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ABSORPTION SPECTRA OF THE PALLADIUM AND PLATINUM TRIADS*

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ABSTRACT

Under certain conditions the continuous spectrum from high potential sparks between metal electrodes immersed in a liquid is interrupted by absorption lines which are identifiable with lines in the arc emission spectrum of the metal. The importance of these lines lies in the fact that in numerous cases where the spectral structures are known, they have been shown to involve the normal state and sometimes low metastable states of the atoms. By extending these observations to unclassified spectra, this method thus permits the identification of the low levels in the spectral structures.

Using electrodes of Ru, Rh, Pd, Os, Ir, and Pt, in the under-water spark, the absorption spectra of these metals were determined down to wave-lengths near 2000A. Analyses of these data reveal the low levels in the arc spectra of the Pd and Pt triads as follows: the lowest energy is represented by a quintet-F term for Ru, by a quartet-F for Rh and by a singlet-S for Pd. A considerable number of the absorption lines for Os, Ir, and Pt have been classified with levels but it is impossible at the present time to recognize their spectral types, except that for Ir the lowest level is probably a doublet-D term and for Pt it is probably a triplet-D. The quantum-theoretical arrangement of low levels as derived from the electron configurations in these atoms is summarized.

1. INTRODUCTION

THE structures of many complex spectra have been revealed by modern methods of analysis which consist of a systematic correlation of various observational data, such as wave numbers, relative intensities, reversal or absorption phenomena, temperature classification and Zeeman effects. The chief difficulty in analyzing the remaining spectra occurs on account of the lack of sufficient descriptive material. Thus for the metals of the Pd and Pt triads no reliable information of the three kinds last named was available when this investigation was begun and even the wave-length and intensity data were incomplete. These defects have now been remedied in some degree, but in no case are the data sufficient to permit an entirely satisfactory classification of the arc spectra of these elements, not to mention their spark spectra which are generally less well known. The purpose of this paper is to present some observations on absorption spectra of the six metals of the Pd and Pt groups, and so far as possible, to draw conclusions concerning the normal states and low metastable terms characterizing the neutral atoms.

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As is well known, a knowledge of the lines which first appear in absorption is of great importance for the analysis of spectra on account of the significance of such lines in describing the normal state and other prominent spectral terms. The ideal arrangement is one in which a continuous spectrum is photographed after passing through a tube of metal vapor at a temperature to produce sufficient vapor pressure without appreciable excitation of the atoms. The continuous spectrum is then crossed by absorption lines which are usually identifiable with prominent lines in the emission spectrum of the electric arc. Such experiments have recently been performed in connection with the analyses of complex spectra, for example, the work of Grotrian[1] on lead, of Gieseler and Grotrian[2] on scandium, titanium and vanadium, of King[3] on chromium, of Angerer and Joos[4] on iron, cobalt and nickel, and of Zumstein[5] on manganese and tin. The study, in this manner, of metals having high boiling points is very difficult and has not been attempted for some of them. More than a year ago we began to investigate the absorption phenomena in under-water spark spectra to determine if they might be controlled so as to be substituted for the regular absorption experiments. Guided by the earlier investigations in this field, an arrangement was employed which was immediately successful, and a considerable number of spectra were photographed. The elements, Fe, Co, Ni, whose spectral structures have been derived from a remarkable correlation of all the descriptive data concerning these spectra, were first examined in order to test our procedure and results. Since these results confirmed the classification of these spectra, the method was extended[6] to the analogous elements, Ru, Rh, Pd, and Os, Ir, Pt, which constitute the subject matter of this paper.

2. UNDER-WATER-SPARK-SPECTRA

Spectral characteristics of sparks between metallic electrodes immersed in liquids have been studied by a considerable number of investigators. The first experiments, those of Wilsing,[7] of Lockyer,[8] and of Hale,[9] were inspired by problems in stellar spectra and were concerned mainly with spectral line displacements due to pressure and other causes. Extensive

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[1] Grotrian, Zeits. f. Physik **18,** 169 (1923).

[2] Gieseler and Grotrian, Zeits. f. Physik **25,** 342 (1924).

[3] King, Astrophys. J. **60,** 282 (1924).

[4] Angerer and Joos, Ann. d. Physik **74,** 743 (1924).

[5] Zumstein, Phys. Rev. **26,** 765 (1925); **27,** 106, 150 (1926).

[6] Cf footnote 5, Science **61,** 635 (1925).

[7] Wilsing, Sitz. d. Akad. Wiss. Berlin, pp. 426–36 (1899).

[8] Lockyer, Astrophys. J. **15,** 190 (1902).

[9] Hale, Astrophys. J. **15,** 132 (1902).

investigations were carried out by Konen,[10] Finger,[11] E. and L. Bloch,[12] and Hulburt.[13] Among these, Finger noted the rule that lines belonging to a spectral series behaved in the same way in respect to changes occurring in under-liquid sparks. This was supported by observations on Cu, Ag, Mg, Ca, Zn, Cd, Al, Tl. Similar conclusions were drawn from the detailed observations of E. and L. Bloch who photographed the under-water spark spectra (5000 to 2200A) of Zn, Cd, Hg, Mg, Ca, Cu, Ag, Al, Tl, Sn, Pb, Bi, Sb and Fe, and found that in general two groups of lines, reversed and bright, appeared, the former being representative of the arc spectrum and the latter of the spark. In addition to series lines in arc spectra, the so-called "single line" (intersystem combination or resonance line) is always absorbed. The suggestion was made that such observations might facilitate the search for spectral regularities.

In Hulburt's experiments the absorption lines were identified in the spectral region 4500–2000A, those appearing in the underwater spark spectra of Al, Bi, Cd, Au, Ir, Pb, Mg, Pt, Rh, Ag, Sn, Zn were those which were reversed in the arc, no more and no less. For the metals Sb, Co, Cr, Cu, Fe, Mo, Ni and W all the lines reversed in the arc appeared as absorption lines and in addition the under-water spark spectra of these elements exhibited altogether more than 400 absorption lines which are not listed as reversed in the arc, but complete details are not given for these.

An investigation of the physical and electrical conditions determining the characteristics of under-water sparks was recently made by Miss Stücklen[14] who studied the effect on Cd spectra of varying (1) external spark gap, 0.5 to 3 cm, (2) self induction to change wave-length from 300 to 1100 m, and (3) diameter of electrodes, 3 to 8 mm, and concluded that the appearance of absorption lines was favored by increasing the frequency, decreasing the potential and increasing the diameter of the electrodes. Under the conditions of Miss Stücklen's experiment, the fundamental spark lines of Cd appeared also in absorption.

The only published results of attempts to correlate the regularities of complex spectra with absorption observations in the under-water spark were those of Sur[15] who discussed his observations with Fe and Cr from this point of view.

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[10] Konen, Ann. d. Physik **9**, 742 (1902).

[11] Finger, Zs. f. wiss. Phot. **7**, 329 and 369 (1909).

[12] E. and L. Bloch, J. d. Physique et le Rad. **3**, 309 (1922).

[13] Hulburt, Phys. Rev. **24**, 129 (1924).

[14] Stücklen, Zeits. f. Physik **30**, 24 (1924).

[15] Sur, Phil. Mag. **1**, 433 (1926).

A general survey of all the published data on lines absorbed in under-water spark spectra of various elements gives the impression that results obtainable by this method are more comparable with those of true absorption experiments than might be expected since the simultaneous appearance of spark lines in emission is evidence that a considerable number of atoms in such a source must be ionized. It appears that the atoms in the outer envelope of the spark are either in normal or low metastable states, and it may be concluded that neither temperature nor photo-ionization are sufficient to energize these atoms.

The lines observed as absorbed in the under-water spark are also remarkably in accord with other observations which have been demonstrated to be very significant in identifying the low levels:

1. All the lines observed as "reversals" in arc emission spectra are always observed as absorption lines in under-water spark spectra and sometimes many more.

2. In so far as temperature classifications of emission lines have been studied in the electric furnace, it is evident that the lines ordinarily absorbed in the under-water spark spectra are always the lines of lowest temperature classes, those first to appear as the furnace temperature rises.

In the determination of absorption spectra by means of the under-water spark, two respects in which this method imposes limitations on the completeness of the results must be mentioned.

1. Bands assigned to water vapor always appear in absorption and these may occasionally obscure absorbed lines characteristic of the metal electrodes. The band at 3063A is especially prominent; it extends nearly to 3200A and contains a large number of lines. This difficulty can be overcome by using some other liquid.

2. It has frequently been mentioned that the lines (both emission and absorption) in under-water spark spectra are widened, some are diffuse and certain ones are displaced as compared with their appearance in ordinary sources. These effects make it difficult to resolve lines which are very close, and sometimes lead to an uncertainty in identifying lines which appear absorbed.

