d^4G_3	.1
7193.56	M	2u	13897.5	b_4'—d^4P_3'	− .1
54.29	M	1	13973.8	b^2D_3'—d^4F_4'	− .1
24.66	M	1	14031.9	b^2D_3'—d^4G_3	− .1
7039.34	M	3	14202.0	$\begin{cases} b^2F_3\text{—}d^4S_2 \\ b^2P_2\text{—}d^4G_3 \end{cases}$	− .1
00.02	M	1u	14281.7	2^2S—a_1'	
6935.80	M	2u	14414.0	b^2D_2'—c^2S_1	
20.09	M	4u	14446.7	b^2F_3—d_3	.2
05.90	M	6	14476.4	b^2F_3—c^2G_4	
6890.90	M	2	14507.9	b^2D_2'—h_2	
89.92	M	2	14510.0	c_2'—d^4S_2	
81.94	M	2	14526.8	b^2F_3—d^4P_3'	
40.99	M	1u	14613.7	b^2D_2'—d^4F_3'	
35.46	M	1	14625.6	b^2D_2'—d^4F_2'	
21.86	M	1u	14654.7	c_2'—c_3	
6781.90	A	0	14741.1	b^2P_1—c^2S_1	
75.64	M	2u	14754.7	c_2'—d_3	.2
49.29	M	2u	14812.3	$\begin{cases} b_4'\text{—}d^4F_4' \\ 2^2S_1\text{—}b^2P_2 \end{cases}$	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation.	ν(calc)−ν(obs)
6741.42	M	7	14829.6	$b^2F_4—c^2G_5$	.2
6672.23	M	3	14983.4	$b^2D_3'—g_4$	− .1
29.67	M	1	15079.6	$b^2D_3'—h_2$	− .2
21.61	M	4	15097.9	$b^2F_4—c^2G_4$	.1
6599.68	A	5	15148.1	$b^2F_4—d^4P_3'$	.3
83.54	A	2	15185.2	$b^2D_3'—d^4F_3'$	
65.54	M	3u	15226.8	$2^2S_1—b^2P_1$	
50.98	M	1	15260.7	$b^2F_4—d^4F_5'$	
44.51	M	1u	15275.8	$b^2F_3—d^4P_2'$	
06.14	A	2u	15365.9	$b^2F_3—d^4G_4$	− .6
6485.18	M	2	15415.5	$b^2F_3—d^4D_3$	.1
74.20	M	3	15441.7	$b^2F_3—d^4F_4'$	
27.57	M	1	15553.7	$2^2S_1—b^2D_2'$	.2
15.18	A	1	15583.7	$c_2'—d^4P_2'$	.1
6358.09	A	2u	15723.7	$c_2'—d^4D_3$	− .1
25.45	A	4	15804.8	$a^2D_3—c^4D_4$	.1
6292.86	A	2	15886.6	a_1' —d^4F_3' ?	− .7
68.30	A	6u	15948.9	$\begin{cases} b^2F_4—d^4G_5 \\ b^2P_1—e^4D_3\ ? \end{cases}$	.1
53.37	A	2u	15987.0	$b^2F_4—d^4G_4$	− .1
33.79	A	1u	16037.2	$b^2F_4—d^4D_3$	
23.66	A	3u	16063.3	b^2F_4 —d^4F_4'	
20.94	A	2u	16070.3	$d_2'—d_3$	.2
6147.31	A	4u	16262.8	$d_2'—d^4F_5'$	
27.73	A	2u	16314.8	$e_3'—d_3$?	− .7
6064.69	A	1u	16484.3	$e_3'—d^4D_4$	− .3
32.33	A	2u	16572.8	$b^2D_2'—c^2P_2'$	− .2
5857.03	Ed.	1	17068.8	$a^2P_2—c^4D_3$	.2
5782.158	H	8	17289.8	$m^2D_2—2^2P_1$	
32.36	H	1u	17440.0	$a^2F_4—c^4D_4$	
00.249	H	6	17538.2	$m^2D_2—2^2P_2$	
