Energy levels of singly ionized cesium (Cs II)

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The system of observed energy levels of Cs II of Wheatley and Sawyer has been reinterpreted through the use of Hartree-Fock calculations and published Zeeman effect and hyperfine-structure measurements. Of the 80 known levels, 30 have been rejected as being not real. A revised list of 54 observed levels of Cs II is presented that includes the $5p^5 5d\,^1P_1$ level recently found by Reader and Epstein and three levels of the $5p^5 6d$ configuration that were located with the aid of Sommer's line list. Percentage compositions and Slater parameters are given for the $5p^5(5d+6s)$, $6p$, and $(6d+7s)$ configurations. Severe configuration mixing is found for levels of the $5p^5(5d+6s)$ group. The measured g values of the $5p^5(5d+6s)$ levels provide evidence of a strong term dependence for the parameter $G^1(5p5d)$. By taking into account displacements of the $5p^5ns$ levels due to configuration interaction, the ionization energy is revised to be $186\,600 \pm 150$ cm^{-1} (23.14 ± 0.02 eV).

The singly ionized cesium atom Cs II is isoelectronic with Xe I and thus has a rare-gas-like energy-level structure. Its ground state is $5p^6\,^1S_0$ and its excited configurations are all of the type $5p^5nl$. The early work on the analysis of Cs II was due to Sommer,[1] Laporte, Miller, and Sawyer,[2] and Olthoff and Sawyer.[3]

The list of energy levels for Cs II given by Moore[4] in the *Atomic Energy Levels* (AEL) compilation was obtained from Wheatley and Sawyer.[5] In their paper, as well as in its predecessors, no effort was made to give term assignments to the excited levels. Rather, the levels were assigned J values, numbered serially, and separated according to general configuration groups. For the AEL compilation, Moore[4] assigned tentative $J_1 l$ term names to levels of the $5p^55d$, $6s$, $6p$, $6d$, $7s$, and $7p$ configurations by analogy with Xe I. A number of these term names have been changed in the present work.

The present work is based primarily on two sets of observations for Cs II that were made since AEL was published. In 1966, Zelikina and Semenov[6] measured the Zeeman splittings for 45 lines of Cs II, from which they derived g values for 32 excited levels. More recently, this author and Epstein[7] made new observations of the resonance lines of Cs II, and in so doing found a new $J=1$ level belonging to the $5p^55d$ configuration. On the basis of our isoelectronic comparisons, Epstein and I gave new term designations to most of the known $J=1$ levels. We also derived a value for the ionization energy that was some 15 000 cm^{-1} lower than the previous value.[8]

By combining the above results with earlier hyperfine-structure measurements[8,9] and *ab initio* level-structure calculations, I have now revised and reinterpreted a large portion of the energy-level system of Cs II. On the basis of these revisions, 30 of the 80 presently known levels have been rejected as being not real. Three new levels of $5p^56d$ have been located with the aid of Sommer's line list. Including the new $5p^55d\,^1P_1$ level of Ref. 7, this brings the total number of levels for Cs II to 54. Seven of these levels are considered to be questionable. These results should be of use in interpreting the absorption spectrum of Cs I in the vacuum ultraviolet,[10] in understanding the ionization of neutral Cs by electron impact,[11,12] and in observing metastable excited core states of Cs I in atomic beams.[13]

The revised list of energy levels for Cs II is given in Table I, which also contains the measured g values and magnetic hyperfine-splitting constants a. The level values are those of Wheatley and Sawyer,[5] increased by 8.91 cm^{-1} to put them on an energy scale relative to the ground state indicated by the measurements of Ref. 7.

CONFIGURATIONS

$5p^5(5d+6s)$ configurations

The structure of the $5p^5(5d+6s)$ group of levels is shown in Fig. 1. The $5p^55d$ levels are drawn as solid bold lines, the $5p^56s$ levels as dashed lines, and the predicted positions of unknown levels of $5p^55d$ as thin lines. The interpretation of these levels was carried out in the following way.

First, *ab initio* values for the Slater parameters were calculated with the Hartree-Fock (HF) program of C. Froese Fischer.[14] These values were then scaled by factors taken from a least-squares

TABLE I. Energy levels of Cs II. The magnetic hyperfine-splitting constants a are given in cm^{-1}.