3. EXPERIMENTAL

The great violence of the powerful electric discharge between electrodes under water showed, in preliminary experiments with improvised apparatus, that it was necessary to build a rugged device for holding and adjusting the metal electrodes. The apparatus constructed for this purpose is shown in Fig. 1. It consists of a block of bakelite to which the two electrode holders are attached. To adjust the electrodes so that they are opposite each other and the proper distance apart, the lower holder is adjustable horizontally and either or both of them may be moved up or down by means of 1/2 mm pitch screws, the latter motion being permitted, and frequently required, during the operation of the spark. This apparatus was placed in a wooden box of about 3 liters capacity, opposite sides of which were furnished with quartz windows. The spark was operated about 5 or 6 cm under water and about 2 cm from the window. Tap water flowed through the box continuously at the rate of 1 to 2 liters per minute to carry off the colloidal metal which would otherwise pollute the water and render it less transparent.

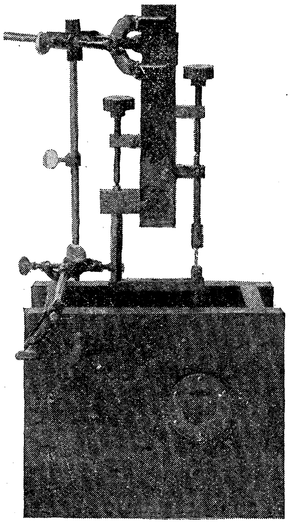
Fig. 1. Under-water spark apparatus.

A 40000 volt transformer was supplied with 10 to 12 amps., 60 cycle, alternating current at 110 volts, and the secondary was connected to the under-water spark with an adjustable air gap in series and some condensers of 0.006 mf capacity in parallel. The external spark gap was between zinc cylinders about 10 mm apart and the distance between the electrodes of the under-water spark was about 1/2 mm. Under the conditions of our arrangement no marked effect assignable to the diameter of the electrodes was observed. For example the same set of platinum lines were absorbed when ingots 5 mm in diameter were used as when the electrodes were wires of Pt-Rh or Pt-Ir alloy slightly more than 1 mm diameter. For the most part ingots averaging 10 to 20 mm^2 cross section were employed.

An image of the under-water spark was focussed with a quartz-condenser upon the slit of the spectrograph. Our concave gratings were used for observations in the visible and ultra-violet to 2400A below which a Hilger quartz spectrograph with lenses of about 60 cm focal length was employed. The exposures were usually only a few minutes, but about an hour was required to extend the spectra below 2300A. Ordinary photographic plates were used except for the shortest waves which were recorded on Schumann plates supplied by Hilger.

As has been shown by others, there are usually several types of lines to be distinguished, (1) emission lines, usually broadened and displaced, (2) symmetrical absorption lines, and (3) partial absorption, very unsymmetrical. The first class belongs to the spectrum of the ionized atom and is of no particular interest here. The latter classes being characteristic of arc spectra were carefully identified and are recorded in the following tables. The partial reversals are always on the violet side of the emission lines; they are designated *p* because of a suspicion that they might be penultimate lines in the sense that this word was proposed by Russell.[16] It appears that such lines actually involve some one of the higher metastable states while lines actually associated with the normal state are broad and symmetrical reversals. These three classes of lines are illustrated in Fig. 2, where portions of the under-water spark spectra of Ru, Rh, Pd and Pt are reproduced.

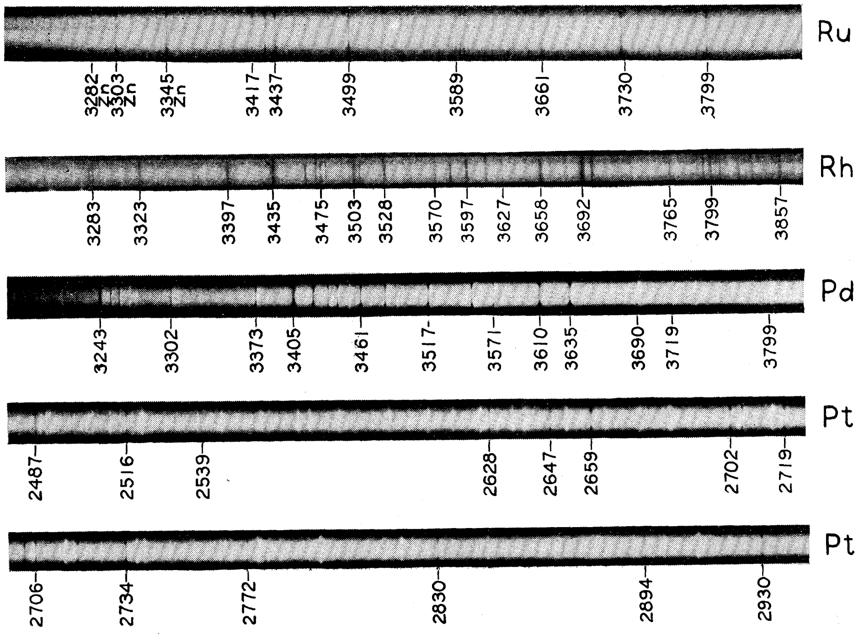

Fig. 2. Under-water spark absorption spectra of ruthenium, rhodium, palladium and platinum.

4. Spectral Regularities

The relation between absorption phenomena and one type of spectral regularity was clearly brought out by Wood,[17] Bevan,[18] Datta,[19] and others, who observed the absorption of a large number of members of the principal series of the alkalies. Extended series are not so readily found,

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[16] Russell, Astrophys. J. **61**, 223 (1925).

[17] Wood, Astrophys. J. **29**, 97 (1909).

[18] Bevan, Proc. Roy. Soc. London **83**, 421 (1910); **85**, 54 (1911).

[19] Datta, Proc. Roy. Soc. London **101**, 539 (1922).

and it is doubtful if they are present, in the more complex spectra, so the interpretation of absorption is more difficult. In fact, the structures of these spectra have not been explained until very recently, although the regularities in many cases have been known for many years. For example, Kayser and Runge[20] described unexplained regularities for Sn, Pb, As, Sb, and Bi in 1894; and similar regularities were announced by Rydberg[21] for Cu and A; by Kayser[22] for Pd, Pt, Ru; and by Snyder[23] for Ni and the entire group of Pd-Pt metals. Similar investigations were later made by Paulson[24] who discovered significant wave-number differences in a large number of spectra. It has since been found that in a few cases, especially in the most complex spectra, purely accidental differences have been mistaken for regularities. but in the majority the results are of real value and are readily explained by the new rules of spectral structure.

These regularities, to distinguish them from regular series, have often been referred to as regularities of another kind. Kayser[25] stated that the success in finding such in various spectra confirmed the suspicion that we are concerned with a quite general property of all spectra in which series are not observed ("Es kann kein Zweifel bestehen, dass wir in den angeführten Thatsachen schon eine grosse Menge von Beobachtungsmaterial für eine allgemeinere und complicirtere Gesetzmässigkeit in Händen haben; es fehlt nur noch der glückliche Blick, der das Gesetz in den Thatsachen erkennt und die vielen einzelnen Beobachurngen zusammanfasst. Wir würden dadurch wohl sehr erheblich gefödert werden").

Systems of wave-numbers such as those given by Snyder and by Paulson consisted of an arrangement of wave-numbers in columns and rows in such a manner that any two wave-numbers in adjacent rows or columns were separated by the same difference. (Two dimensional matrix.) Not all places in such a table are occupied by real lines but the differences between any two lines in any columns or rows whatsoever will, of course, be the same as the separation of any other pair of lines from the same columns or rows.

The wave-numbers were usually written so as to increase in magnitude from left to right and from top to bottom of the tables, and in the same order the columns were designated by alphabetical symbols and the rows by numerical symbols. Snyder noticed in his wave-number system of

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[20] Kayser and Runge, Abhandl. Berl. Akad. (1893), Wiedem. Ann. **52,** 93 (1894).

[21] Rydberg, Astrophys. J. **6,** 239 (1897); **6,** 338 (1897).

[22] Kayser, Abhandl. Berl. Akad (1897).

[23] Snyder, Astrophys. J. **14,** 179 (1901).

[24] Paulson, Dissertation, Lund University (1914).

[25] Kayser, Handbuch der Spectroscopie II, 578 (1902).

Rh that there are what may be called complementary columns, in which the gaps of one correspond to the wave-numbers found in the other, and that there are also groups of rows in which a series of gaps is repeated. It must be admitted that in this statement he came remarkably close to the discovery of Sommerfeld's inner quantum numbers. He also noticed that the wave-numbers of "reversed" spectral lines are to be found only in the final columns of the table and stated that this relation seems to be connected with that which determines the distinction between "rows" and "columns" in the table, viz., the number of rows should considerably exceed the number of columns. This is obvious when we recognize that the columns represent low energy levels (the lowest at the extreme right naturally favors reversed or absorbed lines), and the rows represent higher levels which combine with the low set in accordance with the selection rules for l and j. The excess of rows over columns is in accord with the established fact that in most spectra the number of low and metastable terms is usually small compared with the number of higher energy states.

