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Energy levels of neutral platinum (Pt I)

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Résumé. — Le spectre d'émission du platine dans une cathode creuse a été récemment enregistré sur un spectrographe à réseau au N.I.S.T. et par spectroscopie de Fourier à l'observatoire de Kitt Peak et au laboratoire Aimé Cotton. La classification des raies de Pt I est révisée et étendue. Pour 4 des 83 niveaux déjà connus, le nombre quantique J a été corrigé et 119 niveaux nouveaux ont été déterminés. Les identifications de 70 % des niveaux s'appuient sur l'étude théorique par la méthode de Slater-Condon des configurations mélangées $(5d + 6s)^{10}$, $5d^9 6d$, $5d^9 7s$, $5d^9 7d$, $5d^9 8s$, $(5d^9 6p + 5d^8 6s 6p + 5d^7 6s^2 6p + 5d^9 7p)$. La limite d'ionisation $72\,230 \pm 50 \text{ cm}^{-1}$ ($8,956 \pm 0,006 \text{ eV}$) a été déduite des configurations $5d^9 ns$, $5d^9 5f$ et $5d^8 6s 5f$.

Abstract. — The emission spectrum of a platinum hollow cathode lamp has been recently recorded by means of a grating spectrograph at the National Institute of Standards and Technology (N.I.S.T.) and by Fourier transform spectrometry at Kitt Peak National Observatory and at Laboratoire Aimé Cotton. The classification of Pt I lines is revised and extended. One hundred-nineteen new energy levels have been added to the 83 earlier ones, four of which are assigned revised J -values. Seventy percent of the levels are interpreted theoretically by means of Slater-Condon type calculations of $(5d + 6s)^{10}$, $5d^9 6d$, $5d^9 7s$, $5d^9 7d$, $5d^9 8s$ and $(5d^9 6p + 5d^8 6s 6p + 5d^7 6s^2 6p + 5d^9 7p)$. The ionisation limit $5d^9 \text{ } ^2D_{5/2}$ at $72\,230 \pm 50 \text{ cm}^{-1}$ ($8.956 \pm 0.006 \text{ eV}$) has been derived from $5d^9 ns$, $5d^9 6f$ and $5d^8 6s 5f$ levels.

1. Introduction.

The spectrum of neutral platinum has been observed long ago and the first steps in its analysis have been reported by Moore in Atomic Energy Levels Tables [1]. A new impetus for studying platinum spectra came recently from space research. In the I.U.E. satellite and on the High Resolution Spectrograph coupled with the Hubble Space Telescope, a platinum hollow cathode lamp with Ne carrier gas is used as a source of lines for wavelength calibration. The need for very accurate wavelengths led to reobserve the platinum spectrum by Fourier transform spectrometry at Kitt Peak National Observatory (K.P.N.O.) [2] and on the 10.7 m normal incidence spectrograph at the National Institute of Standards and Technology (N.I.S.T.) [3]. The wavelengths of the classified lines led one of us to improve the

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energy level values of Pt I [2]. Many strong lines were still unclassified and the search for new levels started at Laboratoire Aimé Cotton (L.A.C.) by using the complete lists of wavelengths recorded at Kitt Peak and at N.I.S.T. The status of the analysis in 1989 was reported in [4] and new levels have since been found with the help of infrared Fourier transform spectra recorded at L.A.C. All the Pt I classified lines in the region 1 130-4 330 Å will be included in a comprehensive description of the Pt spectrum by Sansonetti *et al.* [5]. This publication is devoted to the interpretation of the Pt I energy levels while a similar report on the analysis of singly-ionized platinum will be published with the platinum atlas [6].

All platinum spectra studied so far were produced from natural mixings of isotopes and the hyperfine structures of the lines are dominated by the most abundant even-even isotopes ^{194}Pt (33 %) and ^{196}Pt (25 %) and by the magnetic hyperfine structure of the odd isotope ^{195}Pt (34 %). Fourier transform spectra provided us with isotope shifts for the lines excited in the hollow cathode light source, hence for low levels in both parities, a zero value being arbitrarily assigned to the shift of the $5d^{10}1S_0$ level at $6\,140\text{ cm}^{-1}$. These shifts and the intensities of the transitions were helpful in a first empirical interpretation of the levels from which the configurations have been studied by means of the Slater-Condon parametric method. Unfortunately, the Zeeman effect of platinum has not been reobserved since 1929 [7] and the J -values of a few levels still remain undetermined. In the early stage of the analysis, unpublished data by Meggers supplied us with a few unclassified lines in the visible [8]. At the present time, 119 new levels have been discovered and are reported with 83 earlier ones in the tables I and II.