5554.94	H	3	17997.0	$a^4D_3'—c^4D_4$	
35.78	H	3u	18059.3	$a^2D_3'—c^2D_3$	− .1
5462.97	Ed.	2	18300.0	$a^2D_2'—c^4D_1$	− .6
32.05	H	2u	18404.2	$a^4D_2'—c^4D_3$	− .1
08.46	H	1u	18484.4	$a^2D_2'—c^2D_3$	.3
5391.67	H	2u	18542.0	$a^4D_3'—c^4D_3$	
60.045	H	1	18651.4	$a^2P_1—c^4D_1$	
55.0	H	1u	18669.0	$a^4D_1'—c^4D_2$	− .3
52.68	H	2	18677.1	$a^2F_3—c^4D_4$	
5292.539	H	4	18889.3	$a^4D_4'—c^4D_4$	
50.5	Ex.	1u	19040.5	$a^4D_2'—c^4D_2$	− .2
20.041	H	6	19151.6	$2^2P_2—3^2D_2$	
18.170	H	10	19158.5	$2^2P_2—3^2D_3$	
12.89	A	1u	19177.9	$a^4D_3'—c^4D_2$	.2
00.87	H	1u	19222.2	$a^2F_3—c^4D_3$	− .1
5153.226	H	8u	19399.9	$2^2P_1—3^2D_2$	.1
44.12	H	1u	19434.3	$a^4D_4'—c^4D_3$	
11.945	H	2	19556.6	$a^4D_1'—c^4D_1$	− .1
05.551	H	8u	19581.1	$m^2D_3—2^2P_2$	
5076.2	H	3u	19694.3	$a^2F_4—c^2D_3$	
34.3	H	2u	19858.2	$a^2F_3—c^4D_2$	.1
16.634	H	3	19928.1	$a^4D_2'—c^4D_1$	
4866.4	H	3u	20543.4	$a^2D_3'—a_3$	.6
42.2	Ex.	1u	20646.0	$a^4F_2—c^4D_3$	− .2
4797.042	H	2	20840.4	$a^4F_3—c^4D_4$	
76.2	H	1u	20931.3	$a^2F_3—c^2D_3$	.1
67.5	H	2u	20969.5	$a^2D_2'—a_3$	
04.598	H	6	21249.9	$a^4F_4—c^4D_4$	− .1
4697.49	H	4u	21282.0	a^4F_2 —c^4D_2	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs.)
4674.76	H	6*u*	21385.5	$a^4F_3—c^4D_3$	− .1
51.13	H	8	21494.2	$a^4F_5—c^4D_4$	− .1
4586.97	H	6*u*	21794.8	$a^4F_4—c^4D_3$	
39.70	H	4*u*	22021.7	$a^4F_3—c^4D_2$	− .1
30.843	H	6*r*	22064.8	$2^2P_2—3^2S$	.1
13.20	H	1*u*	22151.0	$a^2P_1—b_2$	.1
09.386	H	4	22169.8	$a^4F_2—c^4D_1$	
07.5	H	1*u*	22179.0	$a^2F_4—a_3$	.1
4480.376	H	6*r*	22313.3	$2^2P_1—3^2S$	
15.60	H	3*u*	22640.6	$a^4P_1—c^4D_2$	.1
4397.0	Ex.	1*u*	22736.4	$a^4D_3'—a_3$	− .3
78.2	H	6*u*	22834.0	$a^4P_2—c^4D_3$	.2
36.0	Ex.	1*u*	23056.3	$a^4D_1'—b^2$	− .1
28.7	Ex.	1*u*	23095.2	$a^4F_3—c^2D_3$	− .5
4275.131	H	6	23384.5	$a^4P_3—c^4D_4$	.1
67.2	Ex.	1*u*	23428.0	$a^4D_2'—b_2$	− .1
59.43	H	2*u*	23470.7	$a^4P_2—c^4D_2$	− .3
53.34	Ex.	1*u*	23504.3	$a^4F_4—c^2D_3$	− .2
48.969	H	4	23528.5	$a^4P_1—c^4D_1$	