The wave-number systems of all the spectra to be dealt with in this paper we find were extensively investigated by C. P. Snyder more than twenty-five years ago, but only a small portion of his results, viz., the wave-number system of rhodium, was ever published. For ruthenium, his results were later repeated by Paulson,[26] and his work on palladium has been repeated at least three times by different investigators, viz., Paulson,[27] Bechert and Catalán,[28] McLennan and Smith.[29] Hoping to avoid unnecessary duplication of this sort of work, we have made every effort to locate Mr. Snyder but have been unable to trace him after 1908. We have, however, fortunately located some of his correspondence between 1899 and 1901, and find this to be both of real value and of historical interest. It appears that Mr. Snyder began in 1899 to send selected samples of his analyses of spectra to Professor Rowland, who turned the material over to his assistant, Dr. N. E. Dorsey. After the wave-number system of rhodium was published, the more or less fragmentary data which Mr. Snyder furnished for various other spectra remained in possession of Dr. Dorsey who recently loaned them to us and kindly gave permission to compare them with our own data. Practically all of the levels which Snyder proposed for the different spectra have been found to be real and we are pleased to be able to quote some of these in the following pages.

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[26] Paulson, Phys. Zeits. **16,** 81 (1915).

[27] Paulson, Phil. Mag. **29,** 154 (1915).

[28] Bechert and Catalán, Zeits. f. Physik **35,** 449 (1926).

[29] McLennan and Smith, Trans. Roy. Soc. Can. 3rd Series, **20, Part** I, Section III, 157 (1926).

5. RESULTS

For each of the six elements under investigation we give first a table of absorbed lines and their classifications and then a table of low energy levels. In the first type of table, the data presented in succeeding columns are wave-lengths, estimated intensities in absorption (A) and emission (E), vacuum wave-numbers and term combinations. It will be noticed that the estimated relative intensities of the lines in emission are not all on the same scale, those for wave-lengths above ca. 2440A are taken from Exner and Haschek's[30] tables while those for shorter waves are preliminary values obtained from spectrograms which were made in this laboratory. The latter observations were made with Schumann plates the sensitivity and contrast characteristics of which tend to give a much larger scale of intensities than gelatine emulsions in the extreme ultraviolet. The lines which have been recorded as reversed in the arc are marked R as in Kayser's Handbuch.[31] The notation[32] for term combinations is the one which is coming into common use for spectral regularities; the letters S, P, D, F, G, correspond to quantum numbers $l=1, 2, 3, 4, 5$, respectively; the superscript indicates the maximum multiplicity r of the system and the subscript is the inner quantum number j associated with the energy level. The tables of low terms present the values of all the known terms of the first set calculated on the basis of zero energy for the lowest level.

1. RUTHENIUM (Ru = 101.7; $Z=44$)

As electrodes for the under-water spark we used alloys of 5% Ru and 95% Zn kindly prepared for this purpose by Dr. E. Wichers of this Bureau. It was gratifying to find that a large majority of the lines observed in absorption were identifiable with strong emission lines of ruthenium; only 2138, 3282, 3303 and 3345A were ascribable to zinc.

Clark and Cohen[33] observed between 2043.46 and 3802.44A, 62 absorbed lines in the under-water spark spectrum of Ru but identified only 42 of them with known emission lines of the element. Only about 20 of these are identical with lines in our list of 92 lines given in Table I.

In 1901, Snyder[23] stated that he had constructed a wave-number system containing several hundred lines of ruthenium. Unfortunately, Snyder's results for Ru were never published and no trace of them has been found. A similar investigation of the wave-number system of

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[30] Exner and Haschek, Spektren der Elemente bei normalem Druck II, Franz Deuticke, Leipzig and Wien (1911).

[31] Kayser, Handbuch der Spectroscopie V and VI.

[32] Russell and Saunders, Astrophys. J. **61**, 60 (1925).

[33] Clark and Cohen, Trans. Roy. Soc. Can. 3rd series, **20**, Part I, Section III, 55 (1926).

ruthenium was undertaken by Paulson[26] who published in 1915 a table containing 548 lines ordered in 65 rows and 18 columns. Many hundreds of lines comprising only portions of complete groups were omitted, and it is of interest to note that Paulson stated in this connection that it was not improbable that all the lines of the spectrum could be unified in a single system.

TABLE I

Absorption Spectrum of Ruthenium.

λ	Int.		ν	Combination
	A	*E*		
2090.81	2	10	47813.1	
97.16	10	6	668.3	
2098.74	5	10	632.4	$^5F_4-?$
2100.60	2	15	590.3	
04.25	20	6	507.7	
2109.52	1	12	47389.1	
2255.53	4	20	44321.7	$^5F_5-b^5G_5$
59.52	1	15	44243.4	$^5F_5-$
72.09	5	30	43998.7	
78.19	1	20	880.9	$^5F_4-?$
79.57	7	30	854.4	$^5F_5-b^5G_6$
85.37	1	15	743.1	$^5F_5-?$
87.67	1	20	699.1	$^5F_3-?$
2291.16	1	15	632.5	$^5F_4-b^5F_5'$
2302.52	1	20	417.3	$^5F_4-b^5G_4$
17.79	5	35	43131.3	$^5F_4-b^5G_5$
40.69	2	15	42709.3	$^5F_3-b^5G_3$
51.34	3	20	515.9	$^5F_3-b^5G_4$
70.17	1	12	178.2	$^5F_2-b^5G_2$
75.27	2	20	42087.6	$^5F_2-b^5G_3$
2392.42	1	15	41785.9	$^5F_1-b^5G_2$
2609.05	1	3	38316.7	$^3F_3-?$
12.07	2	4	38272.4	$^5F_2-?$
2631.56	1	1	37989.0	
2719.51	2	4	36760.5	$^5F_5-?$
35.71	6	5	542.8	$^5F_5-?$
2763.13	1	2	36180.2	
2810.54	4	8*d*	35569.9	$^5F_4-33_3$
29.14	2	3	336.1	$^3F_4-?$
54.06	1	3	35027.5	$^5F_3-34_2$
61.40	1	3	34937.7	$^3F_4-?$
66.63	1	3	874.0	$^5F_3-?$
74.99	5	10	772.6	
2886.53	2	4	609.6	
2909.24	1	1	363.2	
16.24	3	10	34280.7	$^5F_4-31_4$
65.17	3	3	33715 1	$^5F_3-32_3$
88.96	8	5	446.9	$^5F_5-26_4$
2994.96	1	4	379.9	$^5F_3-31_4$
3006.59	2	5	250.6	$^5F_2-?$
17.24	1	4	133.3	$^5F_1-?$
3020.87	1	3	33093.4	$^5F_2-32_3$
3186.04	1	5	31377.9	$^5F_2-?$
3238.54	1	4	30869.2	
41.23	1	4	843.6	
54.53	2	3	717.6	$^5F_2-25_3$
54.72		3	715.8	
3260.35	1	5	30662.7	$^5F_4-^3G_3$
74.69	2	4	528.5	
3294.13	2	10	348.3	$^5F_5-^3F_4'$
3301.59	3	8	279.8	$^5F_5-^5G_5$
15.22	3	3	155.3	$^5F_4-b^5G_4$
16.38	1	8	30144.7	$^3P_2-?$
39.55	5	10	29935.6	$^5P_3-37_3$
59.09	2	5	761.4	$^5F_3-^3G_3$
68.45	2	8	678.7	$^5F_2-^3F_3'$
3392.51	2	5	468.3	$^5F_5-?$
3401.74	1	5	388.3	
09.28	1	8	323.3	$^5F_3-?$
17.35	10	20*R*	254.1	$^5F_3-b^5G_4?$
28.33	20	20*R*	160.4	
28.65		4	157.7	$^5F_4-^3F_4'$
30.77	1	5	139.6	$^5F_2-^3G_3$
32.77	1	5	122.7	
36.75	30	30*R*	29089.0	$^5F_4-^5G_5$
83.32	1	4	28700.1	$^5F_4-^5G_4$
3498.95	50	50*R*	571.9	$^5F_5-^5G_6$
3514.50	2	3	445.4	$^5F_3-^5G_3$
19.65	1	4	403.8	
37.95	1	5	256.9	$^5F_3-^3F_4'$
39.37	2	4	28245.6	$^5F_2-^5G_2$
89.22	6	5	27853.3	$^5F_1-^5G_2$
93.03	8	20*R*	823.8	$^5F_2-^5G_3$
96.17	10	20*R*	799.5	$^5F_3-^5G_4$
3599.76	2	5	771.7	
3634.94	10	10	502.9	
3661.34	15	6*R*	27304.7	$^5F_4-?$
3726.93	8	10*R*	26824.1	$^5F_4-^5F_4'$
28.02	10	10*R*	816.3	$^5F_5-^5F_5'$
30.44	8	4*R*	798.9	$^5F_3-^5F_3'$
42.29	9	10*R*	714.0	$^5F_2-^5F_2'$
60.03	5	3*R*	588.0	$^5F_1-^5F_1'$
77.58	1	3	464.5	$^5F_1-^5D_0$
86.05	5	10*R*	405.3	$^5F_2-^5D_1$
90.50	10	10*R*	374.3	$^5F_3-^5D_2$
98.90	25	8*R*	316.0	$^5F_4-^5D_3$
3799.34		8*R*	26312.9	$^5F_5-^5D_4$
3925.92	3	10	25464.6	$^5F_5-X_4$
4199.91	2	10*R*	23803.3	$^3F_4-a^3F_4'$
4214.08	2	10	23734.6	$^3F_4-^5G_5$
4554.52	3	10*R*	21950.1	$^3F_4-^3G_5$
4709.49	2	10	21227.8	$^3F_4-b^3F_4'$

The interpretation of this wave-number system of ruthenium has been begun by us[34] and also by Sommer.[35] It appears that Paulson's table contains nearly all of the lower energy levels of the neutral ruthenium atom. A few of these levels have been identified and grouped with the aid of Zeeman effects recently obtained, most of the remainder have been tentatively named under the guidance of interval rules for the complex term levels and intensity rules for the combinations.

