THE ARC SPECTRUM OF PLATINUM

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Abstract

Eight new levels and forty-four new combinations have been found in Pt I. Fifty-six new lines have been measured in the ultra-violet. An examination of the *Zeeman effect* and the subsequent determination of the *g*-values for most of the terms has permitted a reasonable interpretation of many levels. Low structures are d^9s, d^8s^2 and d^{10}; middle terms arise from d^9p and d^8sp; high configurations are $d^9 \cdot s$, $d^8s \cdot s$, with an indication of $d^8s \cdot d$. Quintet terms appear in the middle and high sets. From the failure of the intensity and interval rules and the irregularity of the *g*-values, it is evident that the Russell-Saunders coupling has almost completely broken down, as is to be expected from the position of platinum in the periodic table. There is only an approximate similarity with the theoretically analogous spectrum of Ni I. Ionization potentials are approximately calculated as 8.9 volts for d^9s to d^9 and 9.7 volts for d^9s to d^8s.

THE platinum arc spectrum has received attention from a number of investigators. The more recent contributions are wave-length determinations in the visible by Meggers,[1] the discovery of many of the term values by McLennan and McLay,[2] the examination of the absorption spectrum in the under water spark by Meggers and Laporte,[3] and a more comprehensive analysis with the aid of the Zeeman effect by Haussmann.[4] The purpose of the present investigation was the discovery of new levels, the classification of more lines, further wave-length measurements in the ultra-violet and the determination of *g*-values from Zeeman effects for as many of the levels as possible in order to add to the knowledge of the types of terms involved.

The present paper lists 8 new levels, 44 newly classified lines, 41 remeasured and 56 newly measured lines. The *g*-values for almost all the eighty terms have been found, aiding considerably in their classification. The conclusion of the previous investigators has been confirmed that the outer electron structures are d^{10}, d^8s^2 and d^9s for the low terms, and evidence is presented that the middle terms are due to d^9p and d^8sp, while the high terms come from $d^9 \cdot s$, $d^8s \cdot s$ and probably $d^8s \cdot d$, in conformity with the predictions of Hund. As is to be expected from the position of platinum in the periodic table, the interval rule is found to be useless, the *g*-values depart very markedly from the Landé values (although the *g*-sums, where it is possible to form them, are correct within experimental error) and the intensity rules are satisfied only very approximately.

[1] W. F. Meggers, Scientific Papers, Bur. of Standards **20**, No. 499 (1925).

[2] J. C. McLennan and A. B. McLay, Trans. Royal Soc. of Canada, (3rd series) **20**, (1926).

[3] W. F. Meggers and O. Laporte, Phys. Rev. **28**, 642 (1926).

[4] A. C. Haussmann, Astrophys. J. **66**, 333 (1927).

EXPERIMENTAL PROCEDURE

A Hilger E1 quartz spectrograph was employed, with Cramer Contrast and Hilger Schumann plates. Rods of extremely pure platinum were used as electrodes in photographs for wave-length determinations. Arc and spark pictures were taken, to assist in classification. It was found necessary to use a mechanical vibrator, for with a steady arc in air the cathode became red hot in several seconds and the arc flared up and out. At 250 volts and an arc current of $1\frac{1}{2}$ amperes, exposures ranged from a few seconds for lines near the visible to one and a half hours for those around $\lambda 1900$.

Zeeman effect photographs were taken from $\lambda 3408$ to 2043 with the same instrument and an electromagnet giving a field of about 34700 gauss with pole faces 10 mm in diameter separated by a 3 mm air gap. A platinum wire fused into a bead at the end, attached to the vibrator arm, served as cathode, the anode being a copper plate clamped against one of the pole pieces. This arrangement was found to give the easiest running arc in the magnetic field, and only a few copper lines appeared on the plates. The separation of Cu $\lambda 2442$ ($^2S - {}^4P_{1/2}$) was used to determine the field, all other exposures in different ranges of the spectrograph being taken under identical conditions. Measurements of Cu $\lambda 2356$ and 2276, whose Zeeman patterns could be simply calculated, were consistent with the choice of the field constant. A current of 1 ampere at 115 volts was used for the Zeeman pictures, the exposures lasting from three minutes to an hour. A quartz double image prism separated the parallel and perpendicular components of the patterns.

Haussmann's wave-lengths above $\lambda 4498$ were taken from Meggers's paper, and below that from Kayser's Tables, with Exner and Haschek's values where Kayser listed no lines. In continuing the search to allocate lines, the author has preferred Exner and Haschek's values rather than Kayser's. The wave-length and intensity of most of the lines below $\lambda 2200$ classified by Haussmann were taken from measurements made by Meggers and Laporte, and it was seen that the listed wave-numbers were consistenly higher than the combination of terms predicted, the greatest error of over two units occurring at the short wave-length end of the list. Consequently, all the lines from $\lambda 2246$ to 2039 have been remeasured by the author, with copper arc and spark lines for standards, since their wave-numbers have been fixed to within about two tenths of a unit by Shenstone's use of the combination principle.[5] From $\lambda 2039$ to 1911 the silver spark was used for comparison, with wave-numbers supplied in a private communication from C. W. Gartlein of Cornell University. The new measurements are in much better agreement with the computed wave-numbers.

