Extension of the Arc Spectra of Palladium and Platinum (6500 to 12000 A)

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The arc spectra of palladium and platinum have been reinvestigated photographically in the red and infrared, and extended approximately 2000 angstroms beyond the former limit of observation. The spectra were excited in conventional direct-current arcs between pure-metal electrodes and recorded by modern sensitized emulsions with the aid of diffraction gratings of 640-cm radius. Improved wavelength values and intensity estimates are given for 63 Pd I lines between 6508.42 and 11556.27 A, and for 74 Pt I lines between 6648.32 and 10757.78 A. All of the observed Pd I lines have been explained as transitions between known atomic energy levels, but only 42 of the 74 Pt I lines can be explained in like manner. It is concluded that further progress in the structural analysis of the Pt I spectrum is dependent on making an improved description in the visible and ultraviolet.

1. Introduction

Inspiration for this investigation was provided by the current compilation of NBS Circular 467 on atomic energy levels [1].[1] Such analyses are usually handicapped by the limited range of photographic observation of spectra, especially in the infrared. Thirty years ago one of the present authors [2] recorded some infrared lines in the arc spectra of the platinum elements by sensitizing ordinary photographic emulsions with dicyanin. Although considerable extensions of the arc spectra were thus made, the greatest wavelength then detected photographically with palladium was 9234.02 A, and with platinum, 8762.48 A.

In 1935 new types of photographic emulsions and sensitizing dyes for infrared photography were described [3], and good infrared sensitive photographic plates became commercially available for the first time. By using these plates the arc spectra of many elements were promptly observed to a new limit in the infrared several thousand angstroms beyond the previous limit set by dicyanin. Such observations for some noble metals were recently made for rhodium [4] and ruthenium [5], and are here presented for palladium and platinum. In most cases, as in rhodium, extension of the infrared spectrum has been rewarded by the discovery of new energy levels, and the possibility that this might happen also in palladium and platinum could not be neglected. The present paper has three collaborators: the first made the spectrograms, the second measured the wavelengths, and the third interpreted the spectra.

2. Materials and Methods

Solid, cylindrical electrodes, approximately 6 mm in diameter and 8 mm long, were made by pressing the purest powdered palladium or platinum metal in a Dietert hydraulic press. These electrodes were pinched in slotted copper rods that served as electrode holders. Electric arcs were produced between a pair of electrodes by currents of 6 to 7 amp from a 220-v d-c circuit. In the case of platinum, the arc was extremely unstable and could not be maintained in the slotted copper holders, but the stability was satisfactory when the short platinum electrodes were held by water-cooled brass clamps.

To record the red and near infrared spectra of these metal arcs, three types of sensitized photographic plates were used. The wavelength range 6500 to 8800 A was photographed with Eastman I-N plates, 8500 to 10500 A with Eastman I-Q plates, and 10000 to 12000 A with Eastman I-Z plates. Before use, these plates were hypersensitized by bathing in dilute solutions of ammonia, followed by rinsing in alcohol and rapid drying with an air blower.

The previous infrared spectrograms obtained with dicyanin-stained plates [2] were made with a concave grating, of 640-cm radius, ruled with 7,500 lines per inch; the scale of the spectrum was 10.4 A/mm. Because the commercial infrared-sensitive photographic plates are vastly more sensitive, it was possible to make the new spectrograms with increased dispersion. Accordingly, the range recorded on I-N plates was observed with a grating ruled 30,000 lines per inch and an average reciprocal dispersion of 1.6 A/mm. The ranges covered by I-Q and I-Z plates were photographed with a grating ruled 15,000 lines per inch and reciprocal dispersion of 4.5 A/mm. Both gratings have radii of 640 cm and are illuminated with parallel light in Wadsworth mountings.

The Eastman I-N plates were so extraordinarily sensitive that arc spectra were completely recorded with continuous background in 30 min. Relatively, the I-Q and I-Z plates are much less sensitive, so that exposure times of 2 to 4 hr. were required to record spectra with background. Furthermore, the sensitivity of I-Z plates declines rapidly beyond 11000 A, the background vanishes even with 4-hr exposures, and the estimated relative intensities of observed spectral lines are consequently too low for the longest waves.