The low set of levels is described in Table II, where the energy values are relative to zero energy for the normal state $^5F_5$; Paulson's symbols for these levels and the modern ones indicating the quantum numbers r, l and j are given side by side.

TABLE II

Low terms in the Ru I spectrum.

Value	Difference	Symbol	
		Paulson	Quantum
0.0		R	$^5F_5$
	1190.8		
1190.8		Q	$^5F_4$
	900.9		
2091.7		P	$^5F_3$
	621.7		
2713.4		O	$^5F_2$
	392.2		
3105.6			$^5F_1$
6545.0		N	a^3F_4
7483.0		M	$^5D_4'$
	1539.4		
8044.0		L	$^5P_2$
	1092.6		
8084.4		K	a^3F_3
	727.1		
8575.6		J	$^5D_3'$
	973.4		
8771.1		I	$^5P_3$
	1029.9		
9057.8		H	a^3F_2
	608.2		
9073.2			$^5P_1$
9120.8		G	b^3F_4
9183.8		F	$^5D_2'$
	436.6		
9620.4	1534.2		$^5D_1'$
10624.0		E	$^3P_2$
10655.0		D	b^3F_3
	792.9		
11447.9		C	b^3F_2
13646.4		B	?
	1408.6		
15055.0		A	?

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[34] Meggers and Laporte, Science **61,** 635 (1925); J. Wash. Acad. Sci. **16,** 143 (1926).

[35] Sommer, Die Naturwissenschaften **13,** 840 (1925); Zeits. f. Physik **37,** 1 (1926).

The combinations with these low levels permit the assignment of inner quantum numbers, *j*, to the second set of levels of which Paulson has given 65, but the corresponding *r* and *l* values must in many cases wait upon further Zeeman-effect observations for their correct identification. The classification of absorption lines listed in Table I shows that almost all of these lines involve the low quintet-*F* term; only a few of them originate in the metastable triplet-*F* term; and possibly a few in other low metastable levels. Some of the higher levels are still unnamed, those represented by numbers are taken from Paulson's table in which they have the same numeration.

2. RHODIUM ($Rh = 102.9$; $Z = 45$)

Our first exposures were made with wires of Pt-Rh alloy but there were a few lines observed in absorption which might be ascribed to either one or the other metal. To eliminate this doubt, the observations were repeated with ingots of pure rhodium prepared for this purpose by Dr. Wichers. Table III contains a list of 100 lines observed in absorption in the range 2206–4375A. Clark and Cohen[33] obtained 61 lines, 2212.92 to 3844.61A, 56 of which correspond to recorded emission lines. Only about 34 of their lines are identical with ours.

The classification of rhodium lines in Table III is based on the wave-number system published by C. P. Snyder[23] in 1901. This consists of 19 columns and 54 rows, the former represent a low set of levels and the latter define a higher set with which the low levels combine so that 476 rhodium lines are ordered in this system. The interpretation of this system at the present time is unfortunately unsupported by reliable Zeeman-effect observations but various other considerations make it very probable that the correct quantum numbers have been assigned in most cases. The low levels as presented by Snyder have been calculated in relative value, after assigning zero energy to $^4F_5$, and these are listed in Table IV together with their symbols. Where it has been impossible in Table III to fix the *r* and *l* values of the higher levels the Snyder numeration of the levels is used. Here again it will be observed that most of the absorbed lines involve levels of the low quartet-*F* term, a smaller number of lines relatively weak in absorption involve metastable states, but none at all are associated with levels of this set having values as large as 11000 cm^{-1}. Kayser's Handbuch lists three additional lines (4121.72, 4128.93, 4288.72A) which have been recorded as reversed in the arc. These are classified by Snyder as $^2F_3 - 12_3$, $^2F_3 - 11_4$ and $^2F_3 - a^4G_4$. They might have been expected on our plates, but they were too weak to be detected with certainty

TABLE III

Absorption spectrum of rhodium.

λ	Int.		ν	Combination	λ	Int.		ν	Combination
	A	*E*				*A*	*E*		
2206.03	5	8	45316.1		3280.54	10	20*R*	30474.0	$^4F_4-11_4$
12.77	10	10	45178.1		83.56	15	20*R*	446.0	$^4F_3-b^4G_4$
42.04	25	15	44588.4		3289.13	1	5	394.4	$^4F_2-16_2$
48.74	3	15	455.5		3323.09	25	50*R*	30083.8	$^4F_4-b^4G_5$
2264.14	15	20	44153.2		38.53	1	8	29944.8	$^4F_4-{}^4F_3'$
2361.92	10	10	42325.5	$^4F_5-?$	68.38	2	5	679.4	$^4F_3-{}^4F_2'$
68.30	5	15	42211.5		72.24	5	8	645.4	$^4F_3-b^4G_3$
82.86	10	8	41953.6	$^4F_5-?$	96.82	40	100*R*	430.9	$^4F_5-{}^4F_5'$
83.37		10	944.6		3399.68	4	10	406.1	$^4F_3-11_4$
2386.10	8	10	896.6		3434.90	60	200*R*	29104.6	$^4F_5-b^4G_6$
2407.86	5	6	518.0		55.22	2	5	28933.5	$^4D_3-b^4G_3$
23.98	1	8	241.9		62.04	20	30*R*	876.5	$^4F_3-{}^4F_3'$
27.70	3	7	41178.7	$^4F_3-45$	70.67	12	20*R*	804.7	$^4F_2-{}^4F_2'$
40.35	5	2	40965.3	$^4F_4-42$	74.79	15	20*R*	770.5	$^4F_2-b^4G_3$
49.07	4	2	819.5		78.91	10	15*R*	736.4	$^2D_3-a^4G_3$
50.58	2	2	794.3	$^4F_4-?$	3498.74	5	10	573.6	$^4F_2-a^4G_3$
73.12	1	1	422.5	$^4F_4-?$	3502.54	35	50*R*	542.6	$^4F_5-a^4G_5$
83.34	2	2	256.2		07.32	12	20*R*	503.7	$^4F_3-a^4G_4$
2487.50	1	3	40188.9		28.03	25	30*R*	336.4	$^4F_4-{}^4F_4'$
2502.46	1?	2	39948.6	$^4F_2-44$	38.12	2	4	255.6	$^2F_4-17_4$
05.67	2	1	897.5		43.97	4	10	208.9	$^2D_2-16_2$
09.70	7	2	833.4	$^4F_3-41$	49.53	8	10	164.7	$^2D_3-{}^4F_3'?$
15.74	5	2	737.8	$^2D_3-43$	70.18	6		28001.8	$^4F_2-{}^4F_3'$
36.71	3	2	409.3		83.10	15	10*R*	27900.9	$^4F_4-{}^4F_5'$
55.36	10	3	39121.7	$^2D_3-41$	96.19	10	20*R*	799.3	$^4F_3-{}^4D_2$
2566.05	2	2	38958.7	$^4F_2-41$	3597.15	15	20*R*	791.9	$^2D_3-a^4G_4$
2622.57	5	3	38119.2	$^2D_2-44$	3612.47	15	15*R*	674.0	$^4F_2-{}^4D_1$
34.98	1	2	37939.7		26.61	5	15	566.1	$^4P_3-22_4$
52.65	8	3	686.9	$^4F_3-36_4$	58.00	35	50*R*	329.6	$^4F_4-{}^4D_3$
2680.62	7	2	37293.8	$^2D_3-38_2$	66.23	8	15	268.2	$^4F_3-{}^4F_4'$
2703.72	15	3	36975.1	$^2D_3-36_4$	90.72	6	15*R*	087.3	$^2D_3-{}^4D_2$
18.55	2	2	773.5	$^2D_2-41$	3692.36	50	50*R*	075.3	$^4F_5-{}^4D_4$
20.14	2	2	751.9		3700.91	25	30*R*	27012.7	$^4F_4-a^4G_5$
67.73	3*w*	2	120.0	$^4F_3-28_3$	13.01	2	10*R*	26924.7	$^4F_2-{}^4D_2$
68.24	?	2	113.4		48.23	1	10	671.7	$^4P_2-23_3$
71.52	4	2	36070.7	$^4F_3-27$	65.08	7	15*R*	552.3	$^2F_4-b^4G_4$
2783.04	3	3	35921.4	$^2D_3-31$	88.48	2	15	388.3	$^2D_2-a^4G_3$
2826.42	2	3	370.1		93.21	8	15*R*	355.4	$^2F_4-a^4G_3$
26.69		3	35366.7	$^4P_3-46$	3799.31	15	20*R*	313.1	$^2F_4-11_4$
62.95	5	4	34918.8	$^2D_2-37_3$	3806.77	7	10	261.6	$^4F_3-{}^4D_3$
2878.66	1	3	34728.2	$^2D_3-25_2$	18.20	3	10	182.9	$^4P_3-{}^2D_2$
2968.67	6	4	33675.3	$^2D_3-23_2$	22.25	8	15*R*	155.2	$^2F_3-17_4$
2986.21	7	4	477.5	$^2D_3-22_4$	28.47	5	15	112.7	$^4F_3-{}^2D_3$
3023.90	1	3	33060.3	$^2D_2-28_3$	33.87	4	10*R*	26075.9	$^2F_3-16_2$
3102.51	3	2	32222.6		3856.51	15	10*R*	25922.9	$^2F_4-b^4G_5$
23.70	1	4	32004.1	$^4F_5-11_4$	3934.23	5	10*R*	410.8	$^2F_4-a^4G_4$
91.18	3	8	31327.3	$^2D_2-23_3$	3958.86	7	30*R*	25252.7	$^2F_3-b^4G_4$
3194.54	1?	3	31294.4	$^2F_4-23_3$	4135.30	2	20*R*	24175.2	$^2F_4-{}^4F_4'$
3263.14	4	10	30636.5	$^2D_3-17_4$	4211.15	5	30*R*	23739.8	$^2F_4-{}^4F_5'$
71.61	2	10	557.2	$^2D_3-16_2$	4374.80	5	30*R*	22851.8	$^2F_4-a^4G_5$