ZEEMAN EFFECT ANALYSIS

Of the 225 arc lines examined for Zeeman effect, the vast majority appeared as triplets only, due to the low resolving power of the instrument. However, fairly accurate determinations of the *g*-values from these "blends" were

[5] A. G. Shenstone, Phys. Rev. **29**, 380 (1927).

possible by the use of formulae developed by A. G. Shenstone[6] from considerations of the intensities of the various lines in the parallel and perpendicular components. It is shown that $2\sigma = g_x(J_x+1) - g_y J_y$, where $J_x = J_y+1$ and σ is the separation of the "center of gravity" of the blend from the normal (undeviated) position, in terms of the Lorentz separation as unity. For $J_x = J_y$ the center of gravity lies of course at $2\sigma = g_x + g_y$. For the π components, separated blends occur only when $J_x = J_y$; the ratios of the intensities follow a somewhat more complicated law and Shenstone has shown that the separation of the center of gravity from the normal (again measured on the basis of the Lorentz displacement) is given by $(g_x - g_y)\{1 + C(J-1)\}$ for odd multiplicity, and by $(g_x - g_y)\{\frac{1}{2} + C'(J-\frac{1}{2})\}$ for even multiplicity. C and C' are complicated functions of J, and a table is appended giving their numerical magnitudes for various values of J. Both these expressions can be reduced to a single more convenient form by substituting in the values of C, C' and J. The result is that the separation of the center of gravity of the π components from the normal position is given by $\pi = k(g_x - g_y)$, where

	Even Multiplicity				Odd Multiplicity		
for $J=\frac{1}{2}$	$k=0.50$	$J=3\frac{1}{2}$	$k=2.96$	for $J=1$	$k=1.00$	$J=4$	$k=3.34$
$1\frac{1}{2}$	1.40	$4\frac{1}{2}$	3.70	2	1.80	5	4.08
$2\frac{1}{2}$	2.18	$5\frac{1}{2}$	4.45	3	2.58	6	4.85
						7	5.56

Haussmann's Zeeman patterns were almost always somewhat greater in value than the author's determinations and in many cases were quite self-inconsistent. These may be the patterns "perturbed so that they were no longer symmetrical," mentioned by him. In as much as the author's measurements are much more self-consistent, it is probable that with the greater dispersion of Haussmann's gratings, the components were separated in some cases to such an extent (though still unresolved) that the cross hairs of the comparator would be set nearer to the strongest line than to the center of gravity, and hence the pattern would be amenable neither to a "completely resolved" or a "blended" analysis. Particularly bad disagreements in measurement were found in the lines $\lambda 2929$, 2830 and 2677, for which Haussmann gave the patterns (0)1.64, (0)1.52 and (0)1.71 respectively, while the author obtained (0)1.27, (0)1.37 and (0)1.50. The use of Haussmann's values in such cases gave g-values quite at variance with other determinations, whereas the author's measurements fitted in very nicely. Among the longer wavelengths above the author's range, some of Haussmann's patterns had to be discarded as they could not be interpreted at all; for example, (0) 1.20, 1.80 for $\lambda 3638$ and (.36) 1.41, .92 for $\lambda 4164$. He gives (.44) $\overline{1.27}$, 1.61 for $\lambda 3699$, and assuming g-values of 1.20 and 1.40 from other combinations, calculates the pattern (.20, .$\overline{40}$,) 1.00, $\overline{1.20}$, $\overline{1.40}$, 1.60, which is not at all in accord with his observation.

No attempt was made in the present paper to determine both g's involved in each of the several completely resolved patterns. Instead, g's were as-

sumed to have Landé values for those levels of which there was but one
with a given J in the whole number of levels due to any particular electron
structure; i.e., the g-sum rule was applied to those cases where there was
but one item in the sum. This procedure gave five unambiguous g-values
among the low terms. Then by applying the blend formulae to lines involv-
ing these terms, other g's could be found and averages finally taken.

NOTATION

The notation used in this paper is that recently adopted by an informal
committee, consisting of H. N. Russell, A. G. Shenstone and L. A. Turner,
appointed at a meeting of the Physical Society last spring.[6a]

The type of term is denoted by the customary $SPD \cdots$ corresponding
to the quantum numbers $L = 0\ 1\ 2 \cdots$. The multiplicity is given by a
superscript to the left and the J value by a subscript at the right. Terms
for which the l-sum of the component electrons is odd (an odd number of
p and f electrons) are followed by the superscript°; those for which the
l-sum is even (an even number of p and f electrons) have no such index.
Thus the present notation is

<div align="center">

Even terms $S\ P\ D\ F \cdots$

Odd terms $S°\ P°\ D°\ F° \cdots$

</div>

replacing the older usage of $S\ P'\ D\ F'$ for even and $S'\ P\ D'\ F$ for odd terms.

The arbitrary numerical designation given by Haussmann to unidenti-
fied middle group terms is in conformity with the suggestions of the com-
mittee and so is retained, except that the "°" has been added. Haussmann's
arbitrary capital letters to indicate unclassified high terms are not in strict
accord with the committee's recommendations, but the usage is continued
in this paper as a change would be unnecessarily confusing.

Among the low terms the arbitrary label "a" is prefixed to each of the
different levels; "b", "c", "d", to the following higher terms of the same S,
L and J. Similarly, the middle group levels are marked z, y, x in succession,
and the high group levels e, f, g.

Electron structure in the outermost shells is given by, e.g., $5d^8\ 6s^2$, the
letter indicating the type of electron, the prefix its total quantum number
and the superscript the number of electrons of that type present. As an
abbreviation, a dot before a letter indicates that the total quantum number
of the electron is greater than it is when the electron is in its lowest state.

It seems unnecessary to repeat the wave-length, frequency, intensity
and term combination list given by Haussmann, as the changes made by
this analysis are almost all in the designation given the various levels. Table
I gives the complete list of all terms known in Pt I, with Haussmann's
arbitrary and suggested designations and in addition the author's identifi-
cations and the probable electron structures. To indicate the reality of
the terms, the numbers of combinations they make are also included. The
most probable g-values, obtained by averaging, as explained above, are
given, as well as the theoretical Landé values. The number of π and σ com-
ponents from which the g's were averaged and the mean deviation of the

[6a] H. N. Russell, A. G. Shenstone and L. A. Turner, Phys. Rev. **33**, 900 (1929).

