THE FIRST SPARK SPECTRUM OF CAESIUM (Cs II)

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Abstract

The resonance lines of Cs II have been photographed in the ultraviolet region with the vacuum spectrograph. The mode of excitation was the hollow cathode discharge in helium. The values of the wave-lengths of the ultraviolet lines for Cs II were obtained from second order measurements. With the separations of the resonance lines as guides, it was possible to assign electron configurations to the energy levels given by Sommer and to extend his scheme somewhat. The coupling is that of approximate (jj) type. The characteristic feature of the Cs II spectrum was the decomposition of the levels arising from the various configurations into two distinct groups due to the large separation of the $5p^{5}$ ²P of Cs III. Five of the eight resonance lines found in the ultraviolet region fitted into Sommer's scheme. One new level with J=0has been found in this investigation, thus completing the group of the six $5p^{5}6p$ levels built upon the ${}^{2}P_{11/2}$ limit. The classification, assignment of inner quantum numbers, and the identification of levels agreed with the theoretical considerations as well as with the predictions from the Xe I classification. The remaining three resonance lines appeared to be due to transitions from the $5p^{6} {}^{1}S_{0}$ ground level to new $5p^{5}(s, d)$ levels built upon the ${}^{2}P_{1/2}$ limit. It was possible to separate the ${}^{3}P_{2}$ and ${}^{3}P_{1}$ levels due to $5p^{5}$ $({}^{2}P_{11/2})$ (6s and 7s) from the $5p^{5}({}^{2}P_{11/2})$ (5d and 6d) levels. The ionization potential of Cs II was computed to be approximately 23.4 volts.

I. INTRODUCTION

I N A recent publication the authors have presented a classification of the Rb II spectrum¹ which was made possible by the identification of the resonance lines of the spectrum in spectrograms taken with a vacuum spectrograph of a hollow cathode discharge of rubidium in helium.² The present paper gives the result of a similar undertaking for caesium. The procedure was the same as for rubidium. The caesium metal was placed in a molybdenum hollow cathode and the spectrum excited by a discharge in an atmosphere of helium. It was photographed with a 1 meter vacuum spectrograph and the wave-lengths of the resonance lines determined by measurements in the second order against carbon and helium standards. As reported in a pre-liminary communication,³ eight lines were measured between 962A and 612A. These data were made use of to interpret the material of Sommer,⁴ who photographed the caesium spark spectrum in the region λ 3268–7280 and arranged a number of the lines in a scheme showing recurring frequency differences.

¹ O. Laporte, G. R. Miller, R. A. Sawyer, Phys. Rev. 38, 843 (1931).

² Through a remarkable oversight the potassium arc resonance lines, $\lambda\lambda7664$ and 7698, were classified in the Rb II spectrum. These two lines and the term by which they were classified should be striken out of that paper.

⁸ O. Laporte, G. R. Miller, R. A. Sawyer, Phys. Rev. 37, 845 (1931).

⁴ Sommer, Ann. d. Physik 75, 163 (1924).

The Cs II spectrum is, like that of Rb II, of rare gas type. The lowest term is $5p^{6} {}^{1}S_{0}$ and the higher terms with which we are concerned arise from the excitation of one of the *p*-electrons to an *s*, *p*, *d*, or *f* level of higher quantum number. A tabulation of the number and location of the levels to be expected from each of these configurations on both the Russell-Saunders and the (*jj*) coupling is given in Table I which is repeated here for convenience