42.26	H	1*u*	23565.7	$a^4D_3'—b_2$	
31.0	Ex.	1*u*	23628.4	$a^4D_4'—a_3$	
4177.758	H	4*u*	23929.6	$a^4P_3—c^4D_3$	
23.27	H	2*u*	24245.8	$a^2F_3—b_2$	
21.7	H	1*u*	24255.0	$a^2D_3'—d^4S_2$	
04.233	H	2	24358.2	$a^4P_2—c^4D_1$	
4080.534	H	1*u*	24499.7	$a^2D_3'—d_3$	.2
75.592	H	3	24529.4	$a^2D_3'—c^2G_4$	
73.27	Ex.	1	24543.4	$a^4P_2—c^2D_3$	.1
63.296	H	4*u*	24603.6	$2^2\mathrm{P}_2—4^2\mathrm{D}_2$	
62.694	H	6*u*	24607.3	$2^2P_2—4^2D_3$	
56.7	H	2*Rv*	24643.6	$2^2P_2—4^2F$	.8
50.656	H	1	24680.4	$a^2D_2'—d^4S_2$	.1
22.667	H	6*u*	24852.1	$2^2P_1—4^2D_2$	− .1
4015.8	H	1*u*	24894.6	$2^2P_1—4^2F_3$	−1.8
10.85	Ex.	1	24925.4	$a^2D_2'—d_3$	
03.038	H	2	24974.0	$a^2P_2—d^4S_2$	.1
3997.93	C.T.	1*u*	25005.9	$a^2D_2'—d^4P_3'$	− .6
64.15	Ex.	1	25219.0	$a^2P_2—d_3$	
51.48	C.T.	1	25299.8	$a^2P_2—d^4P_3'$	− .9
46.88	Ex.	1	25329.3	$a^2D_3'—d^4P_2'$	− .5
33.00	Ex.	1	25418.7	$a^2D_3'—d^4G_4$	− .4
25.274	H	1	25468.7	$a^2D_3'—d^4D_3$	− .1
21.274	H	1*u*	25494.7	$a^2D_3'—d^4F_4'$	
3899.1	Ex.	1*u*	25639.7	$a^4P_3—c^2D_3$?	− .8
88.58	C.T.	1	25709.1	$a^2D_2'—d^4P'$?	1.0
81.71	Ex.	1*u*	25754.6	$a^2D_2'—d^4P_2'$	− .3
62.75	Ex.	1	25881.0	$3^2P_2—c^2P_2'$?	− .6
61.755	H	3*u*	25887.7	$2^2P_2—4^2S$	
60.467	H	3	25896.3	$a^2F_4—c^2G_5$	
25.050	H	3	26136.1	$2^2P_1—4^2S$	
20.879	H	2	26164.6	$a^2F_4—c^2G_4$	− .1
17.50	H	1	26187.8	$a^2P_2—d^4D_3$	− .1
13.54	H	1	26214.9	$a^2F_4—d^4P_3'$	
05.30	H	2*u*	26271.7	$a^2P_2—d^4G_3$	.2
00.499	H	2	26304.9	$a^2F_4—d^4D_4$	
3799.88	H	1	26309.2	$a^4D_2'—d^4S_2$	
97.19	C.T.	1	26327.7	$a^2F_4—d^4F_5'$	− .5
85.60	C.T.	1*u*	26408.4	$a^4F_3—b_2$	.7
80.05	Ex.	1	26447.2	$a^4D_3'—d^4S_2$	− .1
71.902	*H*	2	26504.3	$a^2D_3'-g_4$	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
3764.82	Ex.	1	26554.2	a^4D_2'—d_3	− .1
59.495	H	2	26591.8	a^4D_3'—c_3	
45.38	C.T.	1	26692.0	a^4D_3'—d_3	
43.38	C.T.	1	26706.4	a^2D_3'—d^4F_3'	− .2
41.247	H	3	26721.5	a^4D_3'—c^2G_4	
34.23	H	2	26771.7	a^4D_3'—d^4P_3'	.1
3721.70	H	1*u*	26861.8	a^4D_3'—d^4D_4	