It should be mentioned that a note on the structure of the arc spectrum of Rh was published in 1925 by Sommer[36] who apparently was not aware of the earlier work of Snyder.

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[36] Sommer, Die Naturwissenschaften **13,** 392 (1925).

TABLE IV

Low levels in the Rh I spectrum.

Value	Difference			Symbol	
				Snyder	Quantum
0.0				*S*	$^4F_5$
	1529.9				
1529.9				*R*	$^4F_4$
	1068.0				
2597.9				*Q*	$^4F_3$
3309.8				*P*	$^2D_3$
	874.7				
3472.6		2348.1		*O*	$^4F_2$
5657.9				*N*	$^2D_2$
5690.9				*M*	$^2F_4$
	2100.2				
7791.1				*L*	$^2F_3$
9221.1				*K*	$^4P_3$
	1092.2				
10313.3				*J*	$^4P_2$
	692.6				
11005.9				*I*	$^4P_1$
11968.0				*H*	$^2P_2$
12722.8				*G*	$^2G_5$
13520.4	2006.5			*F*	$^2D_3$
13974.5		2064.8		*E*	$^2P_1$
14381.8				*D*	$^2P_2$
			2598.0		
14787.6				*C*	$^2G_4$
	1738.6				
16118.4				*B*	$^2D_2$
16120.4				*A*	$^2P_1$

3. PALLADIUM (Pd = 106.7; $Z = 46$)

Ingots or heavy wires of pure Pd were used as electrodes and 50 lines (2068.68 – 4212.96A) were observed as absorbed, most of which are very wide and intense. Clark and Cohen[33] found 85 lines (2007.6 – 3894.7A) when Pd electrodes were used but only 50 of these were identified with recorded emission lines. About 40 of our lines are identical with theirs.

The first regularities in the arc spectrum of palladium were recognized by Kayser[22] who in 1897 found repeated differences of 1191 and 3967 wave-numbers among the strongest lines. This work was extended by Paulson[27] who showed that 3967 was really the sum of two differences, 1628 and 2339 and he discovered a new one, 7755. It is our duty to remark that this complete system was known to Snyder in 1900. In addition, his statement (loc. cit.) that he had found in this spectrum a sub-system which had the same series of wave-number differences as the principal system, except that the order of differences is reversed, indicates that he recognized some very high levels belonging to the third set. This wave-number system has recently been interpreted and extended by several investigators. The observation of Zeeman effects enabled Beals[37]

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[37] Beals, Proc. Roy. Soc. London **A109**, 369 (1925).

to identify all the low terms and many higher ones. Bechert and Catalán[28] classified 187 Pd lines with 47 energy levels, some absorption observations of Angerer and Joos as well as a preliminary list of our under-water spark absorption lines being available for this analysis. McLennan and Smith[29] with the aid of similar data obtained independently in their laboratory also discussed the structure of this spectrum. They succeeded in classifying 181 lines with 64 levels, 34 of the latter being identical with levels found by Bechert and Catalán. Although there is no ambiguity about the low levels considerable differences of opinion still exist as to the reality and identity of some of the higher levels. In Table V the com-

TABLE V

Absorption spectrum of palladium

λ	Int.		ν	Combination	λ	Int.		ν	Combination
	A	*E*				*A*	*E*		
2068.68	1	10	48324.5		3242.70	100	100*R*	30829.6	$^3D_3-1^3F_3$
77.84	1	6	111.5	^3D-Z	51.62	20	30*R*	745.1	$^3D_1-2^1P_1$
81.01	3	10	038.2		58.78	30	30*R*	677.5	$^3D_1-1^3D_2'$
82.15	4	10	48011.9	$^1D_2-{}^3D_1$?	3287.25	5	10	411.8	$^3D_3-1^1D_2'$
87.84	10	10	47881.1		3302.11	40	30*R*	30275.0	$^3D_1-1^1P_1$
2092.53	3	7	773.8		3373.00	40	30*R*	29638.7	$^3D_2-1^3F_3$
2105.79	10	10	473.0		3404.59	200	100*R*	363.7	$^3D_3-1^3F_4$
08.02	1	4	423.0		21.23	100	50*R*	220.9	$^3D_2-1^1D_2$
18.01	4	6	47199.1	$^3D_3-X$	33.44	40	20*R*	117.0	$^1D_2-2^1P_1$
72.87	5	10	46007.6	$^3D_2-X$	41.40	50	20*R*	29049.6	$^1D_2-1^3D_2'$
2178.23	5	10	45894.4		60.74	75	50*R*	28887.3	$^3D_3-1^1F_3$
2225.26	10	15	44924.6	$^3D_2-Y$	81.16	60	50*R*	717.9	$^3D_1-1^3F_2$
31.56	10	40	797.7	$^3D_2-4^1P_1$	3489.78	20	15*R*	646.9	$^1D_2-1^1P_1$
54.26	20	20	44346.7	$^3D_3-2^3D_3'$	3516.94	60	100*R*	425.7	$^3D_2-1^3P_1$
2296.51	10	40	43530.9	$^3D_1-2^3D_1'$	53.09	50	50*R*	28136.5	$^1D_2-1^3D_3'$
2360.51	2	5	42350.8		3571.15	25	20*R*	27994.2	$^3D_1-1^3P_0$
2447.92	100	8*R*	40838.6	$^1S_0-2^1P_1$	3609.55	100	100*R*	696.4	$^3D_2-1^1F_3$
76.42	75	8*R*	368.7	$^1S_0-1^1P_1$	34.69	200	200*R*	504.9	$^3D_3-1^3P_2$
2488.92	10	4	40166.0		3690.34	10*p*	20*R*	27090.1	$^1D_2-1^3F_2$
2763.10	30	15*R*	36180.6	$^1S_0-1^3P_1$	3718.91	4*p*	15*R*	26882.0	$^3D_1-1^1D_2'$
2922.51	10	10*R*	34207.2	$^3D_3-1^3D_2'$	3799.18	3*p*	10*R*	314.0	$^3D_2-1^3P_2$
3002.66	10	10*R*	33294.1	$^3D_3-1^3D_3'$	3832.30	3*p*	10*R*	26086.6	$^3D_1-1^3P_1$
27.91	20	20*R*	33016.5	$^3D_2-1^3D_2'$	3894.18	5*p*	20*R*	25672.1	$^1D_2-1^3F_3$
3065.30	10	20*R*	32613.8	$^3D_2-1^1P_1$	3958.63	2*p*	20*R*	25254.1	$^1D_2-1^1D_2'$
3114.04	30	30*R*	32103.3	$^3D_2-1^3D_3'$	4212.96	3*p*	20*R*	23729.6	$^1D_2-1^1F_3$

TABLE VI

Low levels in the Pd I spectrum.

Value	Difference	Symbol	
		Synder	Quantum
0.0		*E*	$^1S_0$
	6564.0		
6564.0		*D*	$^3D_3$
	1190.9		
7754.9		*C*	$^3D_2$
	2338.9		
10093.8		*B*	$^3D_1$
	1627.9		
11721.7		*A*	$^1D_2$

binations are taken from the paper by McLennan and Smith with the understanding that some of the higher levels are subject to revision.

The well established set of low levels characteristic of the Pd I spectrum are given in relative value in Table VI. Practically all of the observed absorption lines have been shown to involve these low levels.

4. OSMIUM (Os = 190.9; $Z = 76$)

Electrodes of Zn-Os alloy prepared by Dr. Wichers were first used in these experiments but the osmium content was probaby too low since only about 20 lines could be observed as absorbed. Rods of osmium were later prepared from sponge sintered in hydrogen at 1200°C. Two such rods, each 5 mm in diameter and about 15 mm long, served as electrodes for our final experiments from which we obtained the data on 193 absorption lines (2211.97–4420.47A) listed in Table VII.