Electron configuration			Russ	ell-Sau	nders		(<i>jj</i>))	Number of levels
$4p^5$				^{2}P		~	$2P_{1\frac{1}{2}}$	${}^{2}P_{1\frac{1}{2}}$	
$4p^{6}$				¹ S ₀			()	(1)
$\begin{array}{c} 4p^{\circ}5s \\ 4p^{\circ}6s \\ 4p^{\circ}7s \\ \end{array}$		¹ <i>P</i> ₁			³ P ₂₁₀		12	01	(4)
$egin{array}{c} 4 p^5 5 p \ 4 p^5 6 p \ 4 p^5 7 p \ \end{array} \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	¹ S ₀	¹ <i>P</i> ₁	${}^{1}D_{2}$	³ S ₁	³ P ₂₁₀	³ D ₃₂₁	12 0123	01 12	(10)
$\left. \begin{array}{c} 4 p^5 4 d \\ 4 p^5 5 d \\ 4 p^5 6 d \\ \end{array} \right\}$	¹ <i>P</i> ₁	${}^{1}D_{2}$	${}^{1}F_{3}$	${}^{3}P_{210}$	³ D ₃₂₁	³ F ₄₃₂	0123 1234	12 23	(12)
$\left. \begin{array}{c} 4 p^5 4 f \\ 4 p^5 5 f \\ 4 p^5 6 f \\ - \end{array} ight angle$	¹ D ₂	${}^{1}F_{3}$	¹ G4	³ D ₃₂₁	³ F ₄₃₂	³ G 543	1234 2345	23 34	(12)

TABLE I. Electron configurations and theoretical terms of the Cs II spectrum.

from the rubidium paper. However, whereas in the Rb II spectrum the coupling was of a type intermediate between the Russell-Saunders and (jj) cases, it is to be expected that in Cs II, as found in Xe I⁵, the coupling will be nearly of the (jj) type and that the two groups of terms having as limits ${}^{2}P_{1/2}$ and ${}^{2}P_{1}{}_{1/2}$ of the Cs III spectrum will be completely separated. This indeed is found to be the case and in fact all of the levels found by Sommer are built upon the $5p^{5} {}^{2}P_{1}{}_{1/2}$ term of Cs III.

The scheme given by Sommer consists of transitions between a middle set of terms and a higher and a lower set. Our knowledge of the similar Rb II and Xe I spectra would identify the middle set of terms as belonging to $5p^5$ 6p and the upper and lower sets respectively to a blend of $5p^5$ 5d and 6s and of $5p^5$ 6d and 7s respectively. The ultraviolet lines must be transitions between the lowest term in the spectrum, $5p^{6}$ $^{1}S_{0}$ and the terms of the configurations $5p^{5}$ (6s, 7s, 5d, 6d) having j=1. Five of the ultraviolet lines in fact may be fitted into Sommer's scheme on this assumption. Table II gives the classified lines of Cs II and relative term values based on ${}^{1}S_{0}=0$. The first and second columns contain the spectroscopic notations⁶ of the levels arising from the $5p^{5}$ 5d, $5p^{5}$ 6d, and $5p^{5}6s$, $5p^{6}7s$ configurations respectively, while the third column contains the J values of these levels. The fourth column con-

⁵ Meggers, de Bruin and Humphreys, B. S. Jour. Research 3, 731 (1929).