20.770	H	2	26868.5	m^2D_2—a^4P_2	.1
12.00	H	1	26932.0	a^2D_2'—c^2S_1	
07.16	C.T.	1*u*	26967.2	a^4D_1'—d^4P_1'	
00.532	H	2	27015.5	a^2F_4—d^4G_5	
3699.1	H	1*u*	27025.9	a^2D_2'—h_2	
95.33	C.T.	1*u*	27053.5	a^2F_4—d^4G_4	− .1
87.5	H	3*u*	27111.0	2^2P_2—5^2D_3	
84.925	H	1	27129.9	a^2F_4—d^4F_4'	− .1
84.671	H	2	27131.8	a^2D_2'—d^4F_3'	− .1
71.969	H	2	27225.6	a^2P_2—c^2S_1	
65.740	H	2	27271.9	a^2F_3—c_3	
64.06	C.T.	1*u*	27284.4	a^2P_1—c^2S_1	− .4
59.358	H	2	27319.4	a^2P_2—h_2	.1
56.787	H	1*u*	27338.7	a^4D_2'—d^4P_1'	.1
55.865	H	2	27345.6	a^4D_4'—c^2G_5	
54.3	H	2*u*	27357.3	2^2P_1—5^2D_2	
52.40	H	1*u*	27371.5	$\{2^2P_1$—5^2F ?	1.3
				a^2F_3—d_3	.6
50.864	H	1	27383.0	a^4D_2'—d^4P_2'	
48.385	H	2	27401.6	a^2F_3—c^2G_4	
45.236	H	2	27425.3	a^2P_2—d^4F_3'	
44.05	K	2*u*	27434.2	a^4D_2'—d^4G_5 ?	.4
43.65	C.T.	1	27437.2	a^2P_2—d^4F_2'	
41.693	H	2	27452.0	a^2F_3—d^4P_3'	
35.923	H	3	27495.5	a^2P_1—d^4F_2'	.1
32.56	H	1	27521.0	a^4D_3'—d^4P_2'	− .1
29.794	H	1	27541.9	a^2F_3—d^4D_4	.1
24.236	H	2*u*	27584.2	a^4D_4'—d_3	.1
21.248	H	3	27607.0	a^4D_2'—d^4G_3	
20.346	H	2	27613.8	a^4D_4'—c^2G_4	
14.216	H	2	27660.7	a^4D_3'—d^4D_3	
3613.755	H	3	27664.2	a^4D_4'—d^4P_3'	
10.806	H	2	27686.8	a^4D_3'—d^4F_4'	
09.300	H	2	27698.3	m^2D_2—a^4P_1	
02.038	H	6	27754.2	a^4D_4'—d^4D_4	
3599.135	H	6	27776.6	a^4D_4'—d^4F_5'	− .1
98.01	H	2*u*	27785.3	2^2P_2—5^2S	− .2
94.025	H	2	27816.1	m^2D_3—a^4P_3	
66.14	H	1*u*	28033.6	2^2P_1—5^2S	
46.45	H	1*u*	28189.2	a^4D_1'—c^2S_1	− .1
44.966	H	2	28201.0	a^2F_3—d^4P_2'	
33.744	H	4*u*	28290.5	a^2F_3—d^4G_4	
30.388	H	6	28317.4	m^2D_2—a^4F_3	
27.487	H	4	28340.7	a^2F_3—d^4D_3	.1
24.240	H	4	28366.8	a^2F_3—d^4F_4'	.1
20.032	H	4	28400.7	a^4D_1'—d^4F_2'	
17.029	H	2	28425.0	a^2F_3—d^4G_3	
12.122	H	4*u*	28464.7	$\{2^2P_2$—6^2D_3	
				a^4D_4'—d^4G_5	.1
07.38	Ex.	1	28503.2	a^4D_4'—d^4G_4	− .5
01.52	Ex.	1	28550.9	a^4F_2—d^4S_2	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
3501.31	Ex.	1	28552.6	$a^4D_4'—d^4D_3$	.4
00.314	H	2	28560.7	$a^4D_2'—c^2S_1$	
