Laser-induced-fluorescence lifetime measurements and relativistic Hartree-Fock oscillator strength calculations in singly ionized platinum

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Radiative lifetimes of eight odd-parity states of Pt II, in the energy range from 51 408 to 64 388 cm^{-1}, have been measured by means of the time-resolved laser-induced-fluorescence technique. Free, singly ionized platinum ions were obtained in a laser-produced plasma and a tunable laser with 1.5 ns duration pulse was used to selectively excite the Pt^+ ions. The comparison of the experimental results with relativistic Hartree-Fock calculations emphasizes the importance of valence-valence correlation and of core-polarization effects in this complex ion. A new and extensive set of calculated oscillator strengths and transition probabilities is reported in the present paper.

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I. INTRODUCTION

Radiative data of singly ionized platinum are of great interest in different fields of physics. In astrophysics, platinum, mostly as a singly ionized atom, has been observed to be overabundant in chemically peculiar stars [1,2]. For example, the abundance deduced for platinum in the atmosphere of χ Lupi is about four orders of magnitude larger than the solar photospheric value [2]. In the same star, a platinum isotope anomaly has been observed from the analysis of high-resolution VUV Fourier transform spectra [3]. Accurate spectroscopic data of Pt II (wavelengths, oscillator strengths, radiative lifetimes) are therefore essential for a detailed interpretation of high-resolution stellar spectra.

Platinum-neon hollow-cathode lamps are very stable and emit a large number of sharp lines in the region 113–400 nm. Such lamps are useful for wavelength calibration of spectrometers on orbiting satellites. They were used for calibration of stellar spectra recorded with the Goddard high-resolution spectrograph (GHRS) onboard the Hubble Space Telescope (HST) as well as for a revised calibration of observations with the International Ultraviolet Explorer (IUE) satellite [4–6].

A few decades ago, the Pt II spectrum was analyzed by Shenstone [7] who published an almost complete set of energy levels for the $5d^9$, $5d^86s$, and $5d^86p$ configurations. These level values were compiled by Moore [8] at NIST and were considerably improved from spectrum recorded with a hollow-cathode lamp by Reader *et al.* [9]. More recently, extended analyses of Pt II have been performed by Blaise and Wyart [10] and Wyart *et al.* [11] who used accurate wavelength measurements obtained by Fourier transform spectroscopy at NIST [6] between 113 and 433 nm. Below 113 nm, Wyart *et al.* [11] observed some Pt II lines from sliding spark spectra recorded at the Zeeman Laboratory, Amsterdam and at Antigonish University [12]. These studies led to an extension of the experimentally known level system of Pt II to 73 even and 204 odd levels, most of them belonging to the configurations: $5d^9$, $5d^86s$, $5d^87s$, $5d^86p$, $5d^87p$, $5d^86d$, $5d^76s^2$, and $5d^76s6p$.

Calculated rates for 112 electric dipole transitions from odd levels below 72 000 cm^{-1} have been reported by Wyart *et al.* [11]. These authors used the pseudorelativistic Hartree-plus-statistical-exchange (HXR) method [13] with basis sets including a limited number of interacting configurations.

On the experimental side, the arc measurements of Corliss and Bozman [14] were limited to only one UV transition of Pt II at 279.421 nm. Larsson *et al.* [15] measured radiative lifetimes for three short-lived states excited with picosecond laser pulses and analyzed their data using a time-resolved detection system. By combining these lifetimes with the relative intensities of a large number of spectral lines in the UV region measured by Sansonetti *et al.* [6], oscillator strengths could be deduced for 22 transitions depopulating the three levels investigated.

The *gf* values obtained by Wyart *et al.* [11] were scaled down by means of the lifetime measurements of Larsson *et al.* [15] for the four transitions retained by Kalus *et al.* [3] in their investigation of χ Lupi and HR 7775 spectra.

In the present work, lifetime measurements for eight levels in Pt II are obtained using time-resolved laser-induced fluorescence (LIF). We also report an extensive theoretical analysis of the low lying configurations using the relativistic Hartree-Fock (HFR) method.

II. LIFETIME MEASUREMENTS

The experimental setup used in the present measurements has been described elsewhere (e.g., [16,17]) and only a brief description will be given here.

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TABLE I. Radiative lifetimes (in ns) for low-lying odd-parity levels ($E < 72\,000$ cm^{-1}) in Pt II.

			Theory (this work)		Experiment	
E (cm^{-1})[a]	Configuration[a]	J	HFR(A)	HFR(B)	This work	Previous[b]
51408.370	$5d^8 6p$	7/2	3.5	4.1	3.9 ± 0.3	3.9 ± 0.3
53875.493	$5d^8 6p$	9/2	3.4	3.9	3.6 ± 0.3	
56587.934	$5d^8 6p$	3/2	4.4	5.0	4.9 ± 0.3	
57018.130	$5d^8 6p$	5/2	3.8	4.4	4.1 ± 0.3	
60907.688	$5d^8 6p$	9/2	3.2	3.2		3.5 ± 0.3
61058.490	$5d^8 6p$	11/2	1.9	2.2		
61190.026	$5d^8 6p$	5/2	2.8	3.3	3.1 ± 0.3	
61665.485	$5d^8 6p$	7/2	2.3	2.7		
62781.658	$5d^8 6p$	1/2	3.4	3.9	3.8 ± 0.3	
62820.489	$5d^7 6s6p$	9/2	6.4	10.8		
63738.841	$5d^8 6p$	7/2	2.7	3.1	2.9 ± 0.3	
64388.642	$5d^8 6p$	3/2	3.7	4.3	4.2 ± 0.3	
64757.343	$5d^8 6p$	5/2	3.1	3.4		2.6 ± 0.3
65046.23	$5d^7 6s6p$	11/2	39.7	46.0		
65351.069	$5d^8 6p$	5/2	2.1	2.6		
65587.115	$5d^8 6p$	1/2	5.3	6.0		
66028.014	$5d^8 6p$	3/2	3.2	3.8		
66434.315	$5d^8 6p$	7/2	2.3	2.6		
67780.44	$5d^7 6s6p$	7/2	50.6	58.5		
69235.665	$5d^8 6p$	1/2	2.7	2.9		
69953.317	$5d^8 6p$	5/2	1.6	1.9		
70181.281	$5d^7 6s6p$	9/2	49.1	49.8		
70379.023	$5d^8 6p$	5/2	1.7	2.0		
71021.13	$5d^8 6p$	9/2	2.0	2.4		
71314.594	$5d^8 6p$	7/2	2.3	2.7		
71364.68	$5d^8 6p$	3/2	2.9	3.2		
71948.916	$5d^7 6s6p$	5/2	6.1	7.8		

[a]From Ref. [11].
[b]From Ref. [15].