				1			man fo aroannala				
1				∘dc							Î
$5p^{5}($	${}^{2}P_{1\frac{1}{2}})5a$	l, 6s		¹ S ₀		1_1	2_{2}	33	4_1	52	60
q	S	J-	Î	0			2	3	1	2	0
		\rightarrow	Rel. Term Value	↑		126518.54	128089.83	129107.65	120080.72	130766_00	133153 54
	${}^3P_2^{\circ}$	2	107392.28°	-		19126.12 (8)	20697.48 (6)	21715.33 (10)	22597.42 (2)	23373.78 (9)	4 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
	${}^{3}P_{1}^{\circ}$		107904.93	107905.	(20)	14 18613.42 (6)	07 20184.84 (6)	04	$\begin{array}{c} 0 \\ 22084.85 \ (7) \end{array}$.06 22861.10 (6)	25248.63 (5)
a •		•	1			19	06		.16	.03	.02
11		-	110945.14	110946	(20)	15573.14(2) - 26	17144.51(6) - 18		19044.61(6)	19820.81(6)	22208.49(7)
22°		7	112795.15			2	15294.63 (3)	16312.38 (4)	17194.57(3)	17970.87 (7)	60.
33°		3	113716.65				$ \frac{-0.05}{-0.05} $ $ \frac{-0.05}{-0.06} $	15390.96(3) 04	Ð	17049.36(1).02	
$5p^{5}($	$({}^{2}P_{\frac{1}{2}})5d,$, 6s							5		
	$\frac{1_{1}^{\circ}}{2_{1}^{\circ}}$		$122872 \\ 123645$	$122872 \\ 123645$	(20) (20)						
$5p^{\circ}(\cdot)$	${}^{2}P_{1\frac{1}{2}})6d$, 7s		1S0		11	22	33	41	52	60
q	S	J-	Î			1	2	3	1	2	0
		→	Rel. Term	Î		126518 37	178080 83	120107 65	1 20080 73	130766.00	122152 54
	$^{3}P_{2}^{\circ}$	2	$\frac{149212.24}{149212.24}$		Ì	22693.82 (7)	21122.47 (4)	20104-64 (5)	71.000071	18446 14 (5)	FC. CCICCI
	0 08		110605 27	140604	(12)	12		.05			
	"F1	-	149005.32	-1.32	(71)	25080.95 (4)	(c) 55.51515 04		19615.46(4) - 14	18839.20(3)	16451.65(2)
110		1	152172.11	152172.	(5)	25653.67 (7)	24082.27(4)		22182.32 (2)	21406.02 (4)	01.
22°		7	152791.47	++.		26273.12 (6)	24701.59 (4)	23683.75 (3)	22801.61(5)	22025.41(6)	
32°		2	153302.26		<u> </u>	26783.83 (2)	$\frac{05}{25212.38}(6)$	07 24194.54 (2)	14 23312.46 (7)	06 22536.21 (0)	
4 ₃ °			153556.59			- 00	05 25466.74 (6)	07	08	05 22790.50 (0)	
53°		3	153678.19				25588.30 (4)	24570.52 (6)		22912.15(9)	
6 ₁ °		1	156399.34	1563927.34	(12)		$\frac{-00}{28309.51}$	07	26409.65(5)	25633.22 (0) - 12	23245.86(6)
505($^{2}P_{\frac{1}{2}})6d,$	75									
	110	1	163180	163180	(1)						

11. TABLE II. Classification of lines of Cs

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tains the relative term values of the levels of these configurations and are referred to the $5p^{6} {}^{1}S_{0}$ level. The headings of the remaining columns give the spectroscopic notations⁶ and relative term values (referred to $5p^{6} {}^{1}S_{0}$) of the levels due to the $5p^{6}$ and $5p^{5}({}^{2}P_{1\frac{1}{2}})$ 6p configurations. In the body of the table are the wave numbers of the spectral lines, followed in parenthesis by their intensities. Below each wave number is the discrepancy (observed value minus calculated value) between the observed wave number and the wave number calculated from the positions assigned to the levels. The scheme is essentially that of Sommer with the addition of terms of relative value 122872, 123645, 133153 and 163180 and the lines arising from them.

Table III contains a list of Cs II lines classified in this investigation. In the first two columns are the intensities obtained in the two investigations; in the third column are the λ 's and the wave numbers in vacuum; the last column contains the classification. $(5p^5)$ is omitted in the classification since it