Configuration	Term	J	E (cm^{-1})	g value	a value
$5p^6$	^1S	0	0.0		
$5p^5 6s$	$\frac{3}{2}[\frac{3}{2}]$	2	107 401.24	1.49 ± 0.03	0.0544
	$\frac{3}{2}[\frac{3}{2}]$	1	110 954.09	1.24 ± 0.02	0.0095
	$\frac{1}{2}[\frac{1}{2}]$	0	122 374.42		
	$\frac{1}{2}[\frac{1}{2}]$	1	122 874.94	1.12 ± 0.02	0.168
$5p^5 5d$	^3P	0	107 572.05		
	^3P	1	107 913.92	1.37 ± 0.02	~0
	^3P	2	112 803.99		
	^3F	4	112 245.44		
	^3F	3	113 725.52		
	^3D	1	123 645.35	0.70 ± 0.02	0.0117
	^1P	1	139 249.0 [a]		
$5p^5 6p$	$\frac{3}{2}[\frac{1}{2}]$	1	126 527.45	1.87 ± 0.03	0.0285
	$\frac{3}{2}[\frac{5}{2}]$	2	128 098.74	1.10 ± 0.02	0.0321
	$\frac{3}{2}[\frac{5}{2}]$	3	129 116.56	1.33 ± 0.02	0.0195
	$\frac{3}{2}[\frac{3}{2}]$	1	129 998.63	1.02 ± 0.02	0.0265
	$\frac{3}{2}[\frac{3}{2}]$	2	130 774.91	1.34 ± 0.02	
	$\frac{3}{2}[\frac{1}{2}]$	0	133 162.45		
	$\frac{1}{2}[\frac{3}{2}]$	1	141 564.50	0.68 ± 0.01	0.137
	$\frac{1}{2}[\frac{1}{2}]$	1	143 361.03	1.44 ± 0.03	−0.049
	$\frac{1}{2}[\frac{3}{2}]$	2	143 403.10	1.12 ± 0.03	0.064
	$\frac{1}{2}[\frac{1}{2}]$	0	144 532.36		
$5p^5 7s$	$\frac{3}{2}[\frac{3}{2}]$	2	149 221.16	1.50 ± 0.03	
	$\frac{3}{2}[\frac{3}{2}]$	1	149 614.24	1.18 ± 0.02	
	$\frac{1}{2}[\frac{1}{2}]$	0	163 033.71		
	$\frac{1}{2}[\frac{1}{2}]$	1	163 189.11	1.38 ± 0.02	0.144
$5p^5 6d$	$\frac{3}{2}[\frac{1}{2}]$	0	151 682.30 [b]	0.00 ± 0.04 [c]	
	$\frac{3}{2}[\frac{1}{2}]$	1	152 181.02	1.24 ± 0.02	
	$\frac{3}{2}[\frac{7}{2}]$	4	152 558.43 [b]	1.27 ± 0.04 [d]	
	$\frac{3}{2}[\frac{3}{2}]$	2	152 800.40	1.33 ± 0.02	
	$\frac{3}{2}[\frac{7}{2}]$	3	152 845.23 [b]	1.07 ± 0.03 [e]	
	$\frac{3}{2}[\frac{5}{2}]$	2	153 311.18	0.97 ± 0.02	
	$\frac{3}{2}[\frac{5}{2}]$	3	153 687.08	1.20 ± 0.02	
	$\frac{3}{2}[\frac{3}{2}]$	1	156 408.22	0.89 ± 0.07	
	$\frac{1}{2}[\frac{5}{2}]$	2	166 696.00		
	$\frac{1}{2}[\frac{3}{2}]$	2	166 970.48	1.30 ± 0.03	
	$\frac{1}{2}[\frac{5}{2}]$	3	167 024.88	1.10 ± 0.02	
	$\frac{1}{2}[\frac{3}{2}]$	1	169 192.31		