Table I. — *Even energy levels of Pt I. The deviations $\Delta E = E_{\text{exp}} - E_{\text{th}}$, the leading components of the eigenfunctions and the theoretical g -factors are derived from studies of the groups $(5d + 6s)^{10}$, $5d^96d$, $5d^97s$, $5d^97d$ and $5d^98s$. For other configurations, empirical designations are given in the column « Leading comp. ».*

Note	E_{exp}	J	ΔE	Leading comp.	%	g_{exp}	g_{th}
	0.	3	5	$5d^96s\ 3D$	100	1.333924	1.333
	775.892	2	13	$5d^96s\ 1D$	41.5	1.066574	1.067
	823.678	4	28	$5d^86s^2\ 3F$	95.8	1.23948	1.240
	6140.180	0	0	$5d^{10}\ 1S$	90.1		
	6567.461	2	-35	$5d^96s\ 3D$	42.4	1.11691	1.117
	10116.729	3	-15	$5d^86s^2\ 3F$	100		1.083
	10131.887	1	18	$5d^96s\ 3D$	100		0.500
	13496.271	2	13	$5d^96s\ 1D$	44.4	1.17	1.186
	15501.845	2	17	$5d^86s^2\ 3F$	59.6	0.92	0.97
*	16983.492	0	0	$5d^86s^2\ 3P$	82.6		
	18566.558	1	14	$5d^86s^2\ 3P$	100		1.500
	21967.111	4	1	$5d^86s^2\ 1G$	95.8		1.010
	26638.591	2	15	$5d^86s^2\ 1D$	54.3	0.97	0.993
	52379.375	3	19	$5d^97s\ 3D$	100	1.32	1.333
	52667.213	2	19	$5d^97s\ 1D$	56.6	1.04	1.072
	55640.623	5		$5d^86s7s(3F_4, 3S_1)$		1.41	
	56784.325	4		$5d^86s7s(3F_4, 3S_1)$		1.27	
*G	59591.82	1	24	$5d^96d\ 3S$	56.7	1.72	1.749
J	59731.571	2	4	$5d^96d\ 3P$	52.7	1.3	1.317
J	59751.177	4	-12	$5d^96d\ 3G$	50.4		1.045
	59764.266	3	15	$5d^96d\ 3D$	51.6	1.27	1.197

Table I (continued).

	59782.853	1	29	5d ⁹ 6d 1P	57.0	1.07	0.959
N	59812.72	5	15	5d ⁹ 6d 3G	100		1.200
	59872.140	3	30	5d ⁹ 6d 1F	55.6	1.23	1.087
	59882.421	4	2	5d ⁹ 6d 3F	81.9	1.17	1.205
	59908.170	2	-29	5d ⁹ 6d 1D	58.5	1.02	1.052
	60357.804	1	-25	5d ⁹ 7s 3D	100	0.52	0.500
*	60573.69	0	0	5d ⁹ 6d 1S	51		
	60640.669	2	25	5d ⁹ 7s 3D	56.6	1.08	1.094
	60790.393	3		5d ⁸ 6s7s (3F ₄ , 3S ₁)		1.07	
	60884.001	4		5d ⁸ 6s7s (3F ₄ , 1S ₀)		1.29	
N	62567.995	3	0	5d ⁹ 8s 3D	100		1.333
N	62705.33	2	0	5d ⁹ 8s 1D	58		1.069
N	63922.22	3					
	64128.722	5,4					
	64141.155	6		5d ⁸ 6s6d (3F ₄ , 3D)			
N	64182.29	2					
*	64222.379	7		5d ⁸ 6s6d (3F ₄ , 3D ₃)			
*	64267.43	5		5d ⁸ 6s6d (3F ₄ , 3D)			
*	64312.78	4		5d ⁸ 6s6d (3F ₄ , 3D)			
*	64330.53	6		5d ⁸ 6s6d (3F ₄)			
N	64379.155	5		5d ⁸ 6s6d (3F ₄)			
J	64505.839	3		5d ⁸ 6s7s (3F ₃ , 3S ₁)			
*	64668.46	4		5d ⁸ 6s6d (3F ₄ , 3D)			
*	65132.91	2	177	5d ⁹ 7d 3P	47		1.265
N	65308.53	4	2	5d ⁹ 7d 3G	49		1.041
N	65339.93	5	18	5d ⁹ 7d 3G	100		1.200
N	65346.52	3		5d ⁹ 7d 3F	48		1.127
N	65361.63	1	18	5d ⁹ 7d 1P	59		1.013
N	65381.38	4	9	5d ⁹ 7d 3F	83		1.209
N	65387.03	3	10	5d ⁹ 7d 3D	63		1.156
N	65395.72	2	1	5d ⁹ 7d 1D	58		1.102
N	66967.965	5		5d ⁸ 6s8s (3F ₄ , 3S ₁)			
N	67342.66	4		5d ⁸ 6s8s (3F ₄ , 3S ₁)			
N	68006.95	3	5	5d ⁹ 6d 3G	87.5		0.784
*	68072.245	3	56	5d ⁹ 6d 3F	49.3		1.099
N	68094.74	2	7	5d ⁹ 6d 3F	53.3		0.934
N	68121.56	4	22	5d ⁹ 6d 3G	49.6		1.050
N	68169.42	2	44	5d ⁹ 6d 1D	41.2		1.030
N	68275.31	2					
N	68703.45	4					
N	68716.32	6		5d ⁸ 6s6d (3F ₄ , 1D ₂)			
N	68759.01	4					
N	68831.115	5					
N	68912.21	4					
N	68947.47	3					