Int.) air I A	n vac	Classification
М	S		, , , , , , , , , , , , , , , , , , , ,	Classification
7 12 5 12 20 20 20 20	$\begin{array}{c} 0 \\ 2 \\ 5 \\ 0 \\ 6 \\ 0 \\ 0 \\ 7 \\ 0 \\ 0 \\ 4 \\ 0 \\ 6 \\ 0 \\ 5 \\ 0 \\ 6 \\ 0 \\ 4 \\ 6 \\ 0 \\ 2 \\ 4 \\ 0 \\ 3 \\ 0 \\ 9 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 163180\\ 156392\\ 152172\\ 149604\\ 123645\\ 122872\\ 110946\\ 107905\\ 28309.51\\ 26783.83\\ 26409.65\\ 26276.13\\ 26273.12\\ 26270.85\\ 25656.65\\ 25653.67\\ 25651.31\\ 25633.22\\ 25588.30\\ 25469.74\\ 25466.74\\ 25466.74\\ 25466.74\\ 25466.74\\ 25466.74\\ 25248.63\\ 25212.38\\ 25210.13\\ 24270.52\\ 24568.21\\ 24194.54\\ 24082.27\\ 23686.83\\ 23683.75\\ 23376.73\\ 23373.78\\ \end{array}$	$\begin{array}{c} 5p^{6} {}^{1}S_{0} - ({}^{2}P_{3}6d, 7s)1_{1}^{\circ} \\ 5p^{6} {}^{1}S_{0} - ({}^{2}P_{13}6d)1_{1}^{\circ} \\ 5p^{6} {}^{1}S_{0} - ({}^{2}P_{13}6d)1_{1}^{\circ} \\ 5p^{6} {}^{1}S_{0} - ({}^{2}P_{3}5d, 6s)2_{1}^{\circ} \\ 5p^{6} {}^{1}S_{0} - ({}^{2}P_{3}5d, 6s)1_{1}^{\circ} \\ 5p^{6} {}^{1}S_{0} - ({}^{2}P_{3}5d, 6s)1_{1}^{\circ} \\ 5p^{6} {}^{1}S_{0} - ({}^{2}P_{3}6d)1_{1}^{\circ} \\ ({}^{2}P_{13}6p)2_{2} - ({}^{2}P_{13}6d)3_{2}^{\circ} \\ ({}^{2}P_{13}6p)1_{1} - ({}^{2}P_{13}6d)3_{2}^{\circ} \\ ({}^{2}P_{13}6p)1_{1} - ({}^{2}P_{13}6d)2_{2}^{\circ} \\ ({}^{2}P_{13}6p)1_{1} - ({}^{2}P_{13}6d)2_{2}^{\circ} \\ ({}^{2}P_{13}6p)5_{2} - ({}^{2}P_{13}6d)6_{1}^{\circ} \\ ({}^{2}P_{13}6p)2_{2} - ({}^{2}P_{13}6d)6_{1}^{\circ} \\ ({}^{2}P_{13}6p)2_{2} - ({}^{2}P_{13}6d)6_{1}^{\circ} \\ ({}^{2}P_{13}6p)2_{2} - ({}^{2}P_{13}6d)6_{3}^{\circ} \\ ({}^{2}P_{13}6p)2_{2} - ({}^{2}P_{13}6d)6_{3}_{2}^{\circ} \\ ({}^{2}P_{13}6p)2_{2} - ({}^{2}P_{13}6d)2_{3}^{\circ} \\ ({}^{2}P_{13}6p)2_{2} - ({}^{2}P_{13}6d)2_{3}^{\circ} \\ ({}^{2}P_{13}6p)3_{3} - ({}^{2}P_{13}6d)2_{3}^{\circ} \\ ({}^{2}P_{13}6p)3$

TABLE III. Wave-length list of Cs II lines.

⁵ Since it is impossible to assign L and S values to the levels, the levels were numbered according to their order, and the inner quantum number was given as lower index to this number. The odd configurations are indicated with a small zero as upper index.