TABLE I. *Terms of Pt I. New terms marked*.*

ν (Vac.)	Author's suggested Structure	Author's sugg. desig.	Arbit. designation	Hauss. designation	No. of comb.	g obs.	g Landé	No. of comp. for g	Mean dev. of g
0.0	$5d^96s$	a^3D_3		$^3D_3$	26	(1.33)			
775.9	$5d^96s$	a^3D_2		a^1D_2	29	1.01	1.17	4	0.03
823.7	$5d^86s^2$	a^3F_4		$^3F_4'$	20	1.25	1.25	5	.02
6140.0	$5d^{10}$	a^1S_0		$^1S_0$	8	(0/0)			
6567.5	$5d^86s^2$	a^3P_2		$^3D_2$	34	1.12	1.50	6	.05
10116.8	$5d^86s^2$	a^3F_3		$^3F_3'$	28	(1.08)			
10132.0	$5d^96s$	a^3D_1		$^3D_1$	25	(.50)			
13496.3	$5d^96s$	a^1D_2		$^3P_2'$	35	1.17	1.00	5	.02
15501.8	$5d^86s^2$	a^3F_2		$^3F_2'$	35	.92	.67	6	.00
18566.5	$5d^86s^2$	a^3P_1		$^3P_1'$	21	(1.50)			
21967.1	$5d^86s^2$	a^1G_4		$^1G_4$	12	1.+?	1.00	3	.13
26638.6	$5d^86s^2$	b^1D_2		b^1D_2	15	.97	1.00	7	.03
*30157.0	$5d^86s6p$	$z^5D_4^\circ$	46_4°		6	1.46	1.50	2	.01
32620.0	$5d^96p$	$z^3P_2^\circ$	1_2°	D_2	12	1.39	1.50	3	.02
33680.5	$5d^86s6p$	$z^5G_5^\circ$	2_5°	G_5	7	1.32	1.27	1	
34122.1	$5d^96p$	$z^3F_3^\circ$	3_3°	F_3	13	1.21	1.08	6	.01
35321.7	$5d^86s6p$	$z^5D_3^\circ$	4_3°	D_3 or F_3	13	1.33	1.50	4	.03
*36781.6	$5d^86s6p$	$z^5G_6^\circ$	47_6°		2	1.33	1.33	1	
36844.7	$5d^86s6p$		5_1°	D_1	10	1.09		5	.05
37342.1	$5d^86s6p$		6_2°	D_2	18	1.15		3	.01
37590.7	$5d^96p$	$z^3F_4^\circ$	7_4°	F_4	11	1.25	1.25	2	.02
37769.0	$5d^86s6p$		8_3°	D_3	16	1.17		4	.10
38536.2	$5d^86s6p$	$z^5F_5^\circ$	9_5°	G_5	8	1.30	1.40	1	
38815.9	$5d^96p$	$z^3D_2^\circ$	10_2°	F_2	13	.88	1.17	3	.03
40194.2	$5d^86s6p$	$z^5F_4^\circ$	11_4°	F_4	11	1.21	1.35	2	.00
40516.3	$5d^86s6p$	$z^5D_2^\circ$	12_2°	D_2	13	1.38	1.50	5	.02
40787.9	$5d^86s6p$		13_2°	D_2	11	1.20		5	.07
40873.5	$5d^86s6p$		14_0°	P_0	3		0/0		
40970.1	$5d^96p$	$z^3D_3^\circ$	15_3°	F_3	19	1.12	1.33	5	.02
41802.7	$5d^96p$	$z^3P_1^\circ$	16_1°	P_1	8	.92	1.50	4	.07
42660.2	$5d^86s6p$		17_3°	D_3	14	1.19		4	.01
43187.8	$5d^86s6p$		18_1°	P_1 or D_1	11	1.39		4	.11
43945.7	$5d^86s6p$		19_3°	D_3 or F_3	8	1.21		3	.03
44432.7	$5d^86s6p$		20_4°	F_4	7	1.20		2	.01
44444.4	$5d^96p$	$z^3F_2^\circ$	21_2°	D_2	9	1.21	.67	5	.02
44730.3	$5d^86s6p$		22_3°	F_3	15	1.19		5	.04
45398.4	$5d^86s6p$	$z^5D_1^\circ$	23_1°	P_1	6	1.52	1.50	1	
*46007.3	$5d^86s6p$	$z^5D_0^\circ$	48_0°		2		0/0		
46170.4	$5d^86s6p$		24_2°	D_2	11	1.01		6	.12
46419.4	$5d^86s6p$		25_2°	D_2	11	.87		4	.05
46433.9	$5d^96p$	$z^3P_0^\circ$	26_0°	P_0	3		0/0		
46622.5	$5d^86s6p$		27_3°	F_3	12	1.15		6	.01
*46793.9	$5d^86s6p$		49_3°		3				
46965.1	$5d^86s6p$		28_4°	G_4	5	1.34		1	
47740.6	$5d^86s6p$	$y^3P_1^\circ$ or $^5D_1^\circ$	29_1°	P_1 or D_1	10	1.43	1.50	2	.01
48351.9	$5d^86s6p$		30_4°	G_4	3	1.25		2	.02
48535.6	$5d^86s6p$		31_2°	P_2	8	1.02		2	.05
48779.3	$5d^86s6p$		32_3°	D_3	7	1.22		3	.01
49286.1	$5d^96p$	$z^1F_3^\circ$	33_3°		9	1.19	1.00	6	.04
49544.5	$5d^96p$	$z^1P_1^\circ$	34_1°		7	1.24	1.00	2	.01
49880.8	$5d^86s6p$		35_2°		7	1.12		5	.06
50055.3	$5d^96p$	$z^3D_1^\circ$	36_1°		8	.87	.50	3	.01
*51097.5	$5d^86s6p$		50_3°		6	1.21		3	.02
51286.9	$5d^96p$	$z^1D_2^\circ$	37_2°		8	1.13	1.00	2	.02
51545.5	$5d^86s6p$		38_2°		5	1.25		3	.17
51752.3	$5d^86s6p$		39_2°		5	1.34		4	.02
52071.6	$5d^86s6p$		40_1°		5	1.22		4	.03
52379.3	$5d^97s$	e^3D_3	A_3		9	1.32	1.33	2	.00
52667.2	$5d^97s$	e^3D_2	B_2		8	1.04	1.17	1	
52708.3	$5d^86s6p$	$y^3P_2^\circ$ or $^5D_2^\circ$	41_2°		5	1.46	1.50	3	.02