TABLE VII

Absorption spectrum of osmium

λ	Int.		ν	Combination	λ	Int.		ν	Combination
	A	*E*				*A*	*E*		
2211.97	2	10	45194.4		2327.00	1	10	42960.6	
14.00	3	8	153.0		32.21	2	5	864.6	
14.19		10	45149.1		34.58	1	10	821.1	
25.28	4	5	44924.2		38.67	3	10	746.2	$F-16$
25.44		10	920.9		40.68	1	8	709.5	
27.98	5	12	869.7		43.76	2	8	653.4	
42.10	2	10	587.2		45.77	1	5	616.8	
52.03	15	20	390.6		47.39	1	7	587.4	
55.84	5	30	315.6		49.81	2	5	543.6	
59.66	2	4	240.7		51.58	2	4	511.6	
62.34	3	6	188.3		53.02	3	6	485.6	
64.60	20	25	144.2		56.92	5	3	415.3	
68.30	5	15	072.2		57.26		4	409.1	
70.18	20	20	44035.7		62.77	10	12	310.3	$F-14$
75.39	2	6	43934.9		66.30	1	3	247.1	
76.45	1	5	914.5		69.26	2	8	194.4	
79.11	2	10*d*	863.2		70.69	10	20	168.9	
79.90	1	6	848.0		71.18		15	160.2	
82.25	1	40	802.9		74.34	1	4	104.1	
82.82	1	5	791.9		74.54		4	100.6	
83.68	5	25	775.4		77.05	20	30	056.1	
84.84	3	5	753.2		79.40	6	20	42014.6	
84.91		5	751.9		82.49	1	5	41960.1	
89.32	7	20*d*	667.6		84.62	2	10	922.6	
97.31	5	15	515.7		87.29	10	40	875.7	
2298.49	1	3	493.4		90.97	1?	4	41811.3	
2300.15	2	5	462.0		93.85	2	5	761.0	
00.50		6	455.4		94.30		8	753.1	
01.91	1	6	428.8		95.40	4	8	734.0	
03.32	10	10	402.2		2395.88		10	725.6	$F-12$
08.32	6	15	308.2		2401.14	2	15	634.2	
13.75	1?	10	206.6		03.86	2	10	587.1	
20.20	7	15	086.5		05.45	1	6	559.6	
23.98	7	10	016.4		08.68	2	10	503.9	
24.25		20	43011.4		10.99	1	8	464.1	

TABLE VII (Continued)

λ	Int.		ν	Combination
	A	E		
2411.46	1	2	456.0	
14.56	2	10	402.8	
18.54	10	20	334.7	
25.00	20	20	224.6	
26.83	2	5	193.5	
31.62	5	1	41112.4	
46.04	3	1	40870.0	
50.75	5	1	791.5	
53.91	2	0	739.0	
56.48	3	1	696.3	
61.43	7	3	614.5	
76.83	2	2	362.0	F−10
88.55	20	4	171.9	
2498.42	2	1	40013.2	
2504.40	2	2	39917.7	
13.25	7	2	777.1	
15.05	1	2	748.7	
18.44	4	2	695.2	
19.80	1	1	673.8	
38.00	1	4	389.3	
42.50	3	4	319.6	
46.17	1	2	262.9	
48.11	1	2	39233.0	
66.51	2	3	38951.8	
71.79	1	2	871.8	
81.06	2	2	732.2	
81.94	2	4	719.0	D−17
90.77	4	4	587.0	D−16
2597.23	1	1	491.1	
2609.58	1	2	308.9	
13.08	10	4	257.6	F−7
19.95	1	4	157.3	D−15
21.82	1	2	130.1	F−6
28.28	2	2	38036.4	
37.12	15	4	37908.9	F−5
44.11	6	4	808.7	
47.72	1	2	757.1	
49.33	1	2	734.2	C−17
56.67	1	2	629.9	
58.58	4	4	602.9	C−16
59.82	2	2	585.4	
60.91	1	1	570.0	
74.55	2	2	378.4	
74.87		2	373.9	
89.80	10	4	166.5	C−14
2699.59	2	4	37031.7	
2706.70	2	2	36934.4	
09.85	1	2	891.5	
14.64	10	3	826.4	
15.37	3	2	816.5	
20.03	2	4	36753.4	
21.86	2	4	728.7	
30.68	3	4	610.1	
32.80	3	4	581.7	C−12
61.43	2	2	202.4	D−10
63.27	2	2	178.3	
70.72	4	4	36081.1	
82.56	4	4	35927.5	D−9
86.31	5	4	879.2	
93.99	1	2	780.6	
94.21		2	777.8	
2796.73	5	2	745.5	
2806.91	8	5	615.9	
08.93	1	4	590.3	
11.57	1	2	556.9	
14.21	2	3	523.5	C−11
15.79	1	2	503.6	
29.28	3	2	334.3	
32.23	1	2	297.5	
38.64	10	5	217.8	C−10
41.60	2	4	181.1	
44.39	6	4	146.6	
46.40	2	2	121.8	
46.60		2	119.3	
48.25	1	2	099.0	
50.77	4	4	35068.0	
60.97	5	4	34942.9	C−9
72.42	1	3	803.7	
74.97	1	4	772.8	
2878.41	2	3	731.2	
2909.07	25	6	365.2	
12.36	5	2	326.4	E−7
17.27	2	4	268.6	
19.83	6	4	238.6	C−8
25.60	2	3	171.0	
31.30	2	4	104.6	
34.67	1	3	065.4	
48.22	3	4	34008.9	
49.53	3	3	33893.8	
62.15	2	4	749.4	D−5
62.34		2	747.3	
64.07	2	4	727.6	
70.98	4	3	649.1	
77.64	1	3	573.9	
2982.91	1	3	514.6	
3013.07	2	4	179.1	
18.05	10	4	124.4	
19.38	2	3	33109.8	
30.70	5	4	32986.1	C−6
40.90	10	5	875.5	
58.66	20	6	684.6	F−2
62.18	2	4	647.0	
74.07	1	4	520.7	
74.95	1	4	511.4	
77.71	2	4	482.3	
78.11	1	2	478.1	
78.38	1	2	475.2	
3090.08	1	2	352.3	
3105.99	3	3	186.5	
09.38	3	4	32151.5	
56.24	10	6	31674.1	
3178.05	3	4	31456.8	
3232.07	5	4	30931.0	
62.29	10	6	644.5	D−4
3267.94	15	6	591.5	
3301.55	25	7	30280.1	
36.14	2	4	29966.2	D−3
3370.58	2	4	29660.0	C−4
3528.60	2	10	28331.8	F−1
3560.88	1?	10	28074.9	
3752.54	5	20	26641.1	
3782.19	2	20	26432.2	
4420.47	2*p*	30	22615.7	

Clark and Cohen[33] obtained 48 absorptions (1952.23–2481.08A) with electrodes of osmium but very few of them are identifiable with emission lines of Os and it is doubtful if more than two or three of their lines are the same as ours.

It appears that the data which have thus far been accumulated are not sufficient to describe the structure of the Os I spectrum. Zeeman-effect observations for 32 lines were published by Moore[38] but these results are of a qualitative nature, and of no value in establishing quantum numbers. Snyder's wave-number system for osmium is very fragmentary and it is probable that some low levels are still unrecognized. The component levels of complex quintet- and triplet-terms are expected to be widely separated—3000 to 4000 wave-numbers on the average—so that estimated relative intensities are of no assistance in constructing multiplets. On the other hand the extent to which the rules for intervals between sub-levels and for intensities of lines actually hold in such a spectrum is uncertain. The low levels which have been found are presented in Table VIII, and the absorption lines resulting from combinations of these with higher levels are marked in Table VII.

TABLE VIII

Low levels in the Os I spectrum.

Value	Difference	Symbol	
		Snyder	Quantum
0.0		*F*	?
	3931.0		
3931.0		*E*	?
	228.5		
4159.5		*D*	?
	984.5		
5144.0		*C*	?
	3588.8		
8732.8		*B*	?
	2287.7		
11020.5		*A*	?

5. IRIDIUM (Ir = 193.1; $Z = 77$)

Wires of 10 or 15 percent Ir alloyed with Pt were first used as electrodes but on account of the difficulty in ascribing certain of the observed absorption lines to the proper element the exposures were repeated with ingots of pure iridium. Table IX contains 51 absorption lines of Ir (2127.87 to 3220.79A). Clark and Cohen[33] observed 73 lines (1892.39 to 2174.81A) 60 of which they identify, each with one or more emission lines, but it is doubtful if any of these lines are identical with ours and we are inclined to believe that their observations do not apply to iridium at all.

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[38] Moore, Astrophys. J. **28**, 1 (1908).

Regularities in the arc spectrum of iridium were first found by Snyder in 1900 and from them we have calculated the relative values of low levels given in Table X. In the absence of Zeeman effect observations from which to derive the quantum numbers, the quantum symbols for these levels cannot be given with any certainty at present. It appears significant, however, that the majority of lines observed as absorbed are related among themselves or to relatively strong emission lines by the difference 2835.0 which occurs between the first two levels. None of the

TABLE IX

Absorption spectrum of iridium.