TABLE I *(Continued)*

Configuration	Term	J	E (cm^{-1})	g value	a value
$5p^5 7p$	$\frac{3}{2}[\frac{1}{2}]$	1	155 974.36?		
	$\frac{3}{2}[\frac{5}{2}]$	2	156 124.09?		
	$\frac{3}{2}[\frac{5}{2}]$	3	156 522.07?		
	$\frac{3}{2}[\frac{3}{2}]$	2	156 766.21?		
	$\frac{3}{2}[\frac{3}{2}]$	1	157 071.37?		
	$\frac{3}{2}[\frac{1}{2}]$	0	157 752.19?		
$5p^5 8s$	$\frac{3}{2}[\frac{3}{2}]$	2	164 453.79		
	$\frac{3}{2}[\frac{3}{2}]$	1	164 665.68	1.20 ± 0.02	
$5p^5 7d$	$\frac{3}{2}[\frac{1}{2}]$	1	165 822.61		
	$\frac{3}{2}[\frac{3}{2}]$	2	165 898.99		
	$\frac{3}{2}[\frac{7}{2}]$	3	166 126.63	1.08 ± 0.02	
	$\frac{3}{2}[\frac{5}{2}]$	2	166 140.02	0.93 ± 0.02	
	$\frac{3}{2}[\frac{5}{2}]$	3	166 609.65		
	$\frac{3}{2}[\frac{3}{2}]$	1	167 443.82?		
	$\frac{1}{2}[\frac{3}{2}]$	1	177 252.41		
$5p^5 8d$	$\frac{3}{2}[\frac{3}{2}]$	1	173 816 [a]		

[a] Determined by resonance line of Reader and Epstein, Ref. 7.
[b] New level.
[c] Derived from Zeeman splitting of line at 3974.329 Å.
[d] Derived from Zeeman splitting of line at 4264.675 Å.
[e] Derived from Zeeman splitting of line at 4039.841 Å.

fit of the $5p^5(5d+6s)$ configuration[15] of La IV and used to diagonalize the energy matrix, configuration interaction not being included. The calculated level positions and g values are shown in Fig. 2. In this figure the absolute energies of the $5p^5 5d$ and $5p^5 6s$ configurations have been chosen so as to obtain approximate agreement with the experimental energies of the $J=1$ levels given in Ref. 7. By comparing these results with the experimental level data, a set of 11 levels was extracted from the 16 published levels of this group as being valid. The absolute heights of the calculated $5p^5 5d$ and $5p^5 6s$ configurations were then adjusted to make the level in each configuration least likely to be perturbed by configuration interaction, $6s\,\frac{1}{2}[\frac{1}{2}]_0$ and $5d\,^3F_3$, agree with its experimental position, and the configuration-interaction parameters introduced into the calculation at 90% of their HF values. The new calculated level positions and g values are shown in Fig. 3. As can be seen the level positions and g values in general agree well with the observed levels, thus verifying our initial selection of levels and over-all interpretation.

The main exception to the good agreement between the calculated and observed $5p^5(5d+6s)$ levels occurs for $5p^5 5d\,^1P_1$, where the difference between the calculated and observed positions is nearly 5000 cm^{-1}. Since this discrepancy is closely related to the value of the parameter $G^1(5p5d)$, a new calculation was carried out with a value of $G^1(5p5d)$ reduced to 18 600 cm^{-1} from its initial scaled HF value of 22 000 cm^{-1}. The results are shown in Fig. 4, where by comparison with Fig. 1 the agreement between calculated and observed energies is seen to be very good. However, the agreement between the calculated and observed g values of the $6s\,\frac{1}{2}[\frac{1}{2}]_1$ and $5d\,^3D_1$ levels is now rather poor. Clearly the degree of configuration mixing for these levels indicated by the calculated g values considerably exceeds that indicated by the measured g values.

It might seem that the degree of configuration mixing between $6s\,\frac{1}{2}[\frac{1}{2}]_1$ and $5d\,^3D_1$ could be reduced by varying the configuration-interaction parameters $R^1(5p5d, 6s5p)$ and $R^2(5p5d, 5p6s)$. However, since the configuration interaction between the $6s\,\frac{3}{2}[\frac{3}{2}]_1$ and $5d\,^3P_1$ levels and also between the $6s\,\frac{3}{2}[\frac{3}{2}]_2$ and $5d\,^3P_2$ levels depends almost exclusive-