TABLE I. (continued)

ν (Vac.)	Author's suggested Structure	Author's sugg. desig.	Arbit. designation	Hauss. designation	No. of comb	g-obs.	g Landé	No. of comp. for g	Mean dev. of g
53019.2	$5d^86s6p$		42_1°		6	1.08		4	.08
53955.3	$5d^86s6p$		43_2°		5	1.32		3	.01
54839.2	$5d^86s6p$		44_3°		4	1.21		3	.01
55216.8	$5d^86s6p$		$45_{1\ or\ 2}^\circ$		4	.96		4	.12
55640.7	$5d^86s7s$	e^5F_5	C_5		5	1.41	1.40	2	.01
56784.4	$5d^86s7s$	e^5F_4	D_4		11	1.27	1.35	4	.05
*59731.5			Q_3		10	1.3		1	
59751.2			E_3		7				
59764.3	$5d^86s7s$	e^5F_3	F_3		10	1.27	1.25	6	.12
59782.8			G_1		8	1.07		2	.01
59872.1			H_3		8	1.23		3	.04
59882.4			I_4		7	1.17		2	.01
59908.1			J_2		7	1.02		2	.03
60357.8	$5d^97s$	e^3D_1	K_1		8	.52	.50	4	.04
60640.6	$5d^97s$	e^1D_2	L_2		13	1.08	1.00	3	.03
60790.4			M_3		11	1.07		4	.02
60884.0			N_4		9	1.29		3	.01
*64129.1			$R_{4\ or\ 5}$		3				
*64141.3	$5d^86s6d$	e^5G_6 or $^5H_6$	T_6		3				
64505.9			O_4		7				

Terms	g-sums obs.	g-sums Landé		Terms	g-sums obs.	g-sums Landé
d^9s $J=2$	2.18	2.17		d^9p $J=1$	3.03	3.00
d^8s^2 $J=2$	3.01	3.17		$J=2$	4.61	4.34
$J=4$	2.25?	2.25		$J=3$	3.52	3.41
				$d^9\cdot s$ $J=2$	2.12	2.17

TABLE II. *Newly classified lines*. Remeasured lines. New lines ‡.*

λ (Air)	Int.	Auth.	ν (Vac.)	Combination	ν obs. $-\nu$ calc.
*7830.45	1	M	12767.3	$28_4^\circ - Q_3$	0.9
*7626.27	1	M	13109.0	$27_3^\circ - Q_3$	.0
*7257.76	1u	E	13774.6	$48_0^\circ - G_1$	-.9
*7094.77	7	M	14091.0	$49_3^\circ - N_4$	.9
*6332.88	0	M	15786.2	$19_3^\circ - Q_3$	.4
*5328.60	2	M	18761.4	$15_3^\circ - Q_3$	.0
*5301.02	25	M	18859.1	$47_6^\circ - C_5$	.0
*5117.49	1	E	19535.4	$11_4^\circ - Q_3$	-1.9
*4551.94	3	M	21962.5	$8_3^\circ - Q_3$	.0
*4498.75	20	M	22222.2	$46_4^\circ - A_3$	-.1
*4465.13	1	E	22389.5	$6_2^\circ - Q_3$	.1
*3922.97	10	E	25483.6	$46_4^\circ - C_5$	-.1
*3906.27	1	E	25592.6	$9_5^\circ - R_{4,5}$	-.3
*3904.39	2	E	25605.0	$9_5^\circ - T_6$	-.1
*3903.70	2	E	25609.5	$3_3^\circ - Q_3$	.1
*3687.46	4	E	27111.2	$1_2^\circ - Q_3$	-.3

TABLE II. (continued)