λ	Int. A	Int. E	ν	Combination
2127.43	10	9	46990.2	
27.87		10	980.5	${}^2D_3-22$
42.18	1	10	666.7	
48.16	5	15	536.8	
50.50	2	10	486.1	
54.15	4	8	407.4	
55.77	6	10	372.5	${}^2D_3-21$
58.01	20	40	324.4	
62.84	2	10	220.9	${}^3D_3-20$
72.17	5	12	46022.4	
75.22	5	15	45957.9	${}^2D_3-19$
78.13	10	12	896.5	${}^2D_3-18$
87.45	1	12	701.0	${}^2D_2-26$
91.62	8	12	614.0	
2198.83	10	25	464.5	${}^2D_2-25$
2205.67	1	15	323.5	${}^2D_2-24$
16.00	3	10	112.3	
20.35	4	10	45023.9	${}^2D_2-23$
38.82	5	10	44652.5	${}^2D_3-16$
39.30		8	642.9	${}^2D_3-15$
58.52	2	8	263.0	
58.87		10	256.2	
2264.60	5	15	44144.2	${}^2D_2-22$
2304.20	5	30	43385.6	${}^2D_2-20$
43.18	1	10	42664.0	${}^2D_2-17$
43.60		10	656.3	
2355.00	1	5	42449.8	
56.60	1?	5	421.0	
63.05	3	2	305.2	
72.80	10	3	42131.4	${}^2D_3-14$
90.60	10	2	41817.7	${}^2D_2-16$
2391.20		3	807.3	${}^2D_2-15$
2431.25	10	2	41118.6	${}^2D_3-13$
55.61	4	2	40710.8	${}^2D_3-12$
75.12	15	3	389.9	${}^2D_3-11$
2481.17	7	3	40291.4	${}^2D_3-10$
2502.98	20	3	39940.3	${}^2D_3-9$
2543.97	10	4	39296.8	${}^2D_2-14$
2611.29	1	3	38283.8	${}^2D_2-13$
39.70	20	4	37871.8	${}^2D_3-6$
61.98	5	5	554.9	${}^2D_2-11$
64.77	8	5	515.5	${}^2D_3-5$
92.33	2	4	131.5	
2694.22	10	5	37105.5	${}^2D_2-9$
2797.71	6	5	35733.0	${}^2D_2-8$
2823.17	3	4	410.8	${}^2D_3-4$
24.44	5	6	394.9	${}^2D_2-7$
2849.74	20	8	35080.6	${}^2D_3-3$
2924.80	10	10	34180.4	${}^2D_3-2$
3068.88	6	5	32575.7	${}^2D_2-4$
3220.79	5	15	31039.4	${}^2D_2-1$

TABLE X

Low levels in the Ir I spectrum.

Value	Difference	Symbol Snyder	Symbol Quantum	Value	Difference	Symbol Snyder	Symbol Quantum
0.0		*L*	${}^2D_3$?	11831.7		*F*	?
	2835.0				387.4		
2835.0		*K*	${}^2D_2$?	12219.1		*E*	?
	2950.0				733.2		
5785.0		*J*	?	12952.3		*D*	?
	539.3				136.3		
6324.3		*I*	?	13088.6		*C*	?
	782.9				3015.4		
7107.2		*H*	?	16104.0		*B*	?
	2770.9				2957.5		
9878.1		*G*	?	19061.5		*A*	?
	1953.6						

higher metastable levels combine to produce lines which have been absorbed. This fact has suggested that the two lowest levels may represent a doublet-D term since the analogous spectrum of Rh has such a ^2D term among its low levels. Quantum-theoretical considerations, however, offer two choices, ^4F and ^2D, as representing the normal state, so that the two levels in question may actually be $^4F_4$ and $^4F_5$.

6. PLATINUM ($\mathrm{Pt}=195.2$; $Z=78$)

Ingots of pure Pt were used as electrodes and the lines appearing as absorbed were confirmed by exposures with Pt-Rh, and Pt-Ir alloys. The latter were used for the purpose of determining what Rh and Ir lines are absorbed—before we obtained pure ingots of these metals it was necessary to use the available alloys with Pt, and we thus secured a considerable number of spectrograms from which the absorbed Pt lines could be determined. Table XI contains 107 lines observed in absorption (2030.53 to 3408.14A). Clark and Cohen[33] found 37 lines (2084.9 to 3064.5A) all but one of which correspond closely with lines appearing in the emission spectrum of this element. Finger's[11] table describing the lines of the under-water spark spectrum with Pt electrodes contains 14 reversed lines (2628–3282A). One line, 2794.20A, is given in Kayser's list as 5R but was not observed in absorption. It is probably a spark line involving the lowest energy of the ionized atom.

The first regularities in this spectrum were indicated by Kayser[22] who found the wave-number difference of 776.1 repeatedly among strong, or reversed lines. A fairly complete wave-number system for Pt was sent to Rowland by Snyder in October, 1900. This system contained the low levels A to H now presented in Table XII. Constant differences in this spectrum were investigated also by Paluson.[39] A somewhat more extended wave-number system was worked out by McLennan and McLay[40] during the past few months. Their low levels and suggested values of inner quantum numbers are in excellent agreement with those obtained independently by us, but we have been led by considerations on the general dependence of level separations upon atomic number, to suggest a different assignment of l values, the consequence of which is that a triplet-D level with inner quantum number 3 represents the normal state of the neutral Pt atom.

A large number of the absorption lines in Table XI involve the first five low levels. In this case, at the present time, sufficient data are not

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[39] Paulson, Ann. d. Phys. **46,** 698 (1915).

[40] McLennan and McLay, Trans. Roy. Soc. Can. 3rd series, **20,** Part I, Section III 201 (1926).

TABLE XI

Absorption spectrum of platinum.

λ	Int.		ν	Combination
	A	E		
2030.53	10	10	49232.3	
32.31	10	7	189.2	
35.68	5	5	107.8	
36.35	2	20	091.6	
39.60	4	5	49013.4	
40.22	4	6	48998.5	
49.23	50	6	783.1	
49.30		4	781.4	$^3D_3-30_3$
59.57	6	6	538.2	
60.66	20	7	512.6	$^1D_2-31_3$
62.69	20	8	464.8	$^3F_4-31_3$
66.83	3	9	367.8	
67.40	30	10	354.4	$^3D_3-28_4$
70.84	10	10	274.1	
73.49	1	5	212.4	
82.41	3	9	48005.9	$^1D_2-30_3$
83.24	2	10	47986.8	
2984.50	50	12	957.8	$^3F_4-30_3$
2101.54	2	10	569.0	
03.26	40	10	530.1	$^3F_4-28_4$
09.41	5	6	491.5	
09.58		6	387.7	
22.49	1	7	47099.5	
28.55	30	15	46965.4	$^1D_2-26_1$ $^3D_5-27_4$
35.10	1	8	821.4	
44.18	8	50	623.1	$^3D_3-25_3$
50.60	1	8	484.0	
52.03	2	10	453.1	
53.50	3	20	421.4	$^3D_3-24_2$
65.14	10	30	171.8	$^3D_3-23_2$
66.57	3	15	46141.4	$^3F_4-27_4$
74.64	40	50	45970.2	
80.46	3	15	847.5	$^1D_2-25_3$
82.73	1	10	799.8	$^3F_4-25_3$
2190.12	2	8	645.3	$^1D_2-24_2$
2202.20	6	15	394.9	$^1D_2-23_2$
17.33	2	15	45085.2	
22.60	7	20	44978.3	
34.91	10	20	730.6	$^3D_3-21_2$
44.96	5	15	530.4	
45.51	2	25	519.5	
49.29	9	15	444.7	$^3D_3-20_2$
49.90	7	10	432.6	$^3D_3-19_4$
68.84	3	30	44061.7	
74.09	10	5	43960.0	
74.38	4	20	954.4	$^1D_2-21_2$
74.83	6	10	945.7	$^3D_3-18_4$
76.42	1	10	915.0	
76.86	2	15	906.5	$^3F_4-21_2$
89.27	6	15	668.6	$^1D_2-20_2$
92.38	8	12	609.3	$^3F_4-19_4$
98.36	1?	10	495.9	
2298.78	1	15	487.9	
2303.19	3	30	404.6	
08.04	8	50	313.5	$^3D_2-32_2$
2315.50	2	40	43173.9	
18.29	8	35	43122.0	$^3F_4-18_4$
26.10	2	40	42977.2	
40.18	6	30	718.6	$^3D_2-31_3$
57.09	10	60R	412.2	$^1D_2-17_1$
68.28	5	50R	42211.8	$^3D_2-30_3$
83.65	3	40	41939.7	
2389.54	5	25	836.3	$^3F_4-16_2$
2401.88	1	20	621.4	
03.10	7	40R	600.2	$^1S_0-26_1$
18.07	2	40	342.7	
28.03	4	10	173.1	$^3D_2-26_1$
28.20		30R	170.3	
36.69	7	20R	41026.8	$^1D_2-15_1$
40.08	15	30R	40969.8	$^3D_3-14_2$
50.97	1	3	787.8	$^3D_3-13_2$
67.42	6	6R	515.9	$^3D_3-12_2$
83.22	1?	2	258.1	$^1D_2-14_2$
87.17	10	5R	194.2	$^3D_3-11_4$
90.13	6	3	146.4	$^3F_4-14_2$
95.82	2	3	054.9	$^3D_2-25_3$
2498.50	5	3	40012.0	$^1D_2-13_2$
2508.50	1	3	39852.4	$^3D_2-24_2$
15.58	7	4	740.3	$^1D_2-12_2$
24.32	1	3	602.7	$^3D_2-23_2$
2539.20	3	3	39370.7	$^3F_4-11_4$
2628.02	15	8R	38040.1	$^1D_2-10_1$
39.33	1?	4	37877.1	$^3D_2-20_2$
46.87	10	10R	769.2	$^3D_3-8_3$
50.84	8	8R	712.7	$^3F_4-9_5$
59.44	50	30R	590.7	$^3D_3-7_4$
77.13	6	5R	342.4	$^3D_3-6_2$
2698.40	1?	5	37048.0	$^1S_0-17_1$
2702.38	20	20R	36993.5	$^1D_2-8_3$
05.88	20	20R	945.6	$^3F_4-8_3$
19.02	20	15R	767.1	$^3F_4-7_4$
29.90	1?	4	620.6	$^3D_2-17_1$
33.62	30	2R	570.7	
33.96		5R	566.2	$^1D_2-6_2$
54.90	2p	5	288.3	$^3D_1-24_2$
2771.65	8	5R	36069.0	$^1D_2-5_1$
2803.23	1	6	35662.6	$^1S_0-15_1$
30.29	20	20R	35321.7	$^3D_3-4_3$
93.87	6	10	34545.7	$^1D_2-4_3$
2897.88	4	8	497.9	$^3F_4-4_3$
2929.79	30	20R	34122.2	$^3D_3-3_3$
2997.97	30	30R	33346.2	$^1D_2-3_3$
3002.26	5	10	33298.6	$^3F_4-3_3$
42.63	10	20R	32856.8	$^3F_4-2_5$
3064.70	40	50R	32620.2	$^3D_3-1_2$
3139.37	3	10	31844.3	$^1D_2-1_2$
3204.04	4p	10	31201.6	$^3D_2-8_3$
3301.87	5p	10	30277.2	$^3D_2-5_1$
3408.14	4p	15	29333.1	