Int.		. • т л		
M	S	λ air 1.A.	v vac.	Classification
	0	4287.80	23315.43)	
	7	4288.350	23312.46	$({}^{2}P_{1\frac{1}{2}}6p)4_{1} - ({}^{2}P_{1\frac{1}{2}}6d)3_{2}^{\circ}$
	1	4288.755	23310.26	
	6	4300.636	23245.86	$({}^{2}P_{1\frac{1}{2}}6p)6_{0} - ({}^{2}P_{1\frac{1}{2}}6d)6_{1}^{\circ}$
	4	4330.239	23086.95	$({}^{2}P_{1\frac{1}{2}}6p)1_{1} - ({}^{2}P_{1\frac{1}{2}}7s){}^{3}P_{1}{}^{6}$
	0	4362.70	22915.17	$(2\mathbf{D}, C_{1}) = (2\mathbf{D}, C_{1}) = 0$
	9	4303.275	22912.15	$({}^{2}P_{1\frac{1}{2}}0p)5_{2} - ({}^{2}P_{1\frac{1}{2}}0d)5_{3}^{\circ}$
	6	4303.09	22909.97	$(2P_{1}6_{2})^{3}P^{\circ} (2P_{1}6_{2})^{5}$
	0	4373 43	22858 91	$(-1_{\frac{1}{2}},0,0)$ $(-1_{$
	5	4384.428	22801.61	$({}^{2}P_{11}6p)4_{1} - ({}^{2}P_{11}6d)2_{9}^{\circ}$
	ŏ	4386.566	22790.50	$({}^{2}P_{12}O_{12})^{2} - ({}^{2}P_{12}O_{12})^{2}$
	. 7	4405.253	22693.82)	$({}^{2}P_{11}, 6p)1_{1} - ({}^{2}P_{11}, 7s){}^{3}P_{0}^{\circ}$
	0	4405.69	22691.56	
	2	4424.046	22597.42	$({}^{2}P_{1\frac{1}{2}}6s){}^{3}P_{2}{}^{\circ} - ({}^{2}P_{1\frac{1}{2}}6p)4_{1}$
	0	4436.06	22536.21	$({}^{2}P_{1\frac{1}{2}}6p)5_{2} - ({}^{2}P_{1\frac{1}{2}}6d)3_{2}^{\circ}$
	7	4501.525	22208.49	
	0	4501.98	22206.24	$({}^{2}P_{1\frac{1}{2}}5d)1_{1}{}^{0} - ({}^{2}P_{1\frac{1}{2}}6p)6_{0}$
	0	4502.50	22203.30	(2D (1)) = (2D (1)) = 0
		4500.834	22182.32	$({}^{2}P_{1\frac{1}{2}}0p)4_{1} - ({}^{2}P_{1\frac{1}{2}}0a)1_{1}$
		4520.12	22087.79	$(2P_{1}6s)^{3}P_{1}^{\circ} - (2P_{1}6s)^{4}$
	Ó	4520.725	22084.05	$(-1_{\frac{1}{2}},0,0)$ $(-1_{$
	6	4538.942	22025.41	$({}^{2}P_{14}6p)5_{2} - ({}^{2}P_{14}6d)2_{2}^{\circ}$
	ŏ	4539.40	22023.17	
	0	4603.11	21718.37	
	10	4603.755	21715.33	$({}^{2}P_{1\frac{1}{2}}6s){}^{3}P_{2}{}^{\circ} - ({}^{2}P_{1\frac{1}{2}}6p)3_{3}$
	0	4604.24	21713.04	
	5	4646.508	21515.53	$({}^{2}P_{1\frac{1}{2}}6p)2_{2} - ({}^{2}P_{1\frac{1}{2}}7s){}^{3}P_{1}^{\circ}$
	4	4670.280	21406.02	$({}^{2}P_{1\frac{1}{2}}6p)5_{2} - ({}^{2}P_{1\frac{1}{2}}6d)1_{1}^{\circ}$
	4	4732.975	21122.47	$({}^{2}P_{1\frac{1}{2}}6p)2_{2} - ({}^{2}P_{1\frac{1}{2}}7s){}^{3}P_{2}{}^{\circ}$