λ (Air)	Int.	Auth.	ν (Vac.)	Combination	ν obs. − ν calc.
*3654.00	1	E	27359.5	$47_6{}^\circ - T_6$	− .2
*3643.17	5	E	27440.8	$a^3P_1 - 48_0{}^\circ$	.0
*3431.86	2	E	29130.4	$a^1G_4 - 50_3{}^\circ$	.0
*3408.13	15	E	29333.2	$a^3F_4 - 46_4{}^\circ$	− .1
*3315.03	8	E	30156.9	$a^3D_3 - 46_4{}^\circ$	− .1
*3283.26	4	E	30448.8	$2_5{}^\circ - R_{4,5}$	.2
*3281.96	5	E	30460.9	$2_5{}^\circ - T_6$	.1
*3002.26	10	E	33298.6	$\begin{cases} a^1D_2 - 49_3{}^\circ \\ a^3F_4 - 3_3{}^\circ \end{cases}$	1.0 .2
*2942.77	4	E	33971.7	$46_4{}^\circ - R_{4,5}$	− .4
*2910.46	1	E	34348.8	$46_4{}^\circ - O_4$	− .1
*2808.49	2	E	35595.9	$a^3F_2 - 50_3{}^\circ$	.2
*2658.69	2	E	37601.3	$a^1D_2 - 50_3{}^\circ$	.1
*2614.61	1	E	38235.2	$a^3F_3 - 30_4{}^\circ$	.1
*2439.45	1	K	40980.4	$a^3F_3 - 50_3{}^\circ$	− .3
*2244.93	8	L	44531.0	$a^3P_2 - 50_3{}^\circ$	1.0
‡2241.20	4	L	44605.0		
†2240.31	3	L	44622.7	$a^3D_2 - 23_1{}^\circ$	.2
‡*2235.46	3	L	44719.6	$a^3P_2 - 37_2{}^\circ$	.2
2234.91	8	L	44730.6	$a^3D_3 - 22_3{}^\circ$	.3
‡2227.53	2	L	44892.7		
‡2224.51	4	L	44939.7		
2222.60	8	L	44978.4	$a^3P_2 - 38_2{}^\circ$	.4
2217.33	7	L	45085.2	$a^3D_1 - 45_{1,2}{}^\circ$	.4
‡2213.93	3	L	45154.5		
‡2208.77	2	L	45260.0		
2202.20	8	L	45394.9	$a^3D_2 - 24_2{}^\circ$	.4
2201.08	7	L	45418.1		
‡2199.68	5	L	45446.9		
2196.90	5	L	45504.5	$a^3P_2 - 40_1{}^\circ$	.4
‡2192.49	3	L	45595.9		
‡2190.78	5	L	45631.5		
2190.16	6	L	45644.5	$a^3D_2 - 25_2{}^\circ$	.5
‡2188.33	2	L	45682.7		
2182.76	6	L	45799.1	$a^3F_4 - 27_3{}^\circ$	.3
2180.49	8	L	45846.9	$a^3D_2 - 27_3{}^\circ$	.3
‡2180.31	6	L	45850.7		
‡*2176.46	3	L	45931.7	$a^1S_0 - 40_1{}^\circ$	.1
*2174.64	10	L	45970.2	$a^3F_4 - 49_3{}^\circ$	.0
‡2170.71	4	L	46053.4		
‡2169.25	5	L	46084.3		
2166.62	6	L	46140.3	$\begin{cases} a^3P_2 - 41_2{}^\circ \\ a^3F_4 - 28_4{}^\circ \end{cases}$	− .5 −1.1
2165.14	9	L	46171.8	$a^3D_3 - 24_2{}^\circ$	1.4
‡2164.28	3	L	46190.2		
2153.54	8	L	46420.6	$a^3D_3 - 25_2{}^\circ$	− .7
‡2153.38	2u	L	46423.9		
2152.07	6	L	46452.3	$a^3P_2 - 42_1{}^\circ$	.6
2150.64	5	L	46483.1		
‡2147.38	2	L	46553.6		
‡2145.02	6	L	46604.8		
2144.22	10	L	46622.2	$a^3D_3 - 27_3{}^\circ$	− .3
2135.15	5	L	46820.4		
‡2134.62	3	L	46831.9		
‡*2132.46	2	L	46879.4	$a^1S_0 - 42_1{}^\circ$	.2
‡2131.07	2	L	46910.0		
2128.62	8	L	46963.9	$\begin{cases} a^3D_2 - 29_1{}^\circ \\ a^3D_3 - 28_4{}^\circ \end{cases}$	− .8 1.2
2122.56	5	L	47097.9		
‡2119.88	4	L	47157.5		
‡2114.22	2	L	47283.8		

TABLE II. (continued)

λ (Air)	Int.	Auth.	ν (Vac.)	Combination	ν obs.−ν calc.
*2109.65	7	L	47386.2	$a^3P_2-43_2^\circ$	−1.6
2109.49	6	L	47389.7		
‡2103.48	2u	L	47525.2		
2103.33	6	L	47528.5	$a^3F_4-30_4^\circ$	.3
‡2101.64	5	L	47566.7		
‡2098.75	3	L	47632.3		
‡2097.30	3	L	47665.2		
‡2095.45	2	L	47707.1		
‡2094.71	1	L	47724.1		
‡2094.00	1	L	47740.4		
‡2088.97	4	L	47855.3		
‡2088.32	5	L	47870.0		
2084.62	7	L	47955.0	$a^3F_4-32_3^\circ$	−.6
‡2084.36	3	L	47961.0		
2083.38	5	L	47983.6		
2082.55	5	L	48002.7	$a^3D_2-32_3^\circ$	−.7
‡2076.25	2	L	48148.4		
2073.62	3	L	48209.5		
2070.96	6	L	48271.3	$a^3P_2-44_3^\circ$	−.4
‡2070.36	1	L	48285.2		
2067.53	5	L	48351.4	$a^3D_3-30_4^\circ$	−.5
2066.95	4	L	48364.9		
2062.81	5	L	48462.0	$a^3F_4-33_3^\circ$	−.4
2060.78	5	L	48509.7	$a^3D_2-33_3^\circ$	−.5
2059.70	3	L	48535.1	$a^3D_3-31_2^\circ$	−.5
‡2058.42	1	L	48565.4		
‡*2049.84	3	L	48768.5	$a^3D_2-34_1^\circ$	−.1
2049.38	6	L	48779.6	$a^3D_3-32_3^\circ$	.3
‡2041.47	1	L	48968.6		
2040.33	3	L	48995.9		
2039.70	3	L	49011.1		
2036.46	8	L	49089.0		
2035.79	4	L	49105.2		
2032.42	5	L	49186.5		
2030.64	6	L	49229.5		
‡*2028.58	2	L	49279.6	$a^3D_2-36_1^\circ$	.2
‡*2028.32	1	L	49285.9	$a^3D_3-33_3^\circ$	−.2
‡2025.86	2	L	49345.7		
‡2024.63	1	L	49375.8		
‡2020.90	2	L	49467.1		
‡2016.72	1	L	49569.3		
‡*2004.13	3	L	49880.7	$a^3D_3-35_2^\circ$	−.1
λ (Vac.)					
‡1995.91	3	L	50102.5		
‡1991.59	2	L	50211.2		
‡*1989.11	2	L	50273.7	$a^3F_4-50_3^\circ$	−.1
‡1987.79	1	L	50307.4		
‡*1979.78	2u	L	50510.7	$a^3D_2-37_2^\circ$	−.3
‡*1969.69	2	L	50769.5	$a^3D_2-38_2^\circ$	−.1
‡1963.17	1	L	50938.3		
‡1949.92	1	L	51284.1		
‡*1949.81	1	L	51287.0	$a^3D_3-37_2^\circ$	.1
‡1929.25	3	L	51833.5		
‡1928.85	1	L	51844.4		

E—Exner and Haschek.

K—Kayser.

L—Author.

† By some mistake Haussmann gave to $a^3D_2-23_1^\circ$, instead of the value here shown, the wave-length 2245.51, which is a strong spark line.

various values from their average are given in the last two columns to give an estimate of the reliability. The five low term g-values that were assumed to have Landé values, as explained before, are given in parentheses. New levels found in the present investigation are marked with an asterisk. Table II gives the newly classified lines, and all the lines remeasured below $\lambda2246$, including 64 hitherto not observed. The author's intensity estimates are on the basis of 10 as maximum. Levels are referred to by their arbitrary symbols, except for the lower group, where the author's suggested names are used.