3498.063	H	2	28579.1	$a^4D_4'—d^4F_4'$	
88.864	H	2	28654.5	$a^4D_2'—h_2$	.1
87.565	H	2*u*	28665.1	$a^2D_3'—c^2P_2'$	
83.760	H	4	28696.4	$a^4D_3—g_4$	
81.9	Ex.	1*u*	28711.8	$2^2P_1—6^2D_2$	
75.998	H	4	28760.5	$a^4D_2'—d^4F_3'$	− .1
74.574	H	1	28772.3	$a^4D_2'—d^4F_2'$	
72.136	H	3	28792.5	$a^4D_3'—h_2$	
3463.5	H	1*u*	28864.3	$2^2P_2—6^2S$	− .2
59.424	H	1	28898.3	$a^4D_3'—d^4F_3'$	
57.856	H	3	28911.4	$m^2D_3—a^4P_2$	.1
50.335	H	6	28974.4	$a^2D_3'—n_4$	
40.52	H	3	29057.1	$m^2D_2—a^4F_2$	− .1
36.53	H	1*u*	29090.8	$a^2D_2'—c^2P_2'$	− .2
33.98	Ex.	1	29112.4	$2^2P_1—6^2S$	.1
20.16	H	1*u*	29230.1	$a^2P_2—1_1$	
14.2	Mu.		29281.1	$2^2P_2—7^2D_3$	−1.7
13.34	H	2	29288.5	$a^2P_1—1_1$	
02.222	H	3	29384.2	$a^2P_2—c^2P_2'$	
3396.324	H	1	29435.2	$a^4F_3—c_3$	
95.473	H	2	29442.5	$a^2P_1—c^2P_2'$	
92.95	K	2	29463.2	$a^2P_1-e^4D_2$?	− .3
92.01	H	1*u*	29472.6	$a^2F_3—h_2$	
85.4	Sh.		29530.2	$2^2P_1—7^2D_2$	−2.4
84.815	H	2*u*	29535.3	$a^4F_3—d_3$	.1
81.425	H	3	29564.9	$a^4F_3—c^2G_4$	
79.69	Ex.	1	29580.1	$a^4F_2—d^4P_1'$	.4
75.671	H	2	29615.3	$a^4F_3—d^4P_3'$	
65.353	H	4*r*	29706.1	$a^4F_4—c^2G_5$	
58.76	Ex.	1	29764.4	$a^4F_2—d^4D_3$	.1
58.31	Ex.	1	29768.4	$a^4D_2—e^4D_3$	.1
54.475	H	2*u*	29802.4	$a^4D_4'—d^4F_2'$?	.1
53.8	Mu.		29808.4	$2^2P_2—8^2D_3$	−2.0
49.287	H	4*u*	29848.6	$a^4F_2—d^4G_3$	.1
42.85	K	1*u*	29906.0	$a^4D_3'—e^4D_3$	.4
37.850	H	6	29950.8	$m^2D_3—a^4F_4$ $a^4F_5—c^2G_5$	.1 − .4
35.235	H	3	29974.3	$a^4F_4—c^2G_4$	
29.638	H	4	30024.7	$a^4F_4—d^4P_3'$	
3326.2	Mu.		30055.7	$2^2P_1—8^2D_2$	− .9
19.691	H	4	30114.7	$a^4F_4—d^4D_4$	
17.225	H	4	30137.0	$a^4F_4—d^4F_5'$	
13.2	Mu.		30174.1	$2^2P_2—9^2D_2$?	−6.6
11.00	H	1*u*	30193.7	$a^4D_1'—1_1$	− .1
07.952	H	8	30221.5	$a^4F_5—d^4G_6$	
3292.903	H	3*R*	30359.6	$a^4F_5—d^4D_4$	− .6
.81	K	2	30360.5	$m^2D_3—a^4F_3$	− .2
.392	H	2	30364.3	$a^4F_3—d^4P_2'$	
90.549	H	4	30381.3	$a^4F_5—d^4F_5'$	
82.716	H	4	30453.8	$a^4F_3—d^4G_4$	
79.823	H	3	30480.7	$m^2D_2—a^2F_3$ $a^4D_4'—e^4D_4$	 .4