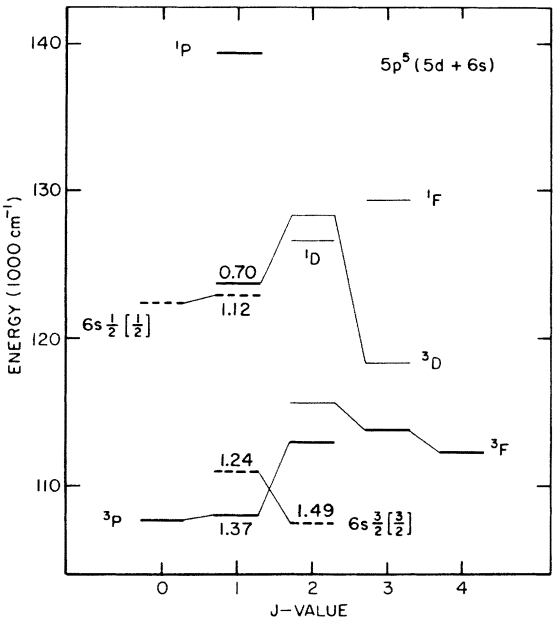

FIG. 1. Experimental energies and g values for levels of the $5p^5 5d$ and $5p^5 6s$ configurations. Levels of $5p^5 5d$, indicated as full lines, are designated in the LS-coupling scheme. Levels of $5p^5 6s$, indicated as dashed lines, are designated in the J_1l-coupling scheme. Predicted positions of the five unknown levels of $5p^5 5d$ are shown as thin lines.

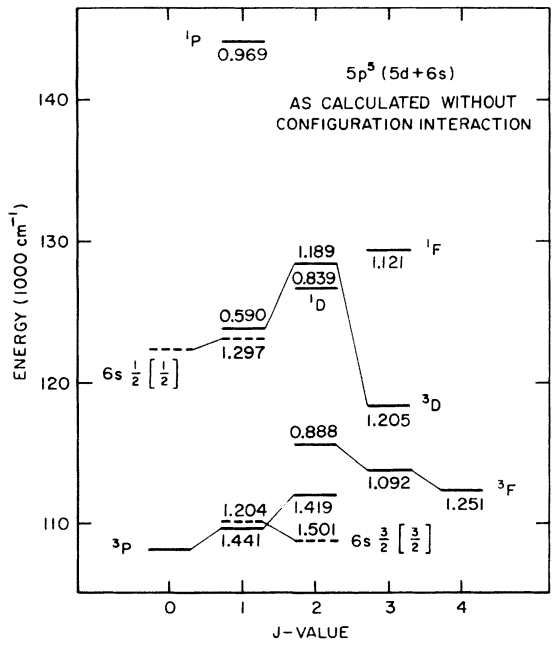

FIG. 2. Calculated level positions and g values of the $5p^5 5d$ and $5p^5 6s$ configurations without configuration interaction. Levels of $5p^5 6s$ are shown as dashed lines. Parameters (in cm^{-1}) used for calculation: $F^2(5p\,5d) = 23\,558$, $G^1(5p\,5d) = 22\,000$, $G^3(5p\,5d) = 16\,630$, $\zeta_{5p}(5p^5 5d) = 8784$, $\zeta_{5d} = 314$; $G^1(5p\,6s) = 3416$, $\zeta_{5p}(5p^5 6s) = 9033$.

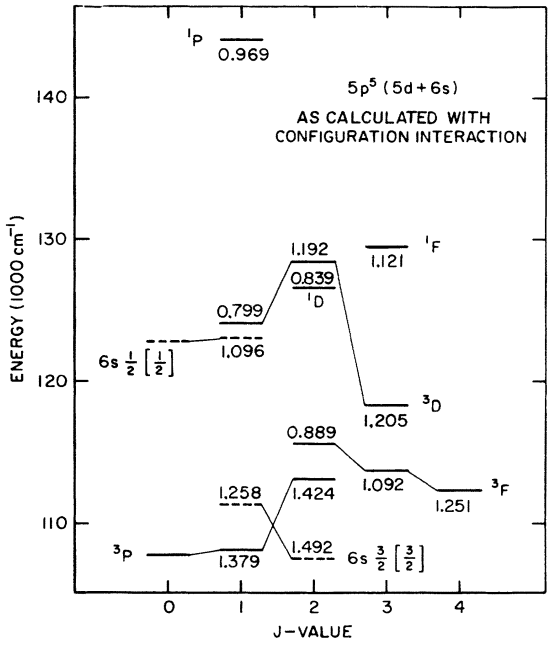

FIG. 3. Calculated level positions and g values of the $5p^5 5d$ and $5p^5 6s$ configurations with configuration interaction. Configuration interaction parameters (in cm^{-1}): $R^2(5p\,5d, 5p\,6s) = -8198$; $R^1(5p\,5d, 6s5p) = -2235$.