The red and infrared arc spectra of palladium and

[1] Figures in brackets indicate the literature references at the end of this paper.

platinum were photographed in the first order of both gratings, and for the measurement of wavelengths the arc spectrum of iron was recorded in juxtaposition. In the I-N region the wavelengths were usually measured relative to the first-order spectrum of iron, but in the I-Q and I-Z ranges the standards were generally taken from the second- and third-order iron spectra, respectively. The spectrograms were measured on a 20-inch Gaertner comparator reading directly to 1 micron.

3. Results

The experimental results of this investigation consist of measured wavelengths and estimated relative intensities of palladium and platinum lines recorded photographically in the red and infrared. The wavelengths result from averaging 2 to 4 independent determinations; their average uncertainty is of the order of ± 0.01 A. Estimated intensities are based largely on the strongest spectrogram; they are given on an open scale ranging from 1 to 2000, to represent approximate relative energies (except beyond 11000 A, where sensitivity of detection falls off rather rapidly). Some of the intensity numbers are accompanied by letters that have been recommended by the Joint Commission for Spectroscopy [6] for the qualitative description of spectral lines. Briefly, *h* stands for hazy, *H* for very hazy, *l* for shaded to longer waves, and *s* for shaded to shorter waves.

In the range of wavelengths reported here, the only spectral impurities detected in palladium and platinum were potassium and calcium. However, the arc spectra of noble metals, especially in the long-wave range, are always contaminated by superposed spectra of atmospheric constituents and metallic compounds. In addition, the arc spectrum of platinum in air is accompanied by fairly complete atomic spectra of nitrogen, oxygen, and a strong background of irregularly spaced lines that represent certain unidentified molecules. That background is usually present in all arc spectra of noble metals, and can therefore be recognized and ignored by recording side by side the arc spectra of two different noble metals and by measuring only the lines that are not common to both.

3.1. Palladium (46 Pd)

Among the six noble metals, palladium is outstanding in possessing the simplest arc spectrum. Following previous workers, Shenstone [7] in 1930 compiled and thoroughly analyzed the arc spectrum of palladium. That compilation lists about 350 Pd I lines with wavelengths ranging from 1945.98 to 9234.02 A. Most of those lines were quoted from published [2] and unpublished data by Meggers. Recently, Shenstone [8] made a new examination of the Pd I spectrum and contributed 75 new lines, mostly in the ultraviolet down to 1683.65 A.

In the present paper only new data for 63 red and infrared lines of the Pd I spectrum are given in table 1. Between 6508 and 8761 A the new list is almost identical with that published by Meggers [2] in 1925, except that the intensity scale has been increased, and the accuracy of wavelengths has been improved. A few faint lines in the early list were not confirmed, but 17 new lines were observed, and the Pd I spectrum has been extended to 11556.27 A in the infrared. All the new lines were immediately explained as transitions between atomic energy levels already published by Shenstone [8], and it must be concluded that the analysis of the Pd I spectrum is practically complete, so that further effort to extend it may not be justified. Incidentally, two forbidden transitions (6915 and 7147 A) between terms of like parity, first discovered by Shenstone [8], were nicely confirmed by the present observations.

TABLE 1. *Extension of the first spectrum of palladium,* Pd I

[*h*, hazy: *H*, very hazy: *l*, shaded to longer waves: *s*, shaded to shorter waves]