In the measurements free platinum ions were generated in a laser-produced plasma by focusing a Nd:YAG laser pulse onto a platinum target. The plasma contained ions in metastable levels and these were used for pulsed selective excitation to the investigated level. Fluorescent light released at the subsequent decay of the levels was captured using a fast detection system. The excitation pulses, produced by a tunable laser system, had a duration of about 1.5 ns and wavelengths in the range 203–214 nm. The fairly high populations of metastable levels up to 16 820 cm^{-1} were utilized, thus avoiding excitations in the VUV wavelength region. The detection system included a low-resolution monochromator and for all the investigated levels we checked that the strongest transitions in [6] were present. This was done as an insurance against level missidentification in this line rich spectrum. The lifetimes obtained are given in Table I. Each value represents an average of at least ten recordings made at two different occasions. The error bars are due to the variation in lifetime between different recordings. As a test the lifetime of one previously investigated level [15] was remeasured with, as shown in the table, a consistent result.

III. RELATIVISTIC HARTREE-FOCK CALCULATIONS

In the present work, two different physical models were considered within the framework of the pseudorelativistic HFR method described by Cowan [13] and modified to include core-polarization (CP) effects [18].

In the first model [HFR(A)], the following configurations were explicitly included in the calculations: $5d^9$, $5d^8 6s$, $5d^8 7s$, $5d^8 6d$, $5d^8 7d$, $5d^7 6s^2$, $5d^7 6p^2$, $5d^7 6d^2$, $5d^7 6s6d$, $5d^7 6s7s$, $5d^7 6d7s$, $5d^6 6s^2 7s$, $5d^6 6s^2 6d$ for the even parity and $5d^8 6p$, $5d^8 7p$, $5d^8 5f$, $5d^8 6f$, $5d^7 6s6p$, $5d^7 6s7p$, $5d^7 6p7s$, $5d^7 6p6d$, $5d^7 6s5f$, $5d^7 6s6f$, $5d^6 6s^2 6p$ for the odd parity. Core-polarization effects, which are expected to be important in this heavy element, were introduced by adding a pseudopotential in the Hartree-Fock equations and a correction to the dipole operator as described in previous papers (see, e.g., [18] for details). For the static dipole polarizability α_d, we used the value corresponding to the ionic core of Pt^{4+} as published in [19], i.e., $\alpha_d = 4.52 a_0^3$, while for the cut-off radius r_c, we adopted a value of $1.55 a_0$, which corresponds to the HFR mean value $\langle r \rangle$ of the outermost $5d$ core orbital.

TABLE II. Calculated oscillator strengths and transition probabilities in Pt II. Only transitions with $E < 72\,000$ cm^{-1} and $\log_{10} gf > -2$ are listed. The number in square brackets denotes the power of 10.