ly on R^2, and since these levels are already very well described by the calculation, the value of R^2 cannot be changed significantly. This leaves only R^1 available for variation. However, in order to

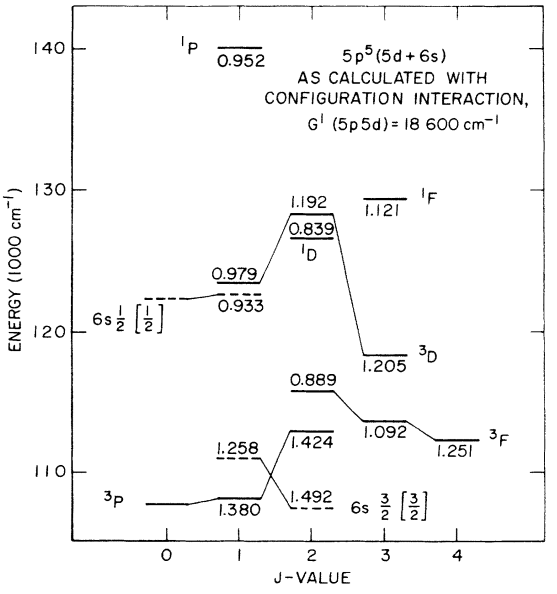

FIG. 4. Calculated level positions and g values of the $5p^5 5d$ and $5p^5 6s$ configurations with configuration interaction and a value of $G^1(5p\,5d)$ reduced to 18 6000 cm^{-1} in order to fit the $5d\,^1P_1$ level.

TABLE II. Energy parameters in cm^{-1} for Cs II. For $5p^5 5d$ and $6s$, the fitted values represent HF values scaled according to La IV. The values of $E_{av}(5p^5 5d)$ and $E_{av}(5p^5 6s)$ were varied to produce a good energy fit. The value of $G^1(5p5d)$ was varied to produce a good fit for g values. $R^2(5p5d, 5p6s)$ and $R^1(5p5d, 6s5p)$ were scaled at 90% of their HF values.

Configuration	Parameter	HF	Fitted	Fitted/HF
$5p^5 5d$	E_{av}	117 654	120 017	
	$F^2(5p5d)$	30 957	23 558	
	$G^1(5p5d)$	34 000	24 750	
	$G^3(5p5d)$	20 839	16 630	
	ζ_{5p}	7 540	8 784	
	ζ_{5d}	293	314	
$5p^5 6s$	E_{av}	115 296	113 493	
	$G^1(5p6s)$	3416(0.41)[a]	3 136	
	ζ_{5p}	7 753	9 033	
Configuration interaction	$R^2(5p5d, 5p6s)$	−9 102(−0.55)	−8 198	
	$R^1(5p5d, 6s5p)$	−2 482(−0.15)	−2 235	
$5p^5 6p$	E_{av}	129 683	133 810± 5	
	$F^2(5p6p)$	9 015	8 318± 51	0.923± 0.006
	$G^0(5p6p)$	1 448(0.20)	1 409± 4	0.973± 0.003
	$G^2(5p6p)$	1 998(0.62)	1 976± 68	0.989± 0.034
	ζ_{5p}	7 824	9 084± 7	1.161± 0.001
	ζ_{6p}	608	1 054± 8	1.735± 0.013
$5p^5 6d$	E_{av}	152 496	157 749± 15	
	$F^2(5p6d)$	6 040	4 527± 82	0.750± 0.014
	$G^1(5p6d)$	5 200	5 125± 40	0.986± 0.008
	$G^3(5p6d)$	3 355	2 873± 159	0.856± 0.047
	ζ_{5p}	7 802	9 070[b]	
	ζ_{6d}	61	69± 8	1.12 ± 0.13
$5p^5 7s$	E_{av}	150 821	154 011± 14	
	$G^1(5p7s)$	956(0.39)	792± 59	0.83 ± 0.06
	ζ_{5p}	7 823	9 094± 24	1.162± 0.003
Configuration interaction	$R^2(5p6d, 5p7s)$	−1 887(−0.48)	−2 668± 275	1.41 ± 0.15
	$R^1(5p6d, 7s5p)$	−260(−0.07)	−367[c]	

[a] Values in parentheses are the ratio of the calculated parameter to a value calculated by using the absolute value of each wave function.