TERM DESIGNATION

McLennan and McLay were of the opinion that the lowest term in the platinum arc spectrum was of the triplet F type, by analogy with the analysis by Bechert and Sommer[7] of the nickel arc, to which the spectrum of platinum should be similar. On that assumption they assigned tentative L-values and multiplicities to the twelve low terms. Shortly thereafter, Meggers and Laporte published their work on the absorption spectrum, but by considerations of the general dependence of level separations on atomic number they were led to a different assignment of L-values, so that the lowest state was named $^3D_3$. Haussmann, from a study of Zeeman patterns, reached the conclusion that the designations suggested by Meggers were preferable to those of McLennan.

The present analysis offers three changes in the names of the low terms and suggests designations for many of the middle and high terms, as well as assigning electron structures in most cases. Considerable assistance was received from a very complete analysis of Ni I recently made by H. N. Russell, confirming and amplifying the results of Bechert and Sommer.

According to Hund's theory the low group (even) structures of platinum and their resulting terms should be $5d^{10}\,^1S_0$; $5d^96s\,^3D_{321}\,^1D_2$; $5d^8\,6s^2\,^3F_{432}$ $^3P_{210}\,^1G_4\,^1D_2\,^1S_0$. Haussmann made an identification of all these with the exception of one $^1S_0$ and the $^3P_0$. The author has made a very thorough search and has also been unable to detect any terms to which these two designations might be applied. It seems probable that the missing $^1S_0$ is from d^8s^2, since that term from such a structure never has been definitely found in other spectra.

It was first pointed out by Grotrian[8] and later shown more extensively by Laporte[9] and by Goudsmit's[10] use of the Γ sum rule, that the total separation of the triplet arising from d^9s or p^5s is (neglecting a small correction in the screening) the same as that of the doublet of the ion d^9 or p^5 of the same atom. The separation of the doublet follows the x-ray regular doublet law of Sommerfeld:

[7] Bechert and Sommer, Bayr. Akad. **7,** 9 (1925).
[8] W. Grotrian, Zeits. f. Physik **8,** 116 (1922).
[9] O. Laporte, Phys. Rev. **29,** 650 (1927).
[10] S. Goudsmit, Phys. Rev. **31,** 496 (1928).

$$\Delta \nu = \frac{R\alpha^2(Z-\sigma)^4}{n^3 l(l+1)}$$

where $R\alpha^2$ is a universal constant, n and l are quantum numbers of the d or p electron lacking from the closed shell d^{10} or p^6, and σ is an empirical screening number depending on n and l but only slightly on the atomic number Z. Goudsmit and Back[11] showed that in the case of the configuration ps the singlet and triplet merge into two pairs of levels, as one considers successively Si $3p4s$, $Z=14$; Sn $5p6s$, $Z=50$; Pb $6p7s$, $Z=82$; i.e., that the triplet separation increases greatly with increasing atomic number and that the relative distance of the singlet from the nearest member of the triplet, compared to the separation of the triplet itself, decreases as Z increases. Recent work by J. E. Mack[12] confirms this, in a study of the d^9s configuration in the spectra of Ni I PdI Pt I, Cu II Ag II Au II, Zn III Cd III Hg III, Ga IV In IV Tl IV, and Ge V Sn V Pb V. Hence it appears that in platinum the structure $5d^96s$ should give $^3D_3$ and $^3D_2$ close together, with $^3D_1$ and $^1D_2$ considerably higher and also near each other. On the basis of the above considerations and the fact that Shenstone[5,13] had found in the $d^9 \cdot ns$ series of Ni I, Cu II, Pd I and Ag II that the $^3D_2$, rather than $^1D_2$, closes in on $^3D_3$, the term at 775.9 in Pt I was changed [14] from Haussmann's designation of $^1D_2$ to $^3D_2$. The present paper suggests the further alteration of the level at 13496.3 from $^3P_2$ to $^1D_2$ to make the assignment conform with the arguments given above. It is true that these names, $^3D_2$ and $^1D_2$, if turned about, would give g-values almost exactly in accord with Landé's predictions, but as the g's throughout the rest of the spectrum are decidedly irregular, it seems plausible that such an agreement is fortuitous. With the present arrangement, the g's for the $J=2$ levels in $5d^96s$ are irregular, but their sum of 2.18 is in good agreement with the Landé sum 2.17.

This assignment means that the term at 6567.5 must be called $5d^86s^2$ $^3P_2$. The g-sum for $J=2$ from this structure comes out as 3.01, differing from the Landé sum of 3.17 by 5 percent, which is about the limit of accuracy to be obtained from these blended patterns. The observed g-value of $5d^8$ $6s^2$ $^3F_4$ is 1.25, exactly the Landé value, so that $^1G_4$ should have a g equal to 1.00 if the g-sum is to be correct. There are but three patterns available for this level, giving computed g-values of 1.00, 1.22, and 1.17, with an average of 1.13, but as they are all Haussmann's determinations, which seem to be consistently too high, it is possible that the g of $^1G_4$ is close to the Landé value of 1.00. With the levels as widely separated as these are—22104 units— it is not surprising that the g's of $^3F_4$ and $^1G_4$ are so close to the theoretical values, although the departures are so great among the rest of the terms.

Among the middle group of terms (odd), the structure $5d^96p$ is to be expected, giving singlet and triplet P° D° F° terms; twelve levels in all.

[11] S. Goudsmit and E. Back, Zeits. f. Physik **40**, 530 (1926).
[12] J. E. Mack, Phys. Rev. **34**, 17 (1929).
[13] A. G. Shenstone, Phys. Rev. **31**, 317 (1928).
[14] J. E. Mack, O. Laporte and R. J. Lang, Phys. Rev. **3** , 748 (1928).