* Level already reported in reference [4]

N New level

J Revised J-value

G New g-value.

Table II. — *Odd energy levels of Pt I. The deviations $\Delta E = E_{\text{exp}} - E_{\text{th}}$, the leading components of the eigenfunctions and the configuration percentages are derived from the study of the mixed group $5d^9 6p + 5d^8 6s 9p + 5d^7 6s^2 6p + 5d^9 7p$. For other configurations, empirical designations are given in the column « Leading comp. ».*

Energy (cm ⁻¹)	J	$E_{\text{exp}} - E_{\text{th}}$	Leading comp. %	5d ⁹ 6p %	5d ⁸ 6s6p %	5d ⁷ 6s ² 6p %	5d ⁹ 7p %	ξ_{exp}	ξ_{th}
30156.854	4	257	B (4F)5D 74	0	98.0	2.0	0	1.46	1.457
32620.018	2	61	A 3P 55	71.9	22.7	5.4	0	1.39	1.404
33680.402	5	225	B (4F)5F 43	0	97.8	2.1	0	1.32	1.311
34122.165	3	220	A 3F 30	59.4	36.0	4.6	0	1.21	1.184
35321.653	3	9	B (4F)5D 42	11.9	85.5	2.6	0	1.33	1.318
36296.310	4	10	B (4F)5G 35	1.9	94.8	3.3	0	1.189	
36781.551	6	83	B (4F)5G 96	0	99.6	0.4	0	1.33	1.328
36844.710	1	88	A 3P 26	38.0	52.9	9.1	0	1.09	1.207
37342.101	2	210	A 3P 20	52.3	43.2	4.5	0	1.15	1.107
37590.569	4	14	A 3F 68	67.9	28.0	4.1	0	1.25	1.240
37769.073	3	194	A 3D 24	52.7	43.3	3.9	0.1	1.17	1.238
38536.160	5	151	B (4F)5F 43	0	91.7	8.3	0	1.30	1.307
38815.908	2	38	B (2D)3F 25	29.8	62.9	7.2	0.1	0.88	0.851
40194.228	4	141	B (4F)5F 25	2.6	79.9	17.5	0	1.21	1.237
40516.243	2	86	B (4F)5D 38	5.9	89.5	4.6	0	1.38	1.312
40787.857	2	81	B (4P)5P 25	21.6	75.1	3.3	0	1.20	1.344
40873.529	0	212	B (2D)3P 33	16.6	70.4	13.0	0		
40970.165	3	25	B (4F)5G 37	16.1	81.2	2.7	0	1.12	1.127
41802.744	1	183	B (2D)3D 27	31.3	65.4	3.3	0	0.92	0.875
42660.058	3	47	B (4F)5D 18	4.3	84.6	11.1	0	1.19	1.198
43187.836	1	4	B (4F)5D 25	33.5	60.2	6.3	0	1.39	1.441
G 43945.543	3	104	B (4P)5P 37	11.0	86.5	2.5	0	1.27	1.347
44432.663	4	254	B (4F)5G 19	4.6	83.3	12.1	0	1.20	1.220
44444.364	2	4	B (4F)5F 31	14.3	79.5	6.2	0	1.21	1.170
44730.313	3	207	B (2F)3D 14	14.4	80.0	5.6	0	1.19	1.164
45348.478	1	251	B (4P)5P 28	3.9	91.0	5.1	0	1.52	1.461
46170.386	2	13	A 3F 36	49.4	47.2	3.4	0	1.01	0.678
46419.962	2	35	B (4P)5D 13	11.3	83.1	5.6	0	0.87	1.150
46433.912	0	7	B (4P)5D 41	31.3	65.7	3.0	0		
46622.489	3	190	B (2F)3D 30	9.7	85.8	4.5	0	1.15	1.162
* 46792.965	5	148	B (4F)3G 57	0	95.1	4.9	0		1.223
*E 46963.670	4	62	B (4P)5D 26	6.7	76.5	16.8	0	1.34	1.302
47740.565	1	81	A 1P 48	51.2	41.1	7.7	0	1.43	1.344
E 48351.94	4	93	B (4F)3F 33	3.3	87.3	9.2	0.2	1.25	1.222
48535.596	2	30	B (4F)5G 15	14.8	69.2	16.0	0	1.02	1.033
48779.337	3	10	B (4F)3D 22	17.1	74.1	8.5	0.3	1.22	1.198
49286.116	3	75	B (4P)5P 18	17.8	74.8	7.2	0.2	1.19	1.211
49544.565	1	131	A 3D 27	33.6	57.7	8.7	0	1.24	1.186
49880.883	2	247	A 3D 18	23.1	70.2	6.7	0	1.12	1.078
* 50010.155	4	152	B (2F)3F 21	0.2	64.1	35.5	0.2		1.258
50055.313	1	15	B (4F)5F 18	34.7	54.4	10.9	0	0.87	1.055
* 50299.385	5	193	C 4F*3G 26	0	13.5	86.5	0		1.251
* 50387.66	0	134	A 3P 38	38.4	51.5	10.1	0		
51097.529	3	137	B (4P)5D 21	11.9	78.4	9.6	0.1	1.21	1.225