77.311	H	2	30504.1	$a^4F_3—d^4D_3$	
73.967	H	10*R*	30535.2	$1^2S—2^2P_1$	
68.278	H	3	30588.4	$a^4F_3—d^4G_3$	− .1
66.014	H	3	30609.6	$a^2F_4—n_4$	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
3252.22	H	2	30739.4	$a^4P_2-d^4S_2$ $a^4D_2'-e^4D_2$?	−.1 .2
47.550	H	10*R*	30783.6	$1^2S—2^2P_2$	
43.160	H	4*u*	30825.3	$a^4F_4—d^4G_5$	
39.16	H	1*u*	30863.3	$a^4F_4—d^4G_4$	−.1
35.712	H	4	30896.2	$a^4F_2—h_2$	.1
33.89	H	2	30913.6	$a^4F_4—d^4D_3$	−.1
31.17	H	4	30939.6	$a^4F_4—d^4F_4'$ $a^4P_1—d^4P_1'$	 −.4
26.60	H	2*u*	30983.5	$a^4P_1—d^4P_2'$	−.1
24.653	H	3	31002.2	$a^4F_2—d^4F_3'$	−.1
23.424	H	3*u*	31014.0	$a^4F_2—d^4F_2'$	
.044	H	1*u*	31017.7	$a^4F_5—d^4P_2'$?	.3
18.23	H	1*u*	31064.0	$a^4P_2—d^4P_3'$	.1
17.64	H	1*u*	31069.7	$a^4F_5—d^4G_5$	−.1
3209.47	H	1*u*	31148.8	$a^4D'_1—e^4D_1$	−.1
08.236	H	4	31160.8	$m^2D_2—a^4D'_3$	
3194.103	H	6	31298.7	$m^2D_2—a^4D_2'$	
71.658	H	1*u*	31520.2	$a^4D_2'—e^4D_1$	.1
69.690	H	4*u*	31539.7	$a^4F_3—g_4$	
60.047	H	2	31636.0	$a^4F_3—h_2$	−.1
56.623	H	3	31670.3	$m^2D_2—a^4D_1'$	
49.501	H	2	31741.9	$a^4F_3—d^4F_3'$	−.2
46.821	H	4*u*	31768.9	$a^4P_2—d^4P_1'$	
42.434	H	6	31813.3	$a^4P_2—d^4P_2'$	−.2
40.318	H	4	31834.7	$a^4P_3—d^4S_2$	
28.692	H	4	31953.0	$a^4P_2—d^4D_3$	−.1
26.106	H	6	31979.4	$a^4P_3—c_3$	
20.452	H	2*u*	32037.4	$a^4P_2—d^4G_3$	−.3
18.355	H	1	32058.9	$a^4D_4'—n_4$	
16.345	H	4*u*	32079.6	$a^4P_3—d_3$	
13.468	H	2	32109.2	$a^4P_3—c^2G_4$	−.1
08.603	H	6*r*	32159.5	$a^4P_3—d^4P_3'$	
3099.922	H	4	32249.6	$a^4P_3—d^4D_4$	−.1
93.993	H	6	32311.3	$m^2D_3—a^4D_4'$	.1
88.121	H	3	32372.8	$a^4P_1—d^4F_2'$	−.1
73.803	H	4	32523.6	$m^2D_3—a^2F_3$	
68.912	H	2	32575.4	$m^2D_2—a^2P_1$	
63.416	H	6	32633.8	$m^2D_2—a^2P_2$	
52.52	Ex.	1	32750.3	$a^4F_3—e^4D_3$	−.5
44.032	H	2	32841.6	$a^4F_4—e^4D_4$	
36.105	H	6	32927.4	$m^2D_2—a^2D_2'$	
30.25	H	2*u*	32991.0	$a^4P_2—c^2S_1$	−.2
24.993	H	2	33048.3	$a^4P_3—d^4D_3$	
22.608	H	3	33074.4	$a^4P_3—d^4F_4'$	
21.56	H	3*r*	33085.9	$a^4F_5—e^4D_4$	