Wave-length	Intensity and character	Wave number, *K* Observed	Wave number, *K* Computed	Spectral-term combination
A		*cm*$^{-1}$	*cm*$^{-1}$	
6508. 42	30	15360. 47	60. 5	$5p\ ^3D^\circ_2-6s\ ^3D_1$
6591. 44	5	15167. 00	67. 1	$5p\ ^1F^\circ_3-5d\ ^3F_4$
6597. 06	1	15154. 08	54. 1	$5p\ ^1F^\circ_3-5d\ ^3F_3$
6603. 03	1	15140. 38	40. 4	$5p\ ^1F^\circ_3-5d\ ^3D_2$
6623. 27	20	15094. 11	94. 2	$5p\ ^3D^\circ_3-6s\ ^1D_2$
6625. 28	10	15089. 53	89. 6	$5p\ ^1F^\circ_3-5d\ ^3D_3$
6662. 87	20	15004. 40	04. 4	$5p\ ^3D^\circ_1-5d\ ^3P_0$
6681. 56	5	14962. 43	62. 5	$5p\ ^1F^\circ_3-5d\ ^3P_2$
6685. 70	3	14953. 17	53. 0	$5p\ ^1F^\circ_3-5d\ ^3G_4$
6686. 80	20	14950. 71	50. 7	$5p\ ^3P^\circ_2-6s\ ^3D_2$
6774. 53	200	14757. 10	57. 0	$5s^2\ ^3F_4-5p\ ^1F^\circ_3$
6784. 51	1000	14735. 39	35. 4	$5p\ ^3P^\circ_2-6s\ ^3D_3$
6833. 41	80*h*	14629. 95	29. 9	$5p\ ^3D^\circ_1-5d\ ^3D_2$
6878. 36	3	14534. 34	34. 3	$5p\ ^1P^\circ_1-5d\ ^3P_0$
6915. 0	5*Hs*	144457. 3	57. 1	$5p\ ^3D^\circ_1-6p\ ^3P^\circ_1$
6916. 53	200*hl*	14454. 13	54. 1	$5p\ ^3D^\circ_1-5d\ ^3P_1$
6917. 53	5	14452. 04	52. 0	$5p\ ^3D^\circ_1-5d\ ^3P_2$
7016. 47	200	14248. 25	48. 3	$5p\ ^3P^\circ_0-6s\ ^3D_1$
7026. 88	2	14227. 15	27. 2	$5p\ ^1D^\circ_2-5d\ ^3D_2$
7037. 58	10	14205. 51	05. 5	$5p\ ^3D^\circ_1-5d\ ^3S_1$

TABLE 1. *Extension of the first spectrum of palladium*, Pd I—Continued

[*h*, hazy: *H*, very hazy: *l*, shaded to longer waves; *s*, shaded to shorter waves]