Table II (continued).

	51286.946	2	39	B (2F) ¹ D	28	3.8	89.9	6.1	0.2	1.13	1.239
J	51545.544	3	353	B (4F) ³ D	30	24.2	61.6	12.6	1.6	1.24	1.214
	51753.317	2	57	B (2F) ³ F	12	17.1	59.6	23.4	0.1	1.34	1.239
	52071.684	1	31	B (4P) ⁵ D	29	21.4	72.1	6.4	0.1	1.22	1.197
N	52438.59	5	18	B (2F) ³ G	74	0	90.2	9.8	0		1.201
*	52520.13	4	90	B (2F) ³ F	29	4.1	60.4	34.9	0.3		1.288
	52708.365	2	145	B (4P) ⁵ D	51	2.6	84.2	13.0	0.2	1.46	1.452
	53019.303	1	58	B (2F) ³ D	16	0.7	82.0	16.8	0.5	1.08	1.104
*	53665.25	1	65	B (2P) ³ D	38	1.5	77.5	20.7	0.3		0.882
	53953.379	2	99	B (2P) ³ P	23	9.1	66.3	23.6	1.0	1.32	1.313
	54011.150	3	1	B (4P) ⁵ P	15	13.0	79.3	7.5	0.2		1.160
	54133.26	2	78	B (4P) ⁵ S	30	0.3	77.9	21.8	0		1.434
*	54178.47	4	133	B (4P) ⁵ D	22	3.2	79.9	16.6	0.3		1.215
	54839.206	3	42	B (4P) ³ D	26	3.1	66.6	29.9	0.4	1.21	1.245
*	55009.37	4	-2	B (2G) ³ H	68	0.4	90.0	9.6	0		0.900
	55216.828	1	25	A ³ D	17	17.3	69.9	12.0	0.8	0.96	0.973
	55536.276	3	1	B (2P) ³ D	18	2.0	70.7	26.6	0.7		1.203
*	55984.51	5	24	B (2G) ³ H	45	0	55.7	44.3	0		1.165
*	56288.65	4	74	B (2G) ³ F	58	0.6	88.2	10.8	0.4		1.186
*	56670.20	2	171	B (4P) ³ P	34	9.0	76.3	7.0	7.7		1.314
*	56794.43	5	110	C 4F* ³ G	24	0	46.1	53.9	0		1.193
*	57041.73	1	175	B (4P) ³ P	22	1.4	78.4	13.8	6.4		1.135
	57506.187	3	18	B (2G) ³ F	33	1.4	76.3	11.1	11.2		1.056
	57987.392	2	30	D ³ P	48	3.5	16.3	3.5	76.7		1.326
*	58101.17	3	65	D ³ F	16	0.9	50.0	17.8	31.3		1.128
*	58326.75	2	102	B (2P) ³ D	19	2.4	76.2	20.0	1.4		1.097
*	58388.47	4	105	C 4F* ⁵ G	32	0.2	22.0	75.3	2.5		1.209
*	58482.14	3	168	D ¹ F	22	0.2	27.8	52.6	44.6		1.134
N	58780.80	1	114	D ¹ P	16	0.7	58.1	11.8	29.4		1.255
*	59127.72	2	68	B (2D) ³ F	21	4.6	50.8	23.9	20.7		0.995
*	59346.33	4		D ³ F	22	0.3	64.3	13.6	21.8		1.172
*	59462.28	2	129	D ¹ D	13	4.1	43.7	30.4	21.8		1.078
N	59492.41	4	86	D ³ F	71	0.0	19.4	10.2	70.4		1.218
*	59686.20	3	76	C 4F* ⁵ G	19	2.9	44.5	52.2	0.4		1.054
*	59792.23	1	19	B (4P) ³ S	13	2.6	49.3	27.3	20.8		1.073
N	59916.97	2	9	D ¹ D	25	3.9	32.6	9.7	53.8		1.122
*	59920.03	3	1	D ³ D	78	0.2	4.7	1.9	93.2		1.270
*	60328.02	3	209	B (4F) ³ F	15	1.6	47.4	40.1	10.9		1.097
*	60423.93	4	215	B (2G) ³ G	27	0	61.1	35.7	3.2		1.110
*	60441.30	1	119	D ¹ P	22	0.7	37.2	22.6	39.5		0.863
*	61097.48	2	67	B (2G) ³ F	28	10.6	69.7	11.0	8.7		1.045
*	61352.25	3	11	B (2G) ³ F	14	3.9	71.5	23.9	0.7		1.023
*	61633.79	5	101	B (2G) ³ G	43	0	68.7	31.3	0		1.174
*	61645.33	2	298	B (2G) ³ F	27	1.9	61.5	31.6	5.0		1.031
N	61942.22	4		5d ⁸ (³ F ₄)6s7p(³ P ₀)							
*	62062.29	2	149	C 4F* ⁵ G	16	0.4	45.3	52.1	2.2		1.043
*	62106.38	3	182	B (4P) ³ D	15	1.3	64.2	32.5	2.0		1.109
*	62321.92	3	38	B (2D) ³ F	21	0.9	70.4	28.7	0		1.085
N	62510.36	4		5d ⁸ (³ F ₄)6s7p(³ P ₁)							