Wavelength[a]		Lower level[b]			Upper level[c]				gA[d]
(nm)	Intensity[a]	Configuration	J	E (cm^{-1})	Configuration	J	E (cm^{-1})	$\log_{10} gf$ [d]	(s^{-1})
138.98750	5400	$5d^9$	5/2	0.00	$5d^76s6p$	5/2	71948.916	−1.04	3.14E [+8]
140.12517	660	$5d^9$	5/2	0.00	$5d^86p$	3/2	71364.68	−1.38	1.41E [+8]
140.22375	880	$5d^9$	5/2	0.00	$5d^86p$	7/2	71314.594	−1.67	7.31E [+7]
[142.0878]		$5d^9$	5/2	0.00	$5d^86p$	5/2	70379.023	−0.70	6.57E [+8]
142.95248	30000	$5d^9$	5/2	0.00	$5d^86p$	5/2	69953.317	−0.44	1.19E [+9]
150.31269	300	$5d^86s$	9/2	4786.611	$5d^86p$	7/2	71314.594	−1.97	3.13E [+7]
150.52462	58000	$5d^9$	5/2	0.00	$5d^86p$	7/2	66434.315	−0.66	6.44E [+8]
155.30689	4500	$5d^9$	5/2	0.00	$5d^86p$	3/2	64388.642	−1.54	8.08E [+7]
156.89021	11000	$5d^9$	5/2	0.00	$5d^86p$	7/2	63738.841	−1.09	2.22E [+8]
157.40819	610	$5d^9$	3/2	8419.822	$5d^76s6p$	5/2	71948.916	−1.96	2.96E [+7]
158.86920	2300	$5d^9$	3/2	8419.822	$5d^86p$	3/2	71364.68	−1.32	1.27E [+8]
161.39882	4000	$5d^86s$	7/2	9356.274	$5d^86p$	7/2	71314.594	−1.05	2.29E [+8]
162.16590	33000	$5d^9$	5/2	0.00	$5d^86p$	7/2	61665.485	−1.02	2.44E [+8]
162.16590	33000	$5d^86s$	7/2	9356.274	$5d^86p$	9/2	71021.13	−0.43	9.44E [+8]
162.21204	5500	$5d^86s$	9/2	4786.611	$5d^86p$	7/2	66434.315	−1.48	8.34E [+7]
163.87331	310	$5d^86s$	7/2	9356.274	$5d^86p$	5/2	70379.023	−2.00	2.49E [+7]
164.43084	7900	$5d^9$	3/2	8419.822	$5d^86p$	1/2	69235.665	−1.08	2.03E [+8]
165.02455	3100	$5d^86s$	7/2	9356.274	$5d^86p$	5/2	69953.317	−1.34	1.13E [+8]
165.94860	20000	$5d^86s$	9/2	4786.611	$5d^76s6p$	11/2	65046.23	−1.42	9.22E [+7]
169.62887	8100	$5d^86s$	9/2	4786.611	$5d^86p$	7/2	63738.841	−1.16	1.61E [+8]
170.59115	4200	$5d^86s$	5/2	13329.227	$5d^76s6p$	5/2	71948.916	−1.41	9.05E [+7]
[172.3085]		$5d^86s$	5/2	13329.227	$5d^86p$	3/2	71364.68	−1.14	1.64E [+8]
172.31314	68000	$5d^86s$	9/2	4786.611	$5d^76s6p$	9/2	62820.489	−0.55	6.38E [+8]
172.45730	4300	$5d^86s$	5/2	13329.227	$5d^86p$	7/2	71314.594	−0.90	2.82E [+8]
173.58642	36000	$5d^9$	3/2	8419.822	$5d^86p$	3/2	66028.014	−0.76	3.85E [+8]
175.28546	2500	$5d^86s$	5/2	13329.227	$5d^86p$	5/2	70379.023	−0.63	5.02E [+8]
175.38286	48000	$5d^9$	5/2	0.00	$5d^86p$	5/2	57018.130	−1.13	1.62E [+8]
175.65046	2600	$5d^9$	3/2	8419.822	$5d^86p$	5/2	65351.069	−1.76	3.75E [+7]
175.81220	8400	$5d^86s$	9/2	4786.611	$5d^86p$	7/2	61665.485	−1.20	1.36E [+8]
176.60328	10000	$5d^86s$	5/2	13329.227	$5d^86p$	5/2	69953.317	−1.56	5.87E [+7]
176.71612	47000	$5d^9$	5/2	0.00	$5d^86p$	3/2	56587.934	−1.38	9.04E [+7]
177.50160	86000	$5d^9$	3/2	8419.822	$5d^86p$	5/2	64757.343	−0.60	5.29E [+8]
177.70866	230000	$5d^86s$	9/2	4786.611	$5d^86p$	11/2	61058.490	0.41	5.35E [+9]
178.07016	1500	$5d^86s$	3/2	15791.276	$5d^76s6p$	5/2	71948.916	−1.76	3.70E [+7]
178.18617	93000	$5d^86s$	9/2	4786.611	$5d^86p$	9/2	60907.688	−0.07	1.82E [+9]
178.58803	13000	$5d^86s$	7/2	9356.274	$5d^86p$	5/2	65351.069	−0.77	3.61E [+8]
[183.1913]		$5d^86s$	3/2	15791.276	$5d^86p$	5/2	70379.023	−1.88	2.61E [+7]
183.33875	10000	$5d^86s$	5/2	16820.894	$5d^86p$	3/2	71364.68	−0.68	4.12E [+8]
183.50745	17000	$5d^86s$	5/2	16820.894	$5d^86p$	7/2	71314.594	−0.41	7.83E [+8]
183.65075	30000	$5d^86s$	5/2	13329.227	$5d^76s6p$	7/2	67780.44	−1.52	6.06E [+7]
183.88246	13000	$5d^86s$	7/2	9356.274	$5d^86p$	7/2	63738.841	−0.90	2.52E [+8]
183.95258	31000	$5d^9$	3/2	8419.822	$5d^86p$	1/2	62781.658	−1.13	1.46E [+8]
185.69688	6000	$5d^86s$	7/2	18097.715	$5d^76s6p$	5/2	71948.916	−1.25	1.10E [+8]
186.71302	30000	$5d^86s$	5/2	16820.894	$5d^86p$	5/2	70379.023	−0.35	8.50E [+8]
187.04100	38000	$5d^86s$	7/2	9356.274	$5d^76s6p$	9/2	62820.489	−0.91	2.41E [+8]
187.11038	11000	$5d^86s$	3/2	15791.276	$5d^86p$	1/2	69235.665	−1.10	1.53E [+8]
187.91031	27000	$5d^86s$	7/2	18097.715	$5d^86p$	7/2	71314.594	−0.15	1.33E [+9]

TABLE II. (*Continued.*)