Arguing by analogy and extrapolation from the behavior of the d^9p levels in the elements mentioned above, Mack has made a tentative identification of all these, (given in this paper), with but four disagreements from Hauss-mann's determinations. The triplets F° and D° are partially re-inverted, while triplet P° is wholly inverted. The g-sums are correct within a few percent, although the individual values are very irregular.

Before discussing the remainder of the middle group of terms, it will be profitable to consider the high set. They are probably due to the configurations $5d^97s$, $5d^86s7s$, $5d^86s6d$, and $5d^96d$, giving a large number of singlet, triplet and quintet *SPDFGHI* terms. In Ni I the lowest level of the group is $d^9 \cdot s$ $^3D_3$ and is thus the second series member of the d^9s structure. The same might be expected in Pt I, and for this reason the term A_3 has been called $5d^97s$ $^3D_3$. Excellent confirmation of this choice is the computed g-value of 1.32, in accord with the Landé value 1.33 (there being but one $J = 3$ level in the configuration.) The levels B_2 and L_2 are then certainly $5d^97s$ $^3D_2$ and $^1D_2$ respectively, their g-sums being correct to within $2\frac{1}{2}$ percent. Level K_1 has a g-value of 0.52 making it appear to be $^3D_1$ from the same structure, in which it is the only $J = 1$ level. The triplet D separation in the low terms is 10132, and this assignement of A_3 and K_1 makes the separation of the second member of the triplet D series only 7978. In the analogous spectra Ni I Cu II Pd I and Ag II this triplet separation is constant to within a few units in the first and second members of the series,[13,5] so the marked diminution in the second member of platinum is another indication of the abnormality of its spectrum.

After d^97s the most important high term should be ^5F due to $d^8s \cdot s$. By analogy with Ni I this should be slightly higher than $d^9 \cdot s$ ^3D but lower than the terms arising from $d^9 \cdot d$ and $d^8s \cdot d$. Actually, the next lowest level of the high terms, after $d^9 \cdot s$ $^3D_3$ and $^3D_2$, has a $J = 5$, and g 1.41 and hence is doubtless $5d^8$ $6s7s$ $^5F_5$ (Landé g 1.40). This assignment is corroborated by the intensities of its combinations with the middle set of terms. With somewhat less assurance the levels D_4 and F_3 may be called $^5F_4$ and $^5F_3$ from the same structure.

Nothing can be said of the remainder of the high terms, except that T_6 is probably either $^5G_6$ or $^5H_6$ from $5d^86s6d$. It may be noted that $\lambda4465.13$, from the combination $6_2^\circ - Q_3$, has a pattern given by Haussman as (.31) 1.24, indicating that it should belong to a transition where $\Delta J = 0$. However, since there are several instances where he has definitely been in error, it is possible that this particular pattern is also incorrect. The wave-length is too great for the Zeeman effect to be determined with the quartz instrument. Haussman classifies $\lambda5108.45$ as $13_2^\circ - K_1$ and $11_4^\circ - F_3$, both very accurately as to wave-number, but the g-value calculated for the high terms show that the main intensity of the line is due to the latter combination. Similarly, $\lambda3925.34$, assigned by Haussman to $^3F_2 - 15_3^\circ$ and to $4_3^\circ - M_3$ without the explicit statement of the duality, gives g-values showing that the former transition is more intense.

Returning to the middle group of terms, one would expect the remainder of them to be due to $5d^8 6s6p$, forming a great many singlets, triplets and quintets. Of these, $^5D_4^\circ$, if it could be found, should combine strongly with the high $^5F_5$ and $^3D_3$ and the low $^3F_4$ and $^3D_3$. In Ni I the lowest level of $d^8 s^2$ is 204 units below the lowest level of d^9s, and in Pt I the lowest level of d^8s^2 is 823 above the lowest of d^9s. Consequently the d^8s ion structure is about 1000 units higher in Pt than it is in Ni, relative to the d^9 basis. In Ni $d^8sp\ ^5D_4^\circ$ lies about 2800 units below $d^9p\ ^3P_2^\circ$ so that in Pt one might expect $^5D_4^\circ$ to appear about 1800 lower than $^3P_2^\circ$, i.e., at 30800. A level with $J=4$ was searched for in that region and 46_4° was found, combining strongly with the terms mentioned above and less intensely with O_4 and $R_{4,5}$ and has therefore been designated $z^5D_4^\circ$. It is the lowest level in the middle group. Its g is close to the Landé value of 1.50; the Zeeman effect of its combination with A_3, measured by Haussmann, is, however, discordant, but there can be no doubt as to the level's reality and nature. The levels 4_3°, 12_2°, 23_1° and 48_0° follow with decreasing assurance as the remainder of the $d^8sp^5D^\circ$ multiplet. The reality of the last named level is somewhat doubtful.

Among the d^8sp terms there should be but two levels with $J=6$, namely $^3H_6^\circ$ and $^5G_6^\circ$. The latter should be lower and might be expected to combine two or three times with the high terms, (strongly with e^5F_5.) Level 47_6° was found and met these requirements and has been labelled $z^5G_6^\circ$. Its combination with e^5F_5 is the strongest line in that region of the spectrum. Level 2_5°, designated as G_5° by Haussmann, is then probably $z^5G_5^\circ$ since it is the lowest $J=5$ level in the middle group, although this means a (partial, at least) re-inversion of the multiplet, which is not the case in nickel. From the strength of its combinations with e^5F_5 and e^5F_4, the level 9_5° seems to be $d^8sp\ ^5F_5^\circ$ rather than the G_5° suggested by Haussmann. Furthermore, it is the only $J=5$ level available to give an inverted partial multiplet with 11_4°, which is doubtless $z^5F_4^\circ$ as it combines quite strongly with the high e^5F_4.

Level 30_4° has been altered from 48353.8 to 48351.9. One of its combinations, with O_4, given by Haussmann, for $\lambda6188.77$, involved the large error of 1.7 wave-numbers, whereas the same line is given also by the combination $22_3^\circ - N_4$ with an error of only 0.1 units. Consequently $30_4^\circ - O_4$ has been abandoned and 30_4° readjusted to give a better fit with its other two combinations and a new one, namely with a^3F_3 to give $\lambda2614.61$.