Table II (continued).

*	62659.30	2	189	B (4P) ³ D	13	3.9	67.3	28.3	0.5	1.143
N	62835.58	5		5d ⁸ (³ F ₄)6s7p(³ P ₁)						
*	63067.47	1	25	B (2D) ³ D	19	3.7	72.6	21.1	2.6	0.774
*	63167.33	3		5d ⁸ (³ F ₄)6s7p(³ P ₁)						
N	63352.91	6		5d ⁸ (³ F ₄)6s7p(³ P ₂)						
*	63466.29	1	48	B (2P) ³ P	16	0.5	74.8	23.9	0.8	0.990
*	63826.31	2	163	C 4F*5G	14	2.8	53.4	43.1	0.7	1.052
N	63945.05	5		5d ⁸ (³ F ₄)6s7p(³ P ₂)						
*	64248.95	2	1	B (2D) ³ D	27	1.9	81.1	16.6	0.4	1.040
N	64319.385	4		5d ⁸ (³ F ₄)6s7p(³ P ₂)						
*	64515.68	2	137	C 4F*5G	13	7.2	42.5	49.5	0.8	1.029
*	64619.64	1	61	B (4P) ³ D	25	2.5	62.1	33.1	2.3	0.615
N	64675.92	3	137	C 4P*5D	17	1.7	36.7	60.2	1.4	1.214
*	64904.25	3		5d ⁸ (³ F ₄)6s7p(³ P ₂)						
N	65306.80	1		5d ⁹ 5f						
N	65315.89	2		5d ⁹ 5f						
N	65318.95	6		5d ⁹ 5f						
N	65325.49	2		5d ⁹ 5f						
N	65331.20	3		5d ⁹ 5f						
N	65332.43	1		5d ⁹ 5f						
N	65333.25	4		5d ⁹ 5f						
N	65336.49	3		5d ⁹ 5f						
N	65339.66	4		5d ⁹ 5f						
N	65341.92	5		5d ⁹ 5f						
N	65510.22	3								
N	65697.70	2,1								
*	65850.11	1								
N	65852.56	4								
N	66198.85	2								
N	66432.56	1								
N	66927.43	2		5d ⁹ 7p(² D _{3/2} , ² P _{1/2})						
*	67121.58	3		5d ⁹ 7p(² D _{3/2} , ² P _{3/2})						
N	67303.64	3,4		5d ⁸ 6s7p						
*	67413.65	5,4		5d ⁸ 6s7p						
N	68266.90	5		5d ⁸ 6s7p						
N	68343.55	3,4		5d ⁸ 6s7p						
N	68606.62	2								
N	68657.42	3								
N	70087.93	7		5d ⁸ (³ F ₄)6s5f						
N	70088.64	5,6		5d ⁸ (³ F ₄)6s5f						
N	70095.52	6		5d ⁸ (³ F ₄)6s5f						
N	70099.57	5		5d ⁸ (³ F ₄)6s5f						