Wavelength[a] (nm)	Intensity[a]	Lower level[b] Configuration	J	E (cm^{-1})	Upper level[c] Configuration	J	E (cm^{-1})	$\log_{10} gf$ [d]	gA[d] (s^{-1})
188.20900	120	$5d^86s$	5/2	16820.894	$5d^86p$	5/2	69953.317	−0.54	5.44E [+8]
188.30587	220000	$5d^86s$	5/2	13329.227	$5d^86p$	7/2	66434.315	−0.12	1.44E [+9]
188.95226	58000	$5d^86s$	7/2	18097.715	$5d^86p$	9/2	71021.13	0.24	3.20E [+9]
189.50088	12000	$5d^9$	3/2	8419.822	$5d^86p$	5/2	61190.026	−1.16	1.27E [+8]
189.75769	11000	$5d^86s$	5/2	13329.227	$5d^86p$	3/2	66028.014	−1.42	7.00E [+7]
191.17092	140000	$5d^86s$	7/2	9356.274	$5d^86p$	7/2	61665.485	0.08	2.21E [+9]
191.27295	3100	$5d^86s$	7/2	18097.715	$5d^86p$	5/2	70379.023	−0.44	6.53E [+8]
192.84320	15000	$5d^86s$	7/2	18097.715	$5d^86p$	5/2	69953.317	−1.11	1.39E [+8]
192.92449	100000	$5d^86s$	7/2	9356.274	$5d^86p$	5/2	61190.026	−0.16	1.25E [+9]
193.98110	53000	$5d^86s$	7/2	9356.274	$5d^86p$	9/2	60907.688	−0.23	1.06E [+9]
194.44617	63000	$5d^86s$	5/2	13329.227	$5d^86p$	5/2	64757.343	−0.66	3.80E [+8]
195.85027	7400	$5d^86s$	5/2	13329.227	$5d^86p$	3/2	64388.642	−1.06	1.52E [+8]
198.37486	18000	$5d^86s$	5/2	13329.227	$5d^86p$	7/2	63738.841	−0.63	3.98E [+8]
199.05751	32000	$5d^86s$	3/2	15791.276	$5d^86p$	3/2	66028.014	−0.77	2.83E [+8]
199.21936	1300	$5d^86s$	3/2	21168.684	$5d^86p$	3/2	71364.68	−1.75	2.96E [+7]
201.356	250	$5d^86s$	1/2	21717.260	$5d^86p$	3/2	71364.68	−1.66	3.56E [+7]
201.49330	78000	$5d^86s$	5/2	16820.894	$5d^86p$	7/2	66434.315	−0.43	6.11E [+8]
203.14397	680	$5d^86s$	3/2	21168.684	$5d^86p$	5/2	70379.023	−1.21	9.99E [+7]
203.64666	98000	$5d^86s$	9/2	4786.611	$5d^86p$	9/2	53875.493	−0.10	1.26E [+9]
204.15751	62000	$5d^86s$	3/2	15791.276	$5d^86p$	5/2	64757.343	−0.44	5.79E [+8]
204.91689	13000	$5d^86s$	3/2	21168.684	$5d^86p$	5/2	69953.317	−0.30	7.91E [+8]
205.70265	39000	$5d^9$	3/2	8419.822	$5d^86p$	5/2	57018.130	−1.00	1.59E [+8]
205.99148	5100	$5d^86s$	5/2	16820.894	$5d^86p$	5/2	65351.069	−0.82	2.39E [+8]
206.17317	1000	$5d^86s$	5/2	23461.503	$5d^76s6p$	5/2	71948.916	−1.37	6.82E [+7]
206.81799	8000	$5d^86s$	5/2	13329.227	$5d^86p$	7/2	61665.485	−0.92	1.88E [+8]
207.54004	33000	$5d^9$	3/2	8419.822	$5d^86p$	3/2	56587.934	−1.21	9.65E [+7]
207.94914	1400	$5d^86s$	3/2	23875.553	$5d^76s6p$	3/2	71948.916	−1.58	4.14E [+7]
207.97676	1700	$5d^86s$	3/2	21168.684	$5d^86p$	1/2	69235.665	−1.74	2.81E [+7]
208.54315	6900	$5d^86s$	5/2	16820.894	$5d^86p$	5/2	64757.343	−1.50	4.79E [+7]
208.68804	1000	$5d^86s$	5/2	23461.503	$5d^86p$	3/2	71364.68	−1.74	2.76E [+7]
208.87282	9300	$5d^86s$	5/2	13329.227	$5d^86p$	5/2	61190.026	−1.06	1.33E [+8]
208.90647	1800	$5d^86s$	5/2	23461.503	$5d^86p$	7/2	71314.594	−1.29	7.76E [+7]
209.74478	74000	$5d^86s$	7/2	9356.274	$5d^86p$	5/2	57018.130	−0.75	2.72E [+8]
210.15979	19000	$5d^86s$	5/2	16820.894	$5d^86p$	3/2	64388.642	−0.65	3.36E [+8]
210.37804	12000	$5d^86s$	1/2	21717.260	$5d^86p$	1/2	69235.665	−0.79	2.43E [+8]
210.50776	1700	$5d^86s$	3/2	23875.553	$5d^86p$	3/2	71364.68	−1.04	1.38E [+8]
211.55823	22000	$5d^86s$	7/2	18097.715	$5d^86p$	5/2	65351.069	−0.37	6.36E [+8]
212.74231	32000	$5d^86s$	3/2	15791.276	$5d^86p$	1/2	62781.658	−0.81	2.29E [+8]
213.07079	26000	$5d^86s$	5/2	16820.894	$5d^86p$	7/2	63738.841	−0.38	6.14E [+8]
214.25054	3900	$5d^86s$	7/2	18097.715	$5d^86p$	5/2	64757.343	−1.28	7.48E [+7]
214.42458	350000	$5d^86s$	9/2	4786.611	$5d^86p$	7/2	51408.370	0.09	1.79E [+9]
214.97007	1100	$5d^86s$	3/2	23875.553	$5d^86p$	5/2	70379.023	−1.26	7.87E [+7]
215.02397	4000	$5d^86s$	5/2	23461.503	$5d^86p$	5/2	69953.317	−0.82	2.20E [+8]
219.03216	40000	$5d^86s$	7/2	18097.715	$5d^86p$	7/2	63738.841	−0.25	7.79E [+8]
220.20165	7900	$5d^86s$	3/2	15791.276	$5d^86p$	5/2	61190.026	−1.17	9.41E [+7]
220.38924	3500	$5d^86s$	3/2	23875.553	$5d^86p$	1/2	69235.665	−1.38	5.66E [+7]
220.67295	5100	$5d^76s^2$	9/2	24879.480	$5d^76s6p$	9/2	70181.281	−1.25	7.64E [+7]

TABLE II. (*Continued.*)