Haussmann classified $\lambda2659.44$ as $a^3D_3 - 7_4^\circ$ although the Zeeman pattern he obtained was (.40) 1.20, which would mean that $\Delta J=0$. The author's measurements gave (0) 1.15, thus confirming Haussmann's classification but showing that his Zeeman separation was in error   In this connection it should be noted that a similar doubt arises for his pattern of (.33) 1.17 for $\lambda4862.40$, classified as $19_3^\circ - O_4$. The author could not settle this point as the resolution was not great enough to be of value at that wave length.

The pattern of $\lambda2144.22$, $a^3D_3 - 27_3^\circ$ is (0) 1.32, giving a g-value for 27_3° of 1.31, calculated from the unambiguous Landé value of 1.33 for a^3D_3. This is decidedly anomalous, as six other patterns give for g of 27_3° the values

1.16, 1.15, 1.15, 1.14, 1.14, 1.14. Including 1.31 the average is 1.17; excluding it, it is 1.15, which is the value given in Table I. If the assignment of this line is correct, the intensities of its Zeeman components may be irregular.

Levels 40°, 42°, and 45°, given with J either 1 or 2 by Haussmann, may now definitely be assigned the J value of 1, due to their Zeeman patterns with a^3D_1 and the combination of the first two with a^1S_0. However, $\lambda2217.33$, $a^3D_1-45_1°$, is very peculiar, since its pattern, (.54) .81, gives g of $45_1°$ to be 1.08 as the average computed from the π and σ components, whereas combinations with a^1D_2 and a^3F_2 show that g of $45_1°$ is .81 and .88 respectively. The value given in Table I is the average of the four determinations. Because of their g-values, the levels $29_1°$ and $41_2°$ have been designated $5d^86s6p$ $^3P°$ or $^5D°$.

The spectrum of an atom of so heavy an atomic weight and so complicated an electron structure can be expected to exhibit very wide deviations from the Russell-Saunders coupling. In other words, the spectrum is approaching the condition of jj-coupling wherein there are no resultant L and S vectors for the atom and hence the assignment of term names becomes meaningless. In such cases it has usually been found possible to designate some of the levels with considerable certainty, but in general there will be a large number of levels to which J-values only can be assigned. This is the case in platinum. The evidence has been given for the assignment of L and S-values to a few of the levels; the remainder do not yield to the methods ordinarily employed in multiplet analysis. This is particularly evident among the middle terms, where half of the levels are still unidentified. They are probably due to the configuration d^8sp and will include the representatives of further singlet, triplet and quintet terms. Comparison with spectra of the same structure usually assists in identification, and such a method has been used here with Ni I and Pt I, but the similarity does not lead very far.

IONIZATION POTENTIALS

The application of a Rydberg formula to the two members of the series $5d^96s$ $^3D_3$ and $5d^97s$ $^3D_3$ puts the limit at 74821 wave-numbers. This corresponds to an energy of 9.2 volts for the removal of an electron from d^9s to form the ion d^9. The limits similarly calculated from the $^3D_2$, $^3D_1$ and $^1D_2$ series are 75003, 82369 and 82402 respectively, indicating that $^3D_3$ and $^3D_2$ are approaching a common limit of about 74912, while $^3D_1$ and $^1D_2$ converge to a limit of about 82385. The closeness with which the four series converge to two limits is additional evidence for the correctness of the assignment of the second series members. The difference of the two average limits, 7473, should be the approximate separation of the $5d^9$ ^2D ion of Pt II. A check on this prediction will be afforded when the analysis of the spark spectrum, now in progress, is completed.

The use of a Rydberg formula, however to a series due to the removal of an s electron usually gives too high a limit. H. N. Russell has given[15]

[15] H. N. Russell, Astrophys. J. **65**, 233 (1927).

an empirical equation to correct such a computation for elements in the first long period, obtained from comparison of the limits given by the Rydberg and the more accurate Ritz formulae in cases where there were three series members known:

$$\text{Percent error} = 4.5 \times 10^{-5} \times \text{length of series.}$$

Applying this to the value of the $^3D_3$ series given above, we obtain 72300 or 8.9 volts. It should be noted that the application of this formula to the platinum spectrum is without justification except in the fact that the spectra are of such similar structure. A better approximation might be expected from the readjustment of the factor 4.5 from data taken from spectra in the same row of the periodic table as platinum. For Au I the factor is 4.8 and for Hg I it is 5.5, giving an average of 5.2. The use of this number, however, introduces a change in the ionization potential only in the second decimal place, beyond the accuracy of a Rydberg formula, so that the correction is trivial.

There will also be an ionizing potential corresponding to the removal of an s electron from the configuration d^8s^2. In cases of this sort, the limit is usually calculated from the lowest term of $d^{n-2}s^2$ and the term of the same type and multiplicity in $d^{n-2}s \cdot s$. Empirically it is found, however, in cases where it can be checked, that a much better approximation to the correct ionization potential is obtained by using as the second member the term of the same type but of higher multiplicity, which is always present. For example, in Ca I $s^2\ ^1S$ and $s \cdot s\ ^3S$ put the limit only 127 units higher than the Ritz equation, and in Ni I the use of $d^8s^2\ ^3F_4$ and $d^8s \cdot s\ ^5F_5$ places it 154 too high, whereas a Rydberg formula applied in the usual way gives errors of 2133 and 2557 in the two cases. The method has been tested on other spectra of a similar nature and always gives a limit much nearer the Ritz value, although it is sometimes too high and sometimes too low. Thus in platinum, using $5d^8 6s^2\ ^3F_4$ and $5d^8 6s7s\ ^5F_5$, we obtain the limit 77730, and adding 824, by which a^3F_4 lies above the lowest term, $(5d^9 6s\ ^3D_3)$ the energy difference between d^9s and d^8s is 78554 or 9.7 volts.

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