* Level already reported in reference [4]

E Revised energy

N New level

G Revised g-factor

J Revised J-value.

2. Theoretical interpretation of the energy levels.

2.1 THE CONFIGURATIONS $5d^{10}$, $5d^96s$ AND $5d^86s^2$. — The low even levels were already studied by means of the Slater-Condon parametric method. The levels of $5d^{10} + 5d^96s + 5d^86s^2$ (3P_0 and 1S_0 being still unknown in the last configuration of this group) had been included in a survey of all $(5d + 6s)^N$ configurations from Hf I to Pt I by means of generalized least-squares for fitting the energy parameters [9]. A specific study of $5d^86s^2 + 5d^96s$ led Grethen *et al.* [10] to eigenfunctions in intermediate coupling for a first theoretical interpretation of the isotope shifts in the framework of the phenomenological approach described in [11]. New values of 4 isotope shift parameters were later derived from more accurate measurements involving 5 levels only [12].

The discovery of the 3P_0 level at $16\,983\text{ cm}^{-1}$ led us to resume the study of the low even group. The parameter $R^2(5d^2, 6s^2)$ is determined to fit the interval $6\,140\text{--}16\,983\text{ cm}^{-1}$ and is 1.19 times larger than the $R^2(5d6s, 6s5d)$ exchange Slater integral of $5d^96s$. They should be equal if the radial wavefunctions for 6s and 5d electrons were the same in all three configurations. The deviations $E_{\text{exp}} - E_{\text{calc}}$ and the leading components of the eigenfunctions are given in table I and the fitted energy parameters are collected with those of other even configurations in table III.

Table III. — Fitted energy parameters and their standard errors (in cm^{-1}) for the even configurations of neutral platinum.

Parameter	$5d^{10}$		$5d^96s$		$5d^86s^2$		$5d^97s$		$5d^96d$		$5d^98s$		$5d^97d$	
E	8 094	219	6 605	57	12 338	44	56 967	165	63 088	12	66 356	112	68 648	11
$F^2(5d, nd)$					49 074	361			417	114			162	112
$F^4(5d, nd)$					37 309	508			225				87	
$G^0(5d, nd)$									162	11			80	
$G^2(5d, nd)$									415	102			100	73
$G^4(5d, nd)$									224				54	
$G^2(5d, ns)$			13 553	233			1 398	183			579	126		
			4 043.3	23	4 227.6	17	3 208.9	15	3 305.8	10	3 209		3 305	
									28.5	12			23.1	10
α			25.7	5					2.6	1.8			0.67	
β			- 187	f										
Configuration interaction :														
					$R^2(5d^2, 5d6s) =$	- 13 903	281							
					$R^2(5d^2, 6s^2) =$	16 151	707							

2.2 UPPER EVEN CONFIGURATIONS. — Most of the upper even levels decay preferentially either to $5d^96p$ or to $5d^86s6p$ and could be attributed empirically to $5d^9nl$ ($nl = 7s, 8s, 6d$ and $7d$) and to $5d^86snl$ ($nl = 7s, 8s$ and $6d$). The interpretation of Pt II levels which are the limits of the Rydberg series $5d^9nl$ and $5d^86snl$ has shown [6, 13] that a strong mixing prevails within the group $5d^9 + 5d^86s + 5d^76s^2$. The interaction parameters $R^2(5d^2, 5d6s)$ and $R^2(5d^2, 6s^2)$ are expected to mix the upper configurations of Pt I as well. The group of configurations $5d^9(6d + 7s)$ is fairly well isolated in the sequence Au II-Bi VI and we started its study in Pt I from extrapolated values of energy parameters $R^2(5d7s, 5d6d)$ and $R^2(5d7s, 6d5d)$ [14]. This led to overestimated configuration mixing effects, the observed g -value of $5d^97s^3D_1(0.52)$ being closer to the unperturbed value 0.50 than to the perturbed

value 0.66 determined by this way. A better approach for describing upper even configurations would be within multiconfigurational bases $(5d + 6s)^9 n\ell$ which involve so far more unknown parameters than known experimental levels. Even if preliminary, the present studies of « isolated » $5d^9 n\ell$ configurations were successful in predicting some levels. The deviations between experimental and theoretical energies are reported in table I and the fitted parameters in table III. Above $63\,000\text{ cm}^{-1}$, some of the levels can be attributed either to $5d^8 6s 7s$ or to $5d^8 6s 6d$. They are reported in table I with empirical designations derived from their transitions. These designations are not always complete.