Wavelength[a] (nm)	Intensity[a]	Lower level[b] Configuration	J	E (cm^{-1})	Upper level[c] Configuration	J	E (cm^{-1})	$\log_{10} gf$ [d]	gA[d] (s^{-1})
222.84978	2100	$5d^86s$	3/2	21168.684	$5d^86p$	3/2	66028.014	−1.68	2.80E [+7]
222.92303	9700	$5d^86s$	5/2	16820.894	$5d^86p$	7/2	61665.485	−1.13	9.88E [+7]
223.53029	9300	$5d^86s$	7/2	18097.715	$5d^86p$	9/2	62820.489	−1.46	4.69E [+7]
224.55244	170000	$5d^86s$	7/2	9356.274	$5d^86p$	9/2	53875.493	−0.06	1.16E [+9]
225.06201	9000	$5d^86s$	3/2	21168.684	$5d^86p$	1/2	65587.115	−0.98	1.38E [+8]
225.31210	3500	$5d^86s$	5/2	16820.894	$5d^86p$	5/2	61190.026	−1.64	2.99E [+7]
225.60897	8200	$5d^86s$	1/2	21717.260	$5d^86p$	3/2	66028.014	−1.32	6.23E [+7]
226.26453	8200	$5d^86s$	3/2	21168.684	$5d^86p$	5/2	65351.069	−0.84	1.91E [+8]
226.64082	1900	$5d^86s$	1/2	27255.687	$5d^86p$	3/2	71364.68	−1.04	1.18E [+8]
227.87659	590	$5d^86s$	1/2	21717.260	$5d^86p$	1/2	65587.115	−1.99	1.32E [+7]
228.82050	180000	$5d^86s$	5/2	13329.227	$5d^86p$	5/2	57018.130	−0.41	5.00E [+8]
231.09626	200000	$5d^86s$	5/2	13329.227	$5d^86p$	3/2	56587.934	−0.45	4.48E [+8]
231.30347	4700	$5d^86s$	3/2	21168.684	$5d^86p$	3/2	64388.642	−1.36	5.52E [+7]
231.98869	12000	$5d^86s$	7/2	18097.715	$5d^86p$	5/2	61190.026	−0.89	1.60E [+8]
232.63386	13000	$5d^86s$	5/2	23461.503	$5d^86p$	7/2	66434.315	−1.27	6.54E [+7]
233.02360	830	$5d^76s^2$	9/2	24879.480	$5d^76s6p$	7/2	67780.44	−1.95	1.41E [+7]
233.51888	8800	$5d^86s$	7/2	18097.715	$5d^86p$	9/2	60907.688	−1.00	1.25E [+8]
234.27732	1100	$5d^86s$	1/2	21717.260	$5d^86p$	3/2	64388.642	−1.70	2.45E [+7]
234.85456	6600	$5d^86s$	5/2	23461.503	$5d^86p$	3/2	66028.014	−0.97	1.28E [+8]
237.16165	4200	$5d^86s$	3/2	23875.553	$5d^86p$	3/2	66028.014	−1.62	2.78E [+7]
[237.7247]		$5d^86s$	9/2	29261.967	$5d^86p$	7/2	71314.594	−1.02	1.13E [+8]
237.72773	23000	$5d^86s$	7/2	9356.274	$5d^86p$	7/2	51408.370	−1.04	1.10E [+8]
238.65017	2900	$5d^86s$	5/2	23461.503	$5d^86p$	5/2	65351.069	−0.97	1.25E [+8]
239.66869	7400	$5d^86s$	3/2	23875.553	$5d^86p$	1/2	65587.115	−0.82	1.75E [+8]
240.57269	15000	$5d^76s^2$	9/2	24879.480	$5d^86p$	7/2	66434.315	−0.87	1.57E [+8]
241.03280	780	$5d^86s$	3/2	23875.553	$5d^86p$	5/2	65351.069	−1.52	3.47E [+7]
241.77302	910	$5d^86s$	7/2	29030.479	$5d^86p$	5/2	70379.023	−1.69	2.33E [+7]
242.08161	18000	$5d^86s$	5/2	23461.503	$5d^86p$	5/2	64757.343	−1.02	1.06E [+8]
242.48672	64000	$5d^86s$	3/2	15791.276	$5d^86p$	5/2	57018.130	−0.77	1.94E [+8]
242.93490	7200	$5d^86s$	7/2	29030.479	$5d^76s6p$	9/2	70181.281	−1.27	6.01E [+7]
243.44610	16000	$5d^86s$	1/2	21717.260	$5d^86p$	1/2	62781.658	−0.97	1.21E [+8]
244.26261	9100	$5d^86s$	5/2	23461.503	$5d^86p$	3/2	64388.642	−0.97	1.20E [+8]
245.04390	30000	$5d^86s$	3/2	15791.276	$5d^86p$	3/2	56587.934	−1.21	6.93E [+7]
246.75920	5800	$5d^86s$	3/2	23875.553	$5d^86p$	3/2	64388.642	−1.05	9.84E [+7]
248.20363	1500	$5d^86s$	5/2	23461.503	$5d^86p$	7/2	63738.841	−1.49	3.52E [+7]
248.69827	17000	$5d^86s$	5/2	16820.894	$5d^86p$	5/2	57018.130	−1.27	5.85E [+7]
248.88753	15000	$5d^76s^2$	9/2	24879.480	$5d^76s6p$	11/2	65046.23	−0.86	1.47E [+8]
251.38885	28000	$5d^86s$	5/2	16820.894	$5d^86p$	3/2	56587.934	−1.18	7.13E [+7]
257.26119	3700	$5d^76s^2$	9/2	24879.480	$5d^86p$	7/2	63738.841	−1.05	9.00E [+7]
257.83871	1900	$5d^86s$	1/2	27255.687	$5d^86p$	3/2	66028.014	−1.80	1.57E [+7]
261.67471	2900	$5d^86s$	5/2	23461.503	$5d^86p$	7/2	61665.485	−1.34	4.41E [+7]
262.53264	5100	$5d^86s$	5/2	13329.227	$5d^86p$	7/2	51408.370	−1.62	2.30E [+7]
267.91293	1200	$5d^86s$	3/2	23875.553	$5d^86p$	5/2	61190.026	−1.66	2.01E [+7]
268.00471	110	$5d^76s^2$	7/2	34647.221	$5d^76s6p$	5/2	71948.916	−1.88	1.24E [+7]
269.22265	1400	$5d^86s$	1/2	27255.687	$5d^86p$	3/2	64388.642	−1.60	2.31E [+7]
271.76199	2100	$5d^76s^2$	9/2	24879.480	$5d^86p$	7/2	61665.485	−1.36	3.94E [+7]
272.64128	990	$5d^76s^2$	7/2	34647.221	$5d^86p$	7/2	71314.594	−1.18	5.94E [+7]