	6	4830.161	20697.48	$({}^{2}P_{1\frac{1}{2}}0s){}^{3}P_{2}{}^{\circ} - ({}^{2}P_{1\frac{1}{2}}0p)2_{2}$
	0	4952.835	20184.84	$({}^{2}P_{1\frac{1}{2}}0s){}^{9}P_{1}{}^{\circ} - ({}^{2}P_{1\frac{1}{2}}0p)Z_{2}$
	5	4972.393	20104.04	$({}^{2}P_{12})_{3} = ({}^{2}P_{12})_{3} = ({}^{2}$
		5096 604	19620.81	$({}^{-1}_{1\frac{1}{2}}{}^{-1}_{3}{}^{-1}_{3})_{11} = ({}^{-1}_{1\frac{1}{2}}{}^{-1}_{3}{}^{-1}_{3})_{22}$ $({}^{2}P_{-1}{}^{-1}_{3}{}^{-1}_{3})_{42} = ({}^{2}P_{-1}{}^{-1}_{2}{}^{-1}_{3})_{32} P_{-}^{\circ}$
	8	5227 002	19126 12	$({}^{2}P_{11}6){}^{3}P_{0}{}^{\circ} - ({}^{2}P_{11}6b){}^{1}$
	6	5249.373	19044.61	$({}^{2}P_{12},{}^{3}S_{2}) = ({}^{2}P_{12},{}^{6}D_{2}) + ({}^{2}P_{12},$
	3	5306.609	18839.20	$({}^{2}P_{11})^{2}(0,0)^{2}(2,0)^{2}($
	6	5370.979	18613.42	$({}^{2}P_{1\frac{1}{6}}6s){}^{3}P_{1}{}^{\circ} - ({}^{2}P_{1\frac{1}{6}}6p)1_{1}$
	5	5419.687	18446.14	$({}^{2}\dot{P}_{1\frac{1}{2}}\dot{6}\rho)\dot{5}_{2}-({}^{2}P_{1\frac{1}{2}}\dot{7}s)^{3}\dot{P}_{2}^{\circ}$
	7	5563.019	17970.87	$({}^{2}P_{1\frac{1}{2}}5d)2_{2}^{\circ} - ({}^{2}P_{1\frac{1}{2}}6p)5_{2}$
	0	5563.73	17968.59	
	3	5814.181	17194.57	$({}^{2}P_{1\frac{1}{2}}5d)2_{2}^{\circ} - ({}^{2}P_{1\frac{1}{2}}6p)4_{1}$
	5	5831.159	17144.51	$({}^{2}P_{1\frac{1}{2}}5d)1_{1}^{\circ} - ({}^{2}P_{1\frac{1}{2}}6p)2_{2}$
		5803.701	17049.36	$({}^{*}P_{1\frac{1}{2}}5d)5_{3}$ $({}^{2}P_{1\frac{1}{2}}0p)5_{2}$
		6128 610	10451.05	$({}^{2}P_{12}D_{2}D_{2})O_{0} - ({}^{2}P_{12}J_{3}){}^{3}P_{1}$ $({}^{2}P_{2}D_{3}D_{3}D_{3})O_{1} - ({}^{2}P_{12}J_{3}){}^{3}P_{1}$
	4 2	6410 541	15572 14	$({}^{-r} 1^{\frac{1}{2}} J U) L_2 = ({}^{-r} \Gamma 1^{\frac{1}{2}} U D) J_3$ $(2D, 15d) 1 \circ (2D, 16c) 1$
	3	6495 528	14300 06	$(2P_{11}5d)_{3_{0}}^{\circ} - (2P_{11}6b)_{3_{0}}^{\circ}$
	3	6536.440	15294 63	$({}^{2}P_{11}5d){}^{2}{}^{9}-({}^{2}P_{11}6d){}^{2}{}^{9}$
	4	6955.519	14373.12	$({}^{2}P_{1\frac{1}{2}5d}){}^{3}{}^{\circ}-({}^{2}P_{1\frac{1}{2}6p}){}^{2}{}^{2}$
	-			(-1200/00) $(-120F/02)$