Wave-length	Intensity and char-acter	Wave number, *K*		Spectral-term combination	Wave-length	Intensity and char-acter	Wave number, *K*		Spectral-term combination
		Observed	Com-puted				Observed	Com-puted	
A		cm^{-1}	cm^{-1}		*A*		cm^{-1}	cm^{-1}	
7052. 04	3	14176. 38	76. 4	$5p\ {}^1D_2^\circ-5d\ {}^3D_3$	8599. 13	300	11625. 89	26. 0	$5p\ {}^3D_3^\circ-6s\ {}^3D_2$
7060. 29	50	14159. 82	59. 8	$5p\ {}^1P_1^\circ-5d\ {}^3D_2$	8644. 48	100	11564. 90	65. 0	$5p\ {}^1D_2^\circ-6s\ {}^3D_1$
7115. 82	7	14049. 32	49. 3	$5p\ {}^1D_2^\circ-5d\ {}^3P_2$	8695. 12	60	11497. 55	97. 6	$5p\ {}^1P_1^\circ-6s\ {}^3D_1$
7147. 5	2*Hs*	13987. 0	87. 0	$5p\ {}^1P_1^\circ-6p\ {}^3P_1$	8761. 39	600	11410. 58	10. 7	$5p\ {}^3D_3^\circ-6s\ {}^3D_3$
7149. 00	50*hl*	13984. 12	84. 0	$5p\ {}^1P_1^\circ-5d\ {}^3P_1$	8922. 04	6*h*	11205. 12	04. 9	$6s\ {}^3D_2-\quad 27_2^\circ$
7150. 13	2	13981. 91	81. 9	$5p\ {}^1P_1^\circ-5d\ {}^3P_2$	8984. 04	40	11127. 79	27. 7	$5s^2\ {}^3F_2-5p\ {}^1P_1^\circ$
7242. 91	5	13802. 80	02. 8	$5p\ {}^1D_2^\circ-5d\ {}^3S_1$	9038. 75	5	11060. 44	60. 3	$5s^2\ {}^3F_2-5p\ {}^1D_2^\circ$
7278. 44	4	13735. 42	35. 4	$5p\ {}^1P_1^\circ-5d\ {}^3S_1$	9233. 85	1000	10826. 75	26. 7	$5s^2\ {}^3F_4-5p\ {}^3F_4^\circ$
7310. 08	200	13675. 97	76. 0	$5p\ {}^3F_2^\circ-6s\ {}^1D_2$	9380. 32	200	10657. 69	57. 6	$5s^2\ {}^3F_2-5p\ {}^3D_1^\circ$
7368. 12	1000	13568. 24	68. 2	$5p\ {}^3F_3^\circ-6s\ {}^3D_2$	9433. 02	70	10598. 15	98. 2	$5s^2\ {}^3F_3-5p\ {}^3F_2^\circ$
7391. 92	400	13524. 56	24. 6	$5p\ {}^3F_2^\circ-6s\ {}^3D_1$	9793. 76	150	10207. 78	07. 8	$5p\ {}^3F_2^\circ-6s\ {}^3D_2$
7486. 93	300	13352. 93	52. 9	$5p\ {}^3F_3^\circ-6s\ {}^3D_3$	9852. 14	3	10147. 30	47. 1	$5s^2\ {}^3F_2-5p\ {}^1F_3^\circ$
7763. 99	2000	12876. 43	76. 4	$5p\ {}^3F_4^\circ-6s\ {}^3D_3$	10509. 75	7*h*	9512. 36	12. 4	$6s\ {}^3D_3-\quad 24_{433}^\circ$
7786. 63	500	12838. 99	39. 0	$5p\ {}^3P_1^\circ-6s\ {}^3D_2$	10890. 26	80	9180. 00	80. 0	$5s^2\ {}^3F_3-5p\ {}^3D_3^\circ$
7915. 79	800	12629. 50	29. 6	$5p\ {}^1F_3^\circ-6s\ {}^1D_2$	10985. 03	30	9100. 80	00. 7	$5s^2\ {}^3F_2-5p\ {}^3F_2^\circ$
7961. 03	200	12557. 73	57. 8	$5s^2\ {}^3F_3-5p\ {}^1D_2^\circ$	11175. 09	10	8946. 02	46. 1	$5p\ {}^1F_3^\circ-6s\ {}^3D_3$
8132. 81	400	12292. 49	92. 4	$5s^2\ {}^3F_4-5p\ {}^3D_3^\circ$	11409. 45	8	8762. 26	62. 3	$5s^2\ {}^3F_3-5p\ {}^3D_2^\circ$
8249. 19	50	12119. 07	19. 1	$5p\ {}^3D_1^\circ-6s\ {}^1D_2$	11556. 27	5	8650. 94	50. 9	$5p\ {}^3D_1^\circ-6s\ {}^3D_2$
8300. 82	1000	12043. 69	43. 7	$5p\ {}^3D_2^\circ-6s\ {}^3D_2$					
8353. 58	200	11967. 63	67. 7	$5p\ {}^3D_1^\circ-6s\ {}^3D^1$					
8387. 99	3*h*	11918. 53	18. 5	$6s\ {}^3D_3-5p\ {}^1G_4^\circ$					
8451. 93	10	11828. 37	28. 4	$5p\ {}^3D_2^\circ-6s\ {}^3D_3$					
8532. 76	300	11716. 32	16. 4	$5p\ {}^1D_2^\circ-6s\ {}^1D_2$					
8582. 10	200	11648. 96	49. 0	$5p\ {}^1P_1^\circ-6s\ {}^1D_2$					
8585. 33	20	11644. 58	44. 6	$5s^2\ {}^3F_3-5p\ {}^1F_3^\circ$					

3.2. Platinum (78 Pt)

Although nearly 1,000 lines have been reported for the arc spectrum of platinum, the data must be sought in five different sources, because no one has made a systematic and satisfactory description of this spectrum. Haussman [9] in a report on Zeeman effect and terms in the Pt I spectrum compiled a list of 377 classified lines, quoting wavelengths from Meggers [2], Meggers and Laporte [10], Kayser [11], and Exner and Haschek [12]. The only additional data are wavelengths of 56 ultraviolet lines (2241.20 to 1928.85 A) published by Livingood [13], but most of these remain unclassified.