2.3 ODD PARITY LEVELS. — The isotope shift of the odd levels indicate large configuration mixing effects and was very important for identifying the lowest level of $5d^7 6s^2 6p$ at $50\,299\text{ cm}^{-1}$, characterized by an outstandingly large shift. It was shown recently that $5d^N 6p + 5d^{N-1} 6s 6p + 5d^{N-2} 6s^2 6p$ mixed configurations provide convenient basis sets for describing the lowest odd parity levels of Hf II, Ta II and W II [15]. In Pt I, by means of analogies with the simpler spectrum of Au I, it is expected that $5d^8 6s 6p$ and $5d^7 6s^2 7p$ overlap other configurations, first of them $5d^9 7p$. Therefore we used the basis $5d^9 6p$ eigenfunctions

Table IV. — *Fitted energy parameters and their standard errors (in cm^{-1}) for the lowest odd configurations of Pt I.*

Parameter	$5d^9 6p$		$5d^8 6s 6p$		$5d^7 6s^2 6p$		$5d^9 7p$	
A					71751	214	63275	95
S	26337	512	12725	303				
B			593.92	r	609.15	11		
C			2976.6	r	3052.9	95		
$G^2(d,s)$			15532	317				
$F^2(d,p)$	13005	p	15055	368	17106	945	1750	f
$G^1(d,p)$	4386	p	4918	139	5450	304	750	f
$G^3(d,p)$	3319	p	5071	405	6823	1035	650	f
$G^1(p,s)$			16795	487				
α			2.3	r	2.3	10		
β			-180	f	-180	f		
ζ_{5d}	4069	r	4277	r	4471	30	4150	f
ζ_{6p}	3104	p	3897	63	4689	141	519	140
Configuration interaction								
$5d^9 6p - 5d^8 6s 6p$:		$R^2(5d^2, 5d6s) =$	19726	442			
			$R^2(5d6p, 6s6p) =$	10111	525			
			$R^1(5d6p, 6p6s) =$	7070	369			
$5d^9 6p - 5d^7 6s^2 6p$:		$R^2(5d^2, 6s^2) =$	21352	2779			
$5d^8 6s 6p - 5d^7 6s^2 6p$:		$R^2(5d^2 5d6s) =$	21502	r			
			$R^2(5d6p, 6s6p) =$	16392	452			
			$R^1(5d6p, 6p6s) =$	10516	442			
$5d^8 6s 6p - 5d^9 7p$:		$R^2(5d7p, 6s6p) =$	3500	f			
			$R^1(5d7p, 6p6s) =$	2400	f			

r parameters held in a constant ratio with the same parameter in another configuration

f parameter held fixed

p parameter held by $P(d^9 p) - P(d^8 sp) = P(d^8 sp) - P(d^7 s^2 p)$

+ $5d^86s6p + 5d^76s^26p + 5d^97p$ for the present analysis, starting from the energy matrices already used in [16]. The matrix elements of the Hamiltonian operator depend on 43 parameters, inasmuch as the $5d^96p-5d^97p$ interaction is neglected. The fitted values of these parameters are collected in table IV and illustrate the difficulties encountered in platinum group elements. The « off-diagonal » configuration parameters are larger than several « diagonal » electrostatic parameters and the spin-orbit interactions are of the same order of magnitude as the electrostatic ones. For these two reasons, it is noticed in table II that the leading components represent a small percentage of the whole eigenfunctions and the configuration mixing affects all levels in different ways.