available for the final assignment of absolute quantum numbers and we must be content for a short period with suggested symbols for the recognized levels. It has not been possible to include all the absorption lines in this system so that we are inclined to believe that one or more low levels are still unknown.

TABLE XII

Low levels in the Pt I spectrum.

Value			Difference	Symbol Snyder	 Quantum
0.0				*H*	$^3D_3$
			775.9		
775.9				*G*	$^1D_2$
	6567.5		47.8		
823.7				*F*	$^3F_4$
			5316.3		
6140.0					$^1S_0$
		9293.1	427.5		
6567.5				*E*	$^3D_2$
	3564.5		3549.3		
10116.8				*D*	$^3F_3$
			15.2		
10132.0				*C*	$^3D_1$
		5385.0	3364.3		
13496.3				*B*	$^3P_2$
			2005.5		
15501.8				*A*	$^3F_2$

The quantum-theoretical interpretation of the low levels of the six metals in question, although contained in a paper by Laporte[41] may be briefly given for all the six spectra at once. For atoms with eight, nine and ten valence electrons the following low levels are possible:

	$z=8$ Ru Os	$z=9$ Rh Ir	$z=10$ Pd Pt
$d^{z-2}s^2$	^5D ^3H ^3G	^4F ^4P ^2H ^2G ^2F ^2D	^3F ^3P ^1G ^1D ^1S
$d^{z-1}s^1$	^5F ^3F ^5P ^3P ^3H ^3G	^4F ^2F ^4P ^2P ^2G ^2D ^2S	^3D ^1D
d^z	^3F ^3P ^1G ^1D ^1S	^2D	^1S

Everyone of the configurations furnishes a whole set of terms, the most prominent ones of which are given above, starting at the left with the term which is presumably the lowest of this configuration. In every spectrum all the three configurations will appear, i.e., all the terms in one vertical column will occur; but it cannot be said which one of them will furnish the most conspicuous and stable terms; nor can it be predicted to which of the three configurations the normal state of the atom will belong. Whereas for the iron triad the terms of $d^{z-2}s^2$ are of prevailing stability, it was shown by various investigators that for the palladium group configurations with a lesser number of s electrons are preferred, as the normal states of Ru and Rh are represented by the configurations (d^7s) and (d^8s) respectively and that the Pd by (d^{10}). A comparison of

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[41] Laporte, J.O.S.A. & R.S.I. **13,** 1 (1926).

Ni and Pd seems to prove the high stability of a shell of ten 4_3 electrons compared with a shell of ten 3_3 electrons, a fact which was correlated by Grimm and Sommerfeld[42] with the different chemical properties of Ag and Cu ions. But it was also emphasized by these authors that for Au a structure similar to that of Cu must be expected and that, therefore, in the Pt spectrum not only the configuration (d^{10}) but also (d^9s) will give low terms. The growing tendency of the atoms of the third triad to use configurations with s electrons, as we may formulate this safely, is also supported by Laporte's[43] result that W has as lowest term a ^5D for which one must account with (d^4s^2). We, therefore, expect in the platinum triad that also the configurations $(d^{z-1}s)$ will appear prominently

Our experiments establish definitely the existence of (d^7s) and (d^6s^2) in Ru, and in Rh, so far as the identification of the l values of the levels is possible, the existence of (d^8s) and (d^9). There are indications of another rather high ^4F, which may perhaps belong to (d^7s^2). In Pd our results confirm those of Bechert and Catalán,[28] and of McLennan and Smith,[29] that the normal state is represented by (d^{10}) with higher metastable levels belonging to (d^9s). There is not much evidence for (d^8s^2) in Pd.

As for the platinum group the intervals between the sub-levels of complex terms become so large that it is hardly justified to speak of one term being lower than another when they overlap more or less completely.

If our assignment of l values in the arc spectrum of Pt is correct the ^3D term, although it contains the level with least energy, is so widely separated that it encompasses the terms ^1D, ^1S and ^3F. The fact that in both 74W and 78Pt the configurations $(d^{z-2}s^2)$ and $(d^{z-1}s)$ are the most prominent ones, giving overlapping low terms, suggests for this group of elements an increasing stability of the configurations with n_1 electrons as compared with the preceding period. We may, therefore, expect ^5D and ^5F as the lowest terms for 76Os, and ^4F as the lowest for 77Ir (quite analogous respectively to Fe and Co of the second preceding period).

Bureau of Standards,
Washington, D. C.
July 8, 1926.

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[42] Grimm and Sommerfeld, Zeits. f. Phys. **36**, 36 (1926).

[43] Laporte, Die Naturwissenschaften **13**, 627 (1925).

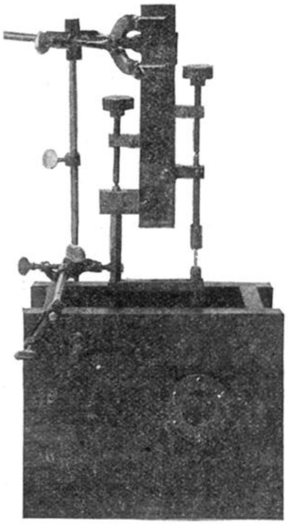

Fig. 1. Under-water spark apparatus.

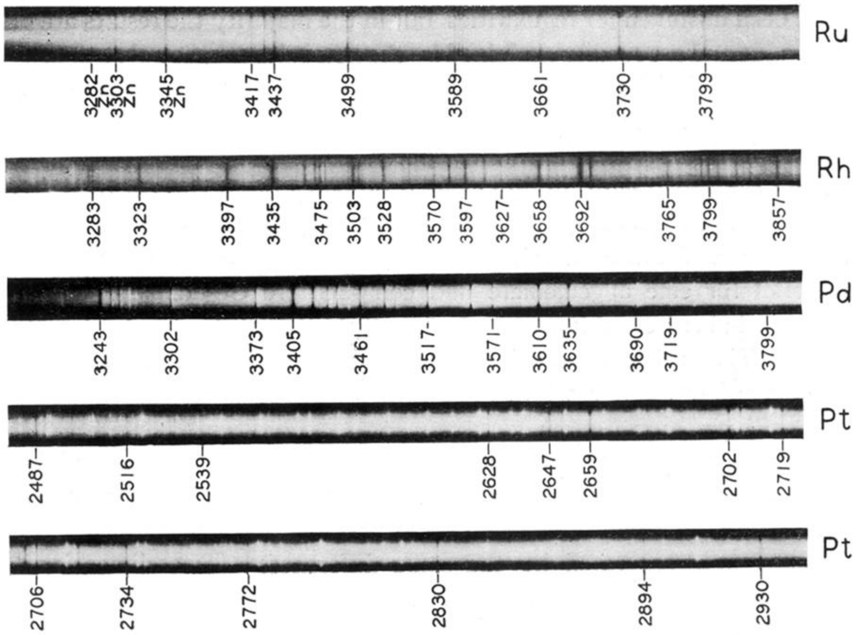

Fig. 2. Under-water spark absorption spectra of ruthenium, rhodium, palladium and platinum.