TABLE III. (Continued).

is common to all configurations lying above the $5p^{6-1}S_0$ ground state. The odd configurations are indicated by an upper index.

II. INDENTIFICATION OF LEVELS AND CONFIGURATIONS IN CS II

At first inspection, the energy level diagram presented in Table II and schematically in Fig. 1 exhibits a marked difference from the corresponding

diagram for rubidium.⁷ The most characteristic dissimilarity is the smaller number of levels which were found by Sommer, e.g., while in all rare-gas-like spectra, the number of the middle group of p terms is ten, Sommer found only five, to which this present investigation added a sixth level. The explanation of this difference is that due to the large separation of $5p^{5}$ ²P term, which is the limit of these p terms, the ten p levels are split into two groups of 6+4,



Fig. 1. Energy diagram for Cs II.

the inner quantum numbers of which are found under heading (jj) coupling in Table I. Comparing this table with the energy diagram for Cs I, it is seen that the six $5p^{5}6p$ levels which are built upon the lower series limit ${}^{2}P_{1\ 1/2}$ are now all located. Likewise, only that part of the other configurations has been found which is built upon ${}^{2}P_{1\ 1/2}$; this is indicated in our notation by including the symbol ${}^{2}P_{1\ 1/2}$ in the spectroscopic notation.

From this point of view, the explanation of the additional resonance lines $\nu = 122872$, $\nu = 123645$, and $\nu = 163180$ is obvious (Fig. 1): they have as initial levels, those of the $5p^{5}(5d, 6s)$ etc., configurations which are built upon ${}^{2}P_{1/2}$. In Fig. 1 all levels which belong to the limit ${}^{2}P_{1/2}$ are drawn as dashed lines and are shifted slightly to the right.

⁷ See Fig. 2 in reference 1.

⁸ See Fig. 3 under reference 1.

The group of six middle levels must be assigned to $5p^{5}({}^{2}P_{1\ 1/2})6p$. In the following diagram, (Fig. 2) we compare the separation of these levels with the corresponding group in Xe I, reducing, however, the Cs II separations by multiplication with 9120/14270, the ratio of the relativistic doublets in the two cases. There is no crossing over of the levels as in the case of Kr. I, Rb II⁸. In the limit of very high ionization, the six levels will form a group of two having the inner quantum numbers 12 and 0123.

The lower group of levels must be then those due to adding a 5*d* and a 6*s* electron. 6*s* can contribute only two levels. They will have j=2 and 1 respectively, lie close together and the one with j=2 will be the deeper. As there is no other alternative, we choose the lowest two levels, namely $\nu 107392.28$, $\nu 107904.93$ as $^{3}P_{2}$ and $^{3}P_{1}$.



Fig. 2. The $5p^{5}(^{2}P_{11/2})6p$ configurations of Xe I and Cs II referred to the center of gravity and reduced to the same magnitude of the relativistic doublet $5p^{5}$.

As far as the identification of the $5p^{5}({}^{2}P_{1})_{1/2}$ levels is concerned, the result is rather incomplete. As Fig. 1 shows, only three more levels with J = 1, 2, 3 are definitely established, while the J values 0,1,1,2,2,3,3,4, are expected. It seems however that the present experimental data are too scant to locate additional levels. It will be remembered that in the present spectrum, only Sommer's data for the visible are available, while in Rb II, Reinheimmer's wave-lengths were supplemented by Otsuka's measurements in the near ultraviolet.¹

As a glance at the energy diagram (Fig. 1) shows, there is but little ambiguity in identifying the two lowest levels of the upper group $\nu 14912.24$, $\nu 149605.31$ as $5p^{5}({}^{2}P_{1\ 1/2})7s$ ${}^{3}P_{2}$ and ${}^{3}P_{1}$. The fact that they lie well separated from the rest of the levels of that group speaks in favour of this assignment.

The result for the $5p^{5}(^{2}P_{1\ 1/2})6d$ levels is much more complete than for the previous series member. We have two levels each with inner quantum numbers 1, 2, 3, which is indeed what should be expected. Only one level with J=0 and another with J=4 remain to be discovered. It should be remembered however that as the latter one gives only one combination, with the J=3

level of $5p^{5}6p$ there is no way to establish its existence conclusively, until additional configurations with which it might combine are known.