In these conditions, many initial values have been tried for the average energies of the configurations and for the configuration interaction parameter before getting a reliable correspondance between experiment and theory for some dozens of levels. At the end of the optimization process, 100 levels are interpreted with an average deviation of 134 cm^{-1} . In the last step, 25 parameters were free to vary and 18 others were held by means of constraints detailed in table IV. All 88 levels found between $30\,156$ and $61\,700 \text{ cm}^{-1}$ are interpreted theoretically. The five unknown levels predicted in this energy range have J -values $J = 0$ and $J = 6$ which make them difficult to be found from only wavenumbers of very few transitions. Above $61\,700 \text{ cm}^{-1}$, seven levels of $5d^8(^3F_4)6s7p$ have been labeled on the basis of relatively strong infrared transitions to $5d^8(^3F_4)6s7s$ and $5d^98p$ might be present also among the known levels. Pending for definitive results on hyperfine structures, only the g -factors are available for checking the eigenfunctions of odd levels but, as far as we could check them, the experimental g -values given in [1] are not very accurate. The overall agreement between g_{exp} and g_{calc} values supports the identifications with some exceptions. The mixing of $J = 1$ levels between $45\,398$ and $50\,055 \text{ cm}^{-1}$ looks unsatisfactory. A similar problem is also seen for the three pairs of close $J = 2$ levels at $40\,516$ and $40\,787 \text{ cm}^{-1}$, $46\,170$ and $46\,419 \text{ cm}^{-1}$, $51\,286$ and $51\,753 \text{ cm}^{-1}$. The g -values of all these levels are very sensitive to small changes of parameter values. The mixing of the overlapping configurations has not been studied above $62\,000 \text{ cm}^{-1}$. The empirical identifications given in table II are sometimes incomplete and should be considered with caution.

Broad infrared lines between $5\,400$ and $6\,000 \text{ cm}^{-1}$ have been interpreted as $5f-6d$ transitions. Their upper levels are built on $5d^9\ ^2D_{5/2}$ and on the first excited level of Pt II, $5d^86s\ ^4F_{9/2}$. By using the fact that the binding energies of the $5f$ levels are very consistent in Au I and Hg I [1], as are also the quantum defects for the $7s$ and $8s$ electrons ($\delta(7s) - \delta(8s) = 0.023$), the first ionization limit of Pt I was determined at $72\,230 \text{ cm}^{-1}$ with an estimated uncertainty of 50 cm^{-1} ($8.956 \pm 0.006 \text{ eV}$), i.e. very close to the less accurate value reported in [1].

3. Conclusion.

The present contribution to the Pt I spectroscopy ends with a clarification of the interpretation and it is shown that very few low levels are still unknown in both parities. Seventeen configurations are now identified and their lowest levels are summarized in table V. We plan to use the eigenfunctions determined presently in a theoretical interpretation of the hyperfine effects. Recent Fourier transform recordings obtained at Aimé Cotton in the infrared and at The Blackett Laboratory (Imperial College, London) in the vacuum ultraviolet [17] are being analyzed. They should provide us with data on the magnetic hyperfine structure of ^{195}Pt and on the isotope shift $^{196}\text{Pt}-^{194}\text{Pt}$ and therefore with further checks of the present work. Finally, the energy parameters determined presently should help for unraveling the odd-parity energy levels in the neighbouring atoms Os I, Ir I and Au I.

Table V. — *Lowest energy levels (in cm⁻¹) of the Pt I configurations with designations in j-j and, eventually, LS coupling.*

Even parity			
5d ⁹ 6s	(5/2,1/2)	³ D ₃	0.000
5d ⁸ 6s ²	(5/2,5/2)	³ F ₄	823.678
5d ¹⁰		¹ S ₀	6140.180
5d ⁹ 7s	(5/2,1/2)	³ D ₃	52379.375
5d ⁸ 6s7s	(⁴ F _{9/2} ,1/2)	⁵ F ₅	55640.623
5d ⁹ 6d	(5/2,3/2)	³ S ₁	59591.82
5d ⁹ 8s	(5/2,1/2)	³ D ₃	62567.995
5d ⁸ 6s6d	(⁴ F _{9/2} ,3/2)	⁵ G ₆	64141.15*
5d ⁹ 7d	(5/2,3/2)	J=2	65132.91*
5d ⁸ 6s8s	(⁴ F _{9/2} ,1/2)	⁵ F ₅	66967.965
Odd parity			
5d ⁸ 6s6p	(³ F ₄ , ³ P ₀)	J=4	30156.854
5d ⁹ 6p	(5/2,1/2)	J=2	32620.018
5d ⁷ 6s ² 6p	(⁴ F _{9/2} ,1/2)	⁵ G ₅	50299.385
5d ⁹ 7p	(5/2,1/2)	J=2	57987.392
5d ⁸ 6s7p	(³ F ₄ , ³ P ₀)	J=4	62510.36
5d ⁹ 5f	(5/2,5/2)	J=1	65306.80*
5d ⁸ 6s5f	(⁴ F _{5/2} ,5/2)	J=7	70087.93*

* This level is maybe not the lowest of its configuration.

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