TABLE II. (*Continued.*)

Wavelength[a] (nm)	Intensity[a]	Lower level[b] Configuration	J	E (cm^{-1})	Upper level[c] Configuration	J	E (cm^{-1})	$\log_{10} gf$ [d]	gA[d] (s^{-1})
276.32173	980	$5d^76s^2$	9/2	24879.480	$5d^86p$	11/2	61058.490	−1.57	2.33E [+7]
277.47838	7900	$5d^76s^2$	9/2	24879.480	$5d^86p$	9/2	60907.688	−0.76	1.53E [+8]
278.86209	2800	$5d^86s$	3/2	21168.684	$5d^86p$	5/2	57018.130	−1.86	1.18E [+7]
279.37012	3400	$5d^86s$	9/2	29261.967	$5d^76s6p$	11/2	65046.23	−1.59	2.16E [+7]
279.78027	550	$5d^76s^2$	7/2	34647.221	$5d^86p$	5/2	70379.023	−1.45	2.99E [+7]
281.33728	4900	$5d^76s^2$	7/2	34647.221	$5d^76s6p$	9/2	70181.281	−1.23	4.88E [+7]
281.40134	2800	$5d^86s$	1/2	27255.687	$5d^86p$	1/2	62781.658	−1.72	1.64E [+7]
281.88604	400	$5d^76s^2$	5/2	36484.028	$5d^76s6p$	5/2	71948.916	−1.61	2.10E [+7]
282.24927	5600	$5d^86s$	3/2	21168.684	$5d^86p$	3/2	56587.934	−1.82	1.29E [+7]
286.608	360	$5d^76s^2$	5/2	36484.028	$5d^86p$	3/2	71364.68	−1.70	1.60E [+7]
289.03725	2600	$5d^86s$	5/2	16820.894	$5d^86p$	7/2	51408.370	−1.96	8.82E [+6]
289.96452	1100	$5d^86s$	9/2	29261.967	$5d^86p$	7/2	63738.841	−1.61	1.97E [+7]
295.85030	1200	$5d^86s$	3/2	32237.007	$5d^86p$	3/2	66028.014	−1.84	1.10E [+7]
300.11675	6800	$5d^86s$	7/2	18097.715	$5d^86p$	7/2	51408.370	−1.45	2.61E [+7]
301.72399	6200	$5d^76s^2$	7/2	34647.221	$5d^76s6p$	7/2	67780.44	−1.58	1.97E [+7]
307.59129	160	$5d^76s^2$	3/2	37877.792	$5d^86p$	5/2	70379.023	−1.92	8.51E [+6]
314.40872	540	$5d^86s$	9/2	29261.967	$5d^86p$	11/2	61058.490	−1.89	8.44E [+6]
315.90704	1800	$5d^86s$	9/2	29261.967	$5d^86p$	9/2	60907.688	−1.61	1.68E [+7]
350.540	80	$5d^76s^2$	5/2	41434.11	$5d^86p$	5/2	69953.317	−1.96	5.98E [+6]
353.58934	2500	$5d^76s^2$	5/2	36484.03	$5d^86p$	5/2	64757.343	−1.94	6.01E [+6]
355.13553	3200	$5d^76s^2$	3/2	37877.792	$5d^86p$	3/2	66028.014	−1.66	1.14E [+7]
397.00530	1800	$5d^76s^2$	5/2	36484.028	$5d^86p$	7/2	61665.485	−1.80	6.56E [+6]
404.64498	2100	$5d^76s^2$	5/2	36484.028	$5d^86p$	5/2	61190.026	−1.61	9.98E [+6]

[a]From Ref. [6]. Wavelengths are given in vacuum (air) below (above) 200.0 nm. Values between brackets are deduced from experimental energy levels.
[b]From Ref. [9].
[c]From Ref. [11].
[d]HFR(B) calculations (this work).

Using a least-squares fitting procedure, the Slater and spin-orbit integrals were adjusted to obtain the best agreement between calculated and experimental energy levels. The fitted parameters were the center-of-gravity energies (E_{av}), the single-configuration direct (F^k) and exchange (G^k) electrostatic interaction integrals, the spin-orbit parameters (ζ_{nl}), and some configuration interaction (R^k) integrals related to the configurations observed experimentally. For the remaining configurations, the F^k, G^k, and R^k integrals were scaled down by a factor of 0.85 as suggested by Cowan [13] while the *ab initio* values of the spin-orbit parameters, ζ_{nl}, computed by the Blume-Watson method, were used without scaling. In addition, the effective interaction parameters α and β were included in the fit to allow specifically for the cumulative effects of distant configurations. All the known even parity levels published by Blaise and Wyart [10] were fitted except the two levels at 119 057.05 cm^{-1} (unidentified designation) and 121 651.19 cm^{-1} (belonging to $5d^76s7s$). All the parameters of the configurations $5d^9$, $5d^86s$, $5d^87s$, $5d^86d$, and $5d^76s^2$ were adjusted with the exception of the α and β effective parameters in $5d^87s$, which were fixed using the values obtained for the $5d^86s$ configuration. For the $5d^76s7s$ for which only a few energy levels have been established experimentally, only the average energy was adjusted. Thus 71 even levels were fitted with 33 free parameters and the mean deviation of the fit $|\Delta E| = |E_{exp} - E_{calc}|$ was 44 cm^{-1}. For the odd parity, all the experimental levels reported by Wyart *et al.* [11] below 110 000 cm^{-1} were introduced in the fitting procedure. The levels situated above 110 000 cm^{-1} are fragmentarily known and therefore some of the designations appear dubious. Moreover, some of these levels overlap unknown levels belonging to higher configurations such as $5d^66s^26p$ and $5d^85f$. Consequently, these energy levels were not included in the fit. For the $5d^86p$ and $5d^76s6p$ configurations, all the parameters including the configuration interaction integrals (R^k) were adjusted. For $5d^87p$ and $5d^66s^26p$, only the average energies were adjusted in view of the scarcity of experimental data. Thus 180 odd levels were fitted using 27 adjustable parameters and the corresponding mean deviation was found to be 108 cm^{-1}.