The present paper is concerned primarily with improved description of the long-wave portion of the Pt I spectrum through the use of photographic plates of greater sensitivity and spectrographs of greater dispersive power. The pioneering work of Meggers [2] produced about 50 Pt I lines with wavelengths greater than 6648 A; now the number is increased to 74 as displayed in table 2. The photographic extension is nearly 2000 A, but the Pt I spectrum appears to be very sparce in the infrared, and no new lines could be detected beyond 10758 A with 4-hr exposures.

Only 42 of the Pt I lines in table 2 can be accounted for as combinations of Haussmann's [9] or Livingood's [10] terms. Attempts to classify the remainder by searching for new atomic energy levels among the unclassified lines were not successful. In fact, a critical examination of the old analyses of the Pt I spectrum raised many doubts about the interpretation of certain levels and the reality of others. A discussion of this will appear in Atomic Energy Levels [1]. It must be concluded that no further progress can be made with the structural analysis of the Pt I spectrum without a more complete and homogeneous description of this spectrum.

TABLE 2. *Extension of the first spectrum of platinum,* Pt I [a]

[*h*, hazy]

Wave-length	Intensity and char-acter	Wave number, *K*		Spectral-term combination
		Observed	Computed	
A		cm^{-1}	cm^{-1}	
6648. 32	100	15037. 24	37. 2	$6^{\circ}_{2}-e\,^{3}D_{3}$
6655. 55	3	15020. 91	20. 9	$22^{\circ}_{3}-E_{3}$
6710. 41	400	14898. 11	98. 2	$8^{\circ}_{3}-e\,^{3}D_{2}$
6760. 01	1000	14788. 80	88. 6	$z\,^{3}F^{\circ}_{4}-e\,^{3}D_{3}$
6820. 21	10	14658. 26	----	--------------
6838. 08	20	14619. 96	20. 0	$24^{\circ}_{2}-M_{3}$
6842. 61	200	14610. 28	10. 3	$8^{\circ}_{3}-e\,^{3}D_{3}$
6896. 73	20	14495. 63	--	--------------
6908. 82	7	14470. 26	70. 2	$24^{\circ}_{2}-e\,^{1}D_{2}$
6956. 85	4	14370. 36	--	--------------
6957. 51	20	14368. 99	--	--------------
6975. 70	15	14331. 53	31. 5	$b\,^{1}D_{2}-z\,^{3}D^{\circ}_{3}$
6989. 83	20*h*	14302. 56	--	--------------
7012. 03	2	14257. 27	--	--------------
7030. 08	10	14220. 67	--	--------------
7056. 28	5	14167. 87	67. 9	$27^{\circ}_{3}-M_{3}$
7065. 57	10	14149. 24	49. 3	$b\,^{1}D_{2}-13^{\circ}_{2}$
7078. 09	8	14124. 21	24. 2	$17^{\circ}_{3}-e\,^{5}F_{4}$
7094. 61	15	14091. 32	--	--------------
7094. 78	100	14090. 98	--	--------------
7113. 73	400	14053. 45	53. 5	$a\,^{3}P_{1}-z\,^{3}P^{\circ}_{2}$
7122. 92	3	14035. 32	--	--------------
7125. 05	5	14031. 12	--	--------------
7131. 64	15	14018. 16	18. 1	$27^{\circ}_{3}-e\,^{1}D_{2}$
7179. 95	4	13923. 84	23. 9	$z\,^{3}P^{\circ}_{0}-e\,^{3}D_{1}$
7217. 57	200	13851. 26	51. 3	$z\,^{3}D^{\circ}_{2}-e\,^{3}D_{2}$