[b] Fixed at HF ratio to ζ_{5p} $(5p^5 7s)$.

[c] Fixed at HF ratio to $R^2(5p6d, 5p7s)$.

obtain good agreement for the g values by varying R^1, R^1 must be increased to nearly three times its scaled HF value. (It might be noted that R^1 and R^2 enter into the energy matrix with opposite signs, which explains the necessity of having to increase the value of R^1 in order to reduce the configuration interaction.) As there is no reason to believe that the HF calculation can be in error to this extent, both as to the value of R^1 and as to the ratio of R^1 to R^2, we conclude that it is not possible to reduce the configuration interaction between $6s\,\frac{1}{2}[\frac{1}{2}]_1$ and $5d\,^3D_1$ by making reasonable variations of R^1 and R^2.

Of course, to a first approximation the two levels involved here do not mix at all, because the $5p^5 6s$ level has a completely pure P character and the $5d\,^3D_1$ level a nearly pure D character. Thus these two levels interact only to the extent that the level designated as $5d\,^3D_1$ contains some admixture of $5p^5 5d\,^3P_1$ or $^1P_1$. Thus the $6s\,\frac{1}{2}[\frac{1}{2}]_1$ level of Cs II acts as an internal probe of the P character of the $5p^5 5d\,^3D_1$ level.

As may be inferred from the calculations already described, the admixture of P type states of $5p^5 5d$ into the $5p^5 5d\,^3D_1$ level is very sensitive to the variation of $G^1(5p5d)$. It is also true that this admixture is rather insensitive to the variation of the other parameters. Thus the presence of the $6s\,\frac{1}{2}[\frac{1}{2}]_1$ level in effect serves to measure the value of $G^1(5p5d)$ applicable to this part of the $5p^5 5d$ configuration. This may be contrasted with the situation found in most $np^5 nd$ configurations,

TABLE III. Calculated energy-level values in cm^{-1}, g values, and percentage compositions for the $5p^5(5d+6s)$ configurations of Cs II. Percentages for $5p^5 5d$ are given in LS coupling; percentages for $5p^5 6s$ are in $J_1 l$ coupling. States of $5p^5 6s$ are denoted by an asterisk. Calculation is described in text.

J	E (obs)	E (calc)	obs − calc	g (obs)	g (calc)	Percent $J_1 l$	Percentage composition
0	107 572	107 703	−131			97% $\frac{3}{2}[\frac{1}{2}]$	97% ^3P; 3% $\frac{1}{2}[\frac{1}{2}]^*$
	122 374	122 380	−6			97% $\frac{1}{2}[\frac{1}{2}]^*$	97% $\frac{1}{2}[\frac{1}{2}]^*$; 3% ^3P
1	107 914	108 027	−113	1.37	1.378	39% $\frac{3}{2}[\frac{1}{2}]$	56% ^3P; 39% $\frac{3}{2}[\frac{3}{2}]^*$; 3% ^3D
	110 954	110 917	37	1.24	1.258	61% $\frac{3}{2}[\frac{3}{2}]^*$	61% $\frac{3}{2}[\frac{3}{2}]^*$; 36% ^3P; 3% ^3D
	122 875	122 798	77	1.12	1.154	81% $\frac{1}{2}[\frac{1}{2}]^*$	81% $\frac{1}{2}[\frac{1}{2}]^*$; 18% ^3D; 1% ^1P
	123 645	123 962	−317	0.70	0.733	39% $\frac{3}{2}[\frac{3}{2}]$	71% ^3D; 17% $\frac{1}{2}[\frac{1}{2}]^*$; 7% ^3P
	139 249	147 467	−8218		0.978	58% $\frac{1}{2}[\frac{3}{2}]$	94% ^1P; 5% ^3D; 1% ^3P
2	107 401	107 454	−53	1.49	1.492	82% $\frac{3}{2}[\frac{3}{2}]^*$	82% $\frac{3}{2}[\frac{3}{2}]^*$; 15% ^3P; 2% ^3D
	112 804	112 869	−65		1.424	76% $\frac{3}{2}[\frac{3}{2}]$	63% ^3P; 17% $\frac{3}{2}[\frac{3}{2}]^*$; 15% ^3D
		115 688			0.889	94% $\frac{3}{2}[\frac{5}{2}]$	44% ^3F; 35% ^1D; 20% ^3D
		126 604			0.839	94% $\frac{1}{2}[\frac{5}{2}]$	55% ^3F; 31% ^1D; 14% ^3D
		128 291			1.192	91% $\frac{1}{2}[\frac{3}{2}]$	50% ^3D; 28% ^1D; 21% ^3P
3	113 726	113 576	150		1.092	77% $\frac{3}{2}[\frac{7}{2}]$	74% ^3F; 17% ^1F; 9% ^3D
		118 281			1.205	80% $\frac{3}{2}[\frac{5}{2}]$	61% ^3D; 39% ^1F
		129 390			1.121	96% $\frac{1}{2}[\frac{5}{2}]$	44% ^1F; 30% ^3D; 26% ^3F
4	112 245	112 230	15		1.251	100% $\frac{3}{2}[\frac{7}{2}]$	100% ^3F