The HFR(A) lifetimes obtained for low-lying odd levels ($E < 72\,000$ cm^{-1}) are presented in Table I and compared with the experimental data measured in the present work and in [15]. With the exception of the level at 64 757.343 cm^{-1},

TABLE III. Comparison between oscillator strengths calculated in the present work [HFR(B)] and the experimental results.

Upper odd level E (cm^{-1})	J	Lower even level E (cm^{-1})	J	Wavelength[a] (nm)	Intensity[a]	$\log_{10} gf$ Experiment [15]	Experiment[b] (this work)	HFR(B) (this work)
51408.370	7/2	4786.611	9/2	214.42458	350000	0.10	0.10	0.09
		9356.274	7/2	237.72773	23000	−0.99	−0.99	−1.04
		13329.227	5/2	262.53264	5100	−1.56	−1.56	−1.62
		16820.894	5/2	289.03725	2600	−1.77	−1.77	−1.96
		18097.715	7/2	300.11675	6800	−1.31	−1.31	−1.45
53875.493	9/2	4786.611	9/2	203.64666	98000		−0.22	−0.10
		9356.274	7/2	224.55244	170000		0.10	−0.06
56587.934	3/2	0.000	5/2	176.71612	47000		−1.29	−1.38
		8419.822	3/2	207.54004	33000		−1.30	−1.21
		13329.227	5/2	231.09626	200000		−0.43	−0.45
		15791.276	3/2	245.04390	30000		−1.20	−1.21
		16820.894	5/2	251.38885	28000		−1.21	−1.18
		21168.684	3/2	282.24927	5600		−1.81	−1.82
57018.130	5/2	0.000	5/2	175.38286	48000		−1.12	−1.13
		8419.822	3/2	205.70265	39000		−1.07	−1.00
		9356.274	7/2	209.74478	74000		−0.78	−0.75
		13329.227	5/2	228.82050	180000		−0.32	−0.41
		15791.276	3/2	242.48672	64000		−0.72	−0.77
		16820.894	5/2	248.69827	17000		−1.27	−1.27
		21168.684	3/2	278.86209	2800		−1.96	−1.86
60907.688	9/2	4786.611	9/2	178.18617	93000	−0.11		−0.07
		9356.274	7/2	193.98110	53000	−0.28		−0.23
		18097.715	7/2	233.51888	8800	−0.90		−1.00
		24879.480	9/2	277.47838	7900	−0.80		−0.76
		29261.967	9/2	315.90704	1800	−1.33		−1.61
61190.026	5/2	8419.822	3/2	189.50088	12000		−1.08	−1.16
		9356.274	7/2	192.92449	100000		−0.14	−0.16
		13329.227	5/2	208.87282	9300		−1.10	−1.06
		15791.276	3/2	220.20165	7900		−1.13	−1.17
		16820.894	5/2	225.31210	3500		−1.46	−1.64
		18097.715	7/2	231.98869	12000		−0.90	−0.89
		23875.553	3/2	267.91293	1200		−1.78	−1.66
		36484.028	5/2	404.64498	2100		−1.18	−1.61
62781.658	1/2	8419.822	3/2	183.95258	31000		−1.00	−1.13
		15791.276	3/2	212.74231	32000		−0.86	−0.81
		21717.260	1/2	243.44610	16000		−1.04	−0.97
		27255.687	1/2	281.40134	2800		−1.68	−1.72
63738.841	7/2	0.000	5/2	156.89021	11000		−1.04	−1.09
		4786.611	9/2	169.62887	8100		−1.11	−1.16
		9356.274	7/2	183.88246	13000		−0.83	−0.90
		13329.227	5/2	198.37486	18000		−0.62	−0.63
		16820.894	5/2	213.07079	26000		−0.40	−0.38
		18097.715	7/2	219.03216	40000		−0.19	−0.25
		23461.503	5/2	248.20363	1500		−1.51	−1.49
		24879.480	9/2	257.26119	3700		−1.09	−1.05
		29261.967	9/2	289.96452	1100		−1.51	−1.61

TABLE III. (*Continued.*)

Upper odd level E (cm^{-1})	J	Lower even level E (cm^{-1})	J	Wavelength[a] (nm)	Intensity[a]	$\log_{10} gf$ Experiment [15]	Experiment[b] (this work)	HFR(B) (this work)
64388.642	3/2	0.000	5/2	155.30689	4500		−1.55	−1.54
		13329.227	5/2	195.85027	7400		−1.14	−1.06
		16820.894	5/2	210.15979	19000		−0.67	−0.65
		21168.684	3/2	231.30347	4700		−1.19	−1.36
		21717.260	1/2	234.27732	1100		−1.81	−1.70
		23461.503	5/2	244.26261	9100		−0.85	−0.97
		23875.553	3/2	246.75920	5800		−1.04	−1.05
		27255.687	1/2	269.22265	1400		−1.58	−1.60
64757.343	5/2	8419.822	3/2	177.50160	86000	−0.43		−0.60
		9356.274	7/2	180.50193	3200	−1.84		(−2.96)[c]
		13329.227	5/2	194.44617	63000	−0.48		−0.66
		15791.276	3/2	204.15751	62000	−0.45		−0.44
		16820.894	5/2	208.54315	6900	−1.38		−1.50
		18097.715	7/2	214.25054	3900	−1.61		−1.28
		21168.684	3/2	229.34678	1800	−1.88		(−2.89)[c]
		23461.503	5/2	242.08161	18000	−0.84		−1.02
		23875.553	3/2	244.53359	1100	−2.04		(−2.44)[c]
		29030.479	7/2	279.81894	1000	−1.96		−2.10
		32237.007	3/2	307.41059	380	−2.30		(−2.70)[c]
		36484.028	5/2	353.58934	2500	−1.36		−1.94