14.84	H	2*u*	33159.6	$a^4F_4—e^4D_3$	−.4
3012.02	H	3*u*	33190.7	$a^4P_2—d^4F_3'$	−.2
10.840	H	5	33203.7	$m^2D_3—a^4D_3'$	
2998.384	H	2	33341.6	$m^2D_3—a^4D_2'$	
97.363	H	4	33353.0	$m^2D_2—a^2D_3'$	−.1
82.77	H	1*u*	33516.1	$a^4D_4'—o_4$	
79.38	H	2*u*	33554.3	$a^4D_4'—p_4$	
78.293	H	2*u*	33566.5	$a^4D_4'—q_4$	
61.177	H	6	33760.5	$m^2D_3—a^2F_4$ $a^4F_2—e^4D_1$	.2 −1.4
51.3	H	1*u*	33873.5	$2^2P_2—c^2D_3$	.4

TABLE X. (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
2923.27	Ex.	1	34198.3	$a^4P_2—e^4D_3$	.3
11.21	H	1u	34340.0	$a^4P_1-e^4D_2$?	− .2
2882.937	H	4	34676.7	$m^2D_3—a^2P_2$	
58.737	H	2	34970.2	$m^2D_3—a^2D_2'$	.1
.233	H	1	34976.4	$a^4P_3—e^4D_4$	
46.49	Ex.	1	35120.7	$a^4P_1-e^4D_1$	
24.375	H	8	35395.7	$m^2D_3—a^2D_3'$	.1
2786.52	Ex.	1	35876.5	$a^4F_4—o_4$	.1
83.55	H	2u	35914.8	$a^4F_4—p_4$	− .1
82.61	H	2u	35926.9	$a^4F_4—q_4$	.1
66.388	H	8	36137.6	$m^2D_2—3^2P_2$	
2630.002	H	2	38011.5	$a^4P_3—o_4$	− .1
27.37	H	1	38049.5	$a^4P_3—p_4$	
26.6	Ex.	1u	38060.7	$a^4P_3—q_4$	1.1
18.381	H	10r	38180.2	$m^2D_3—3^2P_2$	.3
2494.88	K	2	40070.0	$2^2P_2—d^4S_2$?	− .3
92.142	H	8	40114.0	$1^2S—a^4P_2$	
41.625	H	6	40943.9	$1^2S—a^4P_1$	− .2
06.661	H	6	41538.7	$m^2D_2—e_3'$	
2392.629	H	8r	41782.3	$m^2D_2—d_2'$	
69.891	Mi.	6	42183.1	$m^2D_2—4^2F$	− .5
63.21	H.M.	1u	42302.6	$1^2S—a^4F_2$	− .2
19.575	H.M.	4	43098.1	$m^2D_2—c_2'$	− .2
2303.134	Mi.	6	43405.7	$m^2D_2—b^2F_3$	.2
2293.847	H.M.	8R	43581.4	$m^2D_3—e_3'$	.2
81.09	P.M.	2	43825.1	$m^2D_3—d_2'$	.1
63.11	H.M.	6R	44173.3	$m^2D_2—a_1'$	− .1
60.51	H.M.	4	44224.1	$m^2D_3—4^2F$	1.4
44.26	H.M.	2	44544.3	$1^2S—a^4D_2'$	− .2
38.45	H.M.	2u	44659.9	$m^2D_2—5^2F$	2.7
36.24	H.M.	1u	44704.0	$m^2D_2—b^2P_2$	− .2
30.10	H.M.	6R	44827.1	$m^2D_3—b^2F_4$	.1
27.77	H.M.	6R	44874.0	$m^2D_2—b^2D_3'$	− .1
25.691	H.M.	2R	44915.9	$1^2S—a^4D_1'$	− .2
15.68	H.M.	4R	45118.8	$m^2D_2—b^2P_1$	
14.59	H.M.	6R	45141.0	$m^2D_3—c_2'$	− .2
2199.76	Sh.	3R	45445.3	$m^2D_2—b^2D_2'$	.1
.60	Sh.	3R	45448.6	$m^2D_3—b^2F_3$	.2