$5p^{6} {}^{1}S_{0} - 5p^{5}({}^{2}P_{\frac{1}{2}})5d, 6s$	$5p^{5}(^{2}P_{\frac{1}{2}})5d, 6s-$	$-5p^{5}(^{2}P_{\frac{1}{2}})6p$	NALISSING TOLES (1999)	<u> </u>	
122872 (20) 773	18689.34 (3) 770.05	1838.72	20528.06 (6) 770.18	1129.12	21657.19 (3) 770.32
123645 (20)	17919.29 (0)	1838.61	19757.88 (3)	1129.09	20886.87 (3)
$\frac{5p^{6} {}^{1}S_{0} - 5p^{5}({}^{2}P_{\frac{1}{2}})}{6d}, 7s$	$5p^{5}(^{2}P_{\frac{1}{2}})6p-5p^{5}$	$({}^{5}({}^{2}P_{\frac{1}{2}})6d, 7s$			
163180 (7)	21624.51 (4)	1838.60	19785.91 (3)	1129.26	18656.65 (0)

TABLE IV. Classification of levels built upon $5p^{5} {}^{2}P_{\frac{1}{2}}$.

It will be remembered that in the spectrum of Rb II¹, the separation of the $p^{5}s$ from the $p^{5}d$ levels was essentially helped by the consideration of the hyperfine structure. The hypothesis was used that levels due to an *s* electron show wider hyperfine separations than those due to *p* or *d* electrons. In caesium however, a similar consideration failed to give any help; because not only is it to be expected that due to the much higher atomic number of caesium even the *p* electrons will split up into hyperfine structure levels, but also do the experimentally recorded hyperfine structure patterns occur in such an apparently haphazard fashion, that it proved to be impossible to correlate them in any way to the levels. The hyperfine structure data in Cs II seem much less complete than those in Rb II.

From Table II the separations between the first and second series numbers of ${}^{s}P_{2}$ and ${}^{s}P_{1}$ are found to be equal to 41820 cm⁻¹ and 41700 cm⁻¹ respectively. With the aid of the Rydberg term tables for spark spectra,⁹ these differences were each fitted into a Rydberg sequence thus giving two independent determinations of the absolute term values:—

$$5s({}^{2}P_{1\frac{1}{2}}){}^{3}P_{2} - 6s({}^{2}P_{1\frac{1}{2}}){}^{3}P_{2} = 41820; \quad 5s({}^{2}P_{1\frac{1}{2}}){}^{3}P_{1} - 6s({}^{2}P_{1\frac{1}{2}}){}^{3}P_{1} = 41700$$
$${}^{3}P_{2} = 81685 \qquad {}^{3}P_{1} = 81505$$
$$5s({}^{2}P_{1\frac{1}{2}}){}^{3}P_{2} - {}^{3}P_{1} = 512$$
$${}^{3}P_{2} = 82017$$

The agreement is fair. If we take the average value of ${}^{3}P_{2} = 81851$, and subtract from it the $\Delta P({}^{3}P_{2} - {}^{3}P_{1} = 512)$, we obtain the ${}^{3}P_{1}$ absolute value as 81339 cm^{-1} . By adding the frequency of the resonance line $\lambda 926.75$, $\nu 107905$ $({}^{1}S_{0} - {}^{3}P_{1})$ to the ${}^{3}P_{1}$ term value we obtain.

$${}^{1}S_{0} = 189244 \text{ cm}^{-1}$$

as the calculated term of the normal caesium ion which corresponds to an ionizing potential of 23.4 volts. Mohler gives 21.5 ± 0.5 volts. It is however to be expected the limit determined from only the first *s*-terms will be somewhat low. The estimate is tentatively included as it seems to be well-founded.

⁹ F. Paschen, J.O.S.A. and R.S.I. 16, 231 (1928).

It was pointed out above that the additional resonance lines $\nu 122872$, $\nu 123645$ ($\Delta \nu = 773$) have as initial levels, those of the $5p^5(5d, 6s)$, while $\nu 163180$ has that of $5p^5(6d, 7s)$; all three combinations are built upon ${}^2P_{1/2}$. Sommer's data have been gone over thoroughly for the difference 773, but so far except for a few differences given in Table IV, we have been unable to find a satisfactory system of levels. An attempt is now being made in this laboratory to extend the experimental data on the spark spectrum of caesium and it is hoped that it will be possible to locate the terms built on the ${}^2P_{1/2}$ limit.

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