[a]From Ref. [6]. Wavelengths are given in vacuum (air) below (above) 200.0 nm.
[b]Obtained by combining the radiative lifetimes measured in the present work and the relative intensities reported in [6].
[c]Affected by strong cancellation effects.

for which several computed transition probabilities are affected by cancellation effects, the calculated lifetimes are systematically shorter than the measurements (on average by 11%). This is probably due to the fact that the CP model used in our HFR(A) approximation is not sufficient to take into account all the core-valence correlation not included explicitly in the calculations. In order to verify this assumption, a second physical model [HFR(B)] was considered. In this model, the CP contribution was included using the dipole polarizability corresponding to the Pt^{3+} ionic core, i.e., $\alpha_d = 6.27 a_0^3$ [19] while retaining the previous cut-off radius, i.e., $r_c = 1.55 a_0$. Since interactions with configurations of the type $5d^6 nln'l'n''l''$ are supposed to be included in such a CP model, these configurations had to be removed from the multiconfiguration expansions for consistency. Thus, the HFR(B) model included the same configurations as before except the even $5d^6 6s^2 7s$, $5d^6 6s^2 6d$, and the odd $5d^6 6s^2 6p$ configurations. The semiempirical fitting process was then performed in the same way as described above except that the average energy of the $5d^6 6s^2 6p$ could not be adjusted and that only the odd-parity levels below 104 600 cm^{-1} were included in the fit. Thus, 71 even levels were fitted using 33 free parameters and a mean deviation of 44 cm^{-1}, while for the odd parity, 150 levels were fitted using 26 free parameters and the mean deviation of 203 cm^{-1}. The reason why the latter deviation is larger than the one obtained with the HFR(A) model is that the $5d^6 6s^2 6p$ configuration was not included. It is worth noting, however, that this configuration essentially affects the quality of the fit only for higher energy levels, the mean deviation being indeed reduced to 140 cm^{-1} for the odd levels situated below 80 000 cm^{-1}. Table I shows that the radiative lifetimes calculated using the HFR(B) model are in better agreement (within 4% on average) with the experimental values than those obtained with the HFR(A) model. As a consequence, it seems reasonable and justified to adopt as the best results of the present work those obtained using model HFR(B).

IV. OSCILLATOR STRENGTHS AND TRANSITION PROBABILITIES

Computed oscillator strengths and transition probabilities, obtained with the HFR(B) model are reported in Table II for selected transitions in Pt II. In view of the huge number of calculated transitions in the present work, Table II is restricted to the strongest lines ($\log_{10} gf > -2$) involving the levels situated below 72 000 cm^{-1} [21]. Radiative transition probabilities for 112 transitions originating from upper odd levels below 72 000 cm^{-1} were reported by Wyart *et al.* [11] who used the HXR mode of the Cowan code including a limited set of interacting configurations. Those results are systematically larger than the *gA* values obtained in the present work, the mean ratio $gA(\text{Wyart})/gA(\text{present})$ is 1.84 ± 0.24. This is not only due to the fact that explicit intravalence correlation is included in a more extensive way in our work but also to the fact that CP effects are taken into account. It should be emphasized, however, that the main purpose of Wyart *et al.* [11] was the identification of lines in laboratory spectra and not the obtention of refined transition probability values.

Table III shows a comparison between our calculated oscillator strengths and the experimental values published by Larsson *et al.* [15] or deduced in the present work. These experimental *gf* values were obtained by combining the LIF lifetime measurements given in Table I with the relative intensities reported by Sansonetti *et al.* [6]. In view of the uncertainties affecting the measured lifetimes (~10%) and intensities (~20% [6]), we estimate the experimental oscillator strengths to be accurate to about 25%–30%. However, it is important to note that the NIST platinum atlas [6] was primarily intended to provide a wavelength standard for Pt-Ne hollow cathode lamps used on the HST and, even though the intensities were reported as accurate as 20%, serious radiometric calibration errors were discovered in this atlas for Pt I lines by Den Hartog *et al.* [20]. Consequently, although it is difficult to assess the effect of such calibration errors on the Pt II lines, we cannot rule out that some branching fractions deduced in the present work from the NIST experimental intensities can be affected by larger uncertainties.

As seen from Table III, a good agreement is observed between the experimental and theoretical results with the exception of some transitions depopulating the level at 64 757 cm^{-1}. It is worth noting that, for this level, the calculated line strengths for the transitions at $\lambda = 180.501\,93$, 229.346 78, 244.533 59, and 307.410 59 nm are affected by severe cancellation effects while the lines at 208.543 15, and 353.589 34 nm are listed as *unresolved from close line* and *asymmetric* in Ref. [6], which might affect the line intensities used to deduce the experimental $\log_{10} gf$ values in [15].

V. CONCLUSIONS

A first extensive set of oscillator strengths and transition probabilities has been calculated for transitions of Pt II belonging to the $5d^9-5d^86p$, $5d^9-5d^76s6p$, $5d^86s-5d^86p$, and $5d^86s-5d^76s6p$ transition arrays by a HFR approach including valence-valence correlation and CP effects. Comparisons of the theoretical results with lifetime measurements performed with a time-resolved laser-induced-fluorescence technique for selected odd-parity levels illustrate the dramatic importance of CP effects for obtaining accurate radiative parameters for this heavy ion.

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