81.71	H.M.	1u	45821.2	$1^2S—a^2P_1$	− .4
78.95	H.M.	1u	45879.3	$1^2S—a^2P_2$	− .1
69.53	H.M.	2u	46078.4	$m^2D_3—b_4'$	− .2
65.10	H.M.	1u	46172.7	$1^2S—a^2D_2'$	.1
40.66	P.M.	2	46699.8	$m^2D_3—5^2F$??	5.7
38.50	H.M.	1u	46747.0	$m^2D_3—b^2P_2$	− .3
30.76	H.M.	1	46916.7	$m^2D_3—b^2D_3'$	.1
19.87	P.M.	0	47157.7	$m^2D_3—b^2P_1$??	3.5
05.12	Sh.		47488.1	$m^2D_3—b^2D_2'$	.2
2024.33	Sh.		49383.0	$1^2S—3^2P_2$	

Authorities

A	Aretz.	K	Kayser.
C.T.	Crew & Tatnall.	M	Meggers.
Ed.	Eder & Valenta.	Mu.	Mulliken.
Ex.	Exner & Haschek.	R	Randall.
H	Hasbach.	Sh.	Shenstone.

H.M. Hasbach, with Mitra corrections.
P.M. Pina, with Mitra corrections.

able error between calculated and observed wave-numbers has been considered greater where such less reliable measurements have been used. In the ultraviolet below λ2369, the standard measurements of Mitra[9] have been accepted as correct with the exception of λ2148. Hasbach's wave-lengths have then been corrected by interpolation. This amounts to considering that his wave lengths are consistent but have a gradually increasing error. The justification for such a procedure is given by the small error between the calculated and observed wave-numbers. The tables used were Kayser and Konen "Handbuch der Spectroscopie" Vol. VII and Kayser Vol. V. The frequencies have all been re-calculated using Kayser's "Tabelle der Schwingungszahlen."

The number of lines classified is about 350. They include practically every strong line in the spectrum, as well as a great majority of the weak lines. The only comparatively strong unclassified lines from Meggers and Hasbach's lists, are the following:—

3454.70	(4*u*)
3382.899	(3)
3175.73	(3*u*)
2768.89	(3)

In the ultra-violet one low-voltage line alone, λ2171.75, remains unaccounted for, it is undoubtedly due to a term combining either with m^2D_2 or m^2D_3 and with none of the other known trems of the spectrum.

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