7254. 23	5*h*	13781. 26	--	--------------
7407. 44	3	13496. 22	--	--------------
7486. 03	80	13354. 54	54. 6	$a\,^{1}G_{4}-z\,^{0}D^{\circ}_{3}$
7607. 25	10	13141. 74	41. 8	$27^{\circ}_{3}-e\,_{5}F_{3}$
7614. 83	8	13128. 65	28. 7	$27^{\circ}_{3}-E_{3}$
7618. 17	30*h*	13122. 90	--	--------------
7626. 20	4*h*	13109. 08	09. 0	$27^{\circ}_{3}-Q_{3}$
7637. 65	7*h*	13089. 43	--	--------------
7641. 27	2	13083. 23	--	--------------
7644. 11	5	13078. 37	--	--------------
7738. 60	3*h*	12918. 68	--	--------------
7749. 76	40	12900. 07	00. 0	$29^{\circ}_{1}-e\,^{1}D_{2}$
7761. 63	2	12880. 35	--	--------------
7780. 53	70*h*	12849. 06	--	--------------
7786. 77	80	12838. 76	38. 7	$19^{\circ}_{3}-e\,^{5}F_{4}$
7790. 21	5*h*	12833. 09	--	--------------
7830. 42	6*h*	12767. 19	--	--------------
7877. 45	3*h*	12690. 97	--	--------------
7911. 26	20*h*	12636. 73	--	--------------
7977. 35	60	12532. 04	32. 1	$30^{\circ}_{4}-N_{4}$
8093. 86	7	12351. 65	51. 7	$20^{\circ}_{4}-e\,^{5}F_{4}$
8204. 47	90	12185. 13	85. 1	$z\,^{5}F^{\circ}_{4}-e\,^{3}D_{3}$
8224. 78	400	12155. 04	55. 0	$a\,^{1}G_{4}-z\,^{3}F^{\circ}_{3}$
8227. 55	70	12150. 95	50. 9	$z\,^{5}D^{\circ}_{2}-e\,^{3}D_{2}$
8259. 03	7	12104. 63	04. 7	$32^{\circ}_{3}-N_{4}$
8301. 83	20	12042. 23	42. 2	$29^{\circ}_{1}-G_{1}$
8428. 47	4	11861. 29	61. 3	$32^{\circ}_{3}-e\,^{1}D_{2}$
8456. 36	3*h*	11822. 17	22. 2	$31^{\circ}_{2}-e\,^{3}D_{1}$
8619. 91	4*h*	11597. 85	97. 9	$z\,^{1}F^{\circ}_{3}-N_{4}$
8722. 99	6*h*	11460. 81	--	--------------
8762. 47	70	11409. 17	09. 2	$z\,^{3}D_{3}-e\,^{3}D_{3}$
8804. 61	2	11354. 57	54. 5	$z\,^{1}F^{\circ}_{3}-e\,^{1}D_{2}$
8981. 87	8	11130. 48	30. 4	$b\,^{1}D_{2}-8^{\circ}_{3}$
9004. 06	7*h*	11104. 29	--	--------------
9012. 40	3*h*	11092. 78	92. 8	$32^{\circ}_{3}-H_{3}$
9060. 50	1	11033. 89	--	--------------
9100. 87	2	10984. 94	85. 0	$32^{\circ}_{3}-e\,^{5}F_{3}$
9128. 03	2*h*	10952. 26	52. 2	$32^{\circ}_{3}-Q_{3}$
9201. 81	20	10864. 44	64. 5	$z\,^{3}P^{\circ}_{1}-e\,^{3}D_{2}$
9291. 30	3*h*	10759. 80	59. 8	$35^{\circ}_{2}-e\,^{1}D_{2}$
9340. 16	4	10703. 52	03. 5	$b\,^{1}D_{2}-6^{\circ}_{2}$
9460. 64	3*h*	10567. 21	--	--------------
10005. 95	7*h*	9991. 31	91. 3	$35^{\circ}_{2}-H_{3}$
10539. 57	2*h*	9485. 45	--	--------------
10546. 35	20	9479. 35	79. 4	$18^{\circ}_{1}-e\,^{3}D_{2}$
10685. 35	2	9356. 04	--	--------------
10705. 51	4*h*	9338. 42	--	--------------
10757. 78	8	9293. 05	--	--------------

[a] Shenstone has pointed out that many *LS*-designations lack significance because of the effect of *jj*-coupling in Pt. I. In "Atomic Energy Levels" [1] many of the earlier designation assignments are, therefore, being omitted.

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