where the value of $G^1(npnd)$ is determined entirely by the position of the high-lying $^1P_1$ level.

The incompatibility of the value of $G^1(5p5d)$ needed to fit $5d\ ^1P_1$ (~17 800 cm^{-1}) with the value needed to obtain good g values for the $6s\ \frac{1}{2}[\frac{1}{2}]_1$ and $5d\ ^3D_1$ levels (~24 800 cm^{-1}) implies a sizable term dependence of $G^1(5p5d)$ in the $5p^5 5d$ configuration of Cs II. Hansen[16] has discussed the possibility of a term dependence of $G^1(pd)$ for $np^5 nd$ configurations from the point of view of the discrepancies between fitted and HF values of $G^1(pd)$.[17] The energy levels of Cs II provide an example of such a term dependence from an almost purely experimental point of view.[18]

For our final calculation of the $5p^5(5d+6s)$ levels, the value of $G^1(5p5d)$ was chosen to obtain a reasonably good fit for the g values of $6s\ \frac{1}{2}[\frac{1}{2}]_1$ and $5d\ ^3D_1$, without changing the other parameters. The average energies of the two configurations were chosen to obtain a reasonably good over-all fit for the energies, the resultant average absolute difference between the observed and calculated level values being 96 cm^{-1}, not including $5d\ ^1P_1$. A better fit could probably be obtained by varying the other parameters, but until the $5d$ configuration is completed, further adjustment of the parameters would be unwarranted.

The values of the parameters used for the final calculation of $5p^5(5d+6s)$ and the HF values are given in Table II.[19] The calculated level values, g values, and percentage compositions are given in Table III. It should be noted that even though this calculation is somewhat preliminary, the percentage compositions are relatively insensitive to changes in the parameters and thus represent fairly accurately (~±2%) the mixing of states for these levels. A more accurate measurement of the g values would be of considerable importance for the further theoretical interpretation of the $(5d+6s)$ group, because the sum of the experimental g values for the four lower $J=1$ levels, 4.43, does not agree extremely well with the theoretical sum of 4.531. Further work might also be done to account quantitatively for the observed hyperfine-splitting constants in terms of the calculated eigenvectors, but this is beyond the scope of this paper.

$5p^5 6p$ configuration

All of the $5p^5 6p$ levels appear to be valid. The configuration is thus complete. Zelikina and Semenov have measured g values for all ten of its lev-

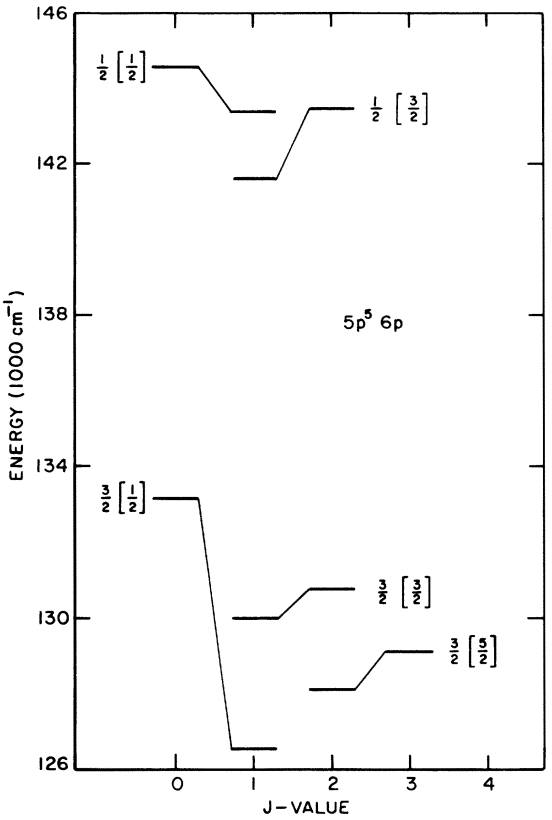

FIG. 5. Structure of the $5p^5 6p$ configuration. The levels are designated in the J_1l-coupling scheme.

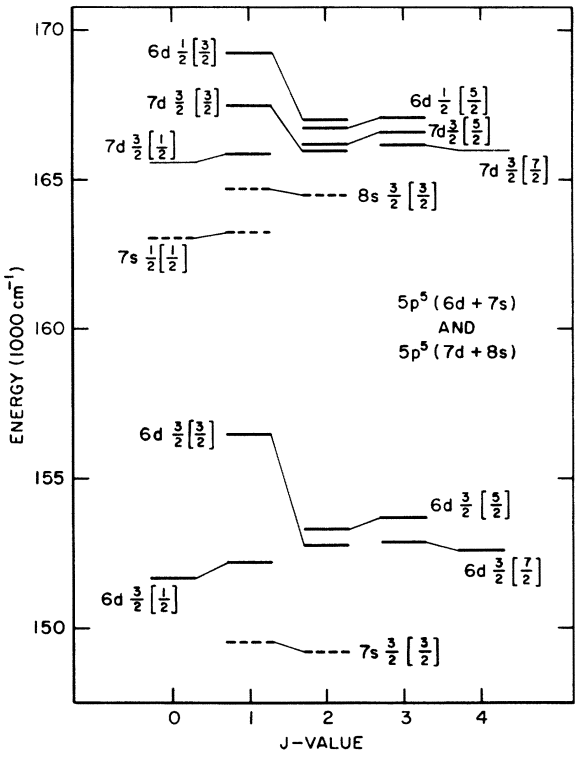

FIG. 6. Structure of the $5p^5 6d$, $7d$, $7s$, and $8s$ configurations. All levels are designated in J_1l coupling. Predicted positions of the $7d\,\frac{3}{2}[\frac{1}{2}]_0$ and $7d\,\frac{3}{2}[\frac{7}{2}]_4$ levels are indicated by thin lines.

els, and their measured values are in good agreement with the calculated values. The hyperfine-splitting constants[8,9] have relative values that are similar to those measured for the analogous levels of $4p^5 5p$ of Rb II by Kopfermann, Steudel, and Trier.[20] The structure of the $5p^5 6p$ configuration of Cs II is shown in Fig. 5.

The results of fitting the energy parameters to

TABLE IV. Calculated energy-level values in cm^{-1}, g values, and percentage compositions for the $5p^5 6p$ configuration of Cs II. Negative eigenvector components are preceded by a minus sign. Mean error of level fit = 15 cm^{-1}.

J	E (obs)	E (calc)	obs − calc	g (obs)	g (calc)	Percent J_1l	Percentage composition—LS
0	133 162	133 161	1			98% $\frac{3}{2}[\frac{1}{2}]$	−52% ^1S + 48% ^3P
	144 532	144 531	1			98% $\frac{1}{2}[\frac{1}{2}]$	52% ^3P + 48% ^1S
1	126 527	126 538	−11	1.87	1.862	93% $\frac{3}{2}[\frac{1}{2}]$	75% ^3S + 23% ^3P
	129 999	130 013	−14	1.02	1.028	94% $\frac{3}{2}[\frac{3}{2}]$	57% ^1P − 21% ^3D − 18% ^3P
	141 564	141 557	7	0.68	0.656	92% $\frac{1}{2}[\frac{3}{2}]$	72% ^3D + 26% ^1P − 1% ^3S
	143 361	143 363	−2	1.44	1.454	91% $\frac{1}{2}[\frac{1}{2}]$	−59% ^3P + 19% ^3S − 16% ^1P
2	128 099	128 094	5	1.10	1.130	89% $\frac{3}{2}[\frac{5}{2}]$	53% ^3D − 39% ^1D + 8% ^3P
	130 775	130 775	0	1.34	1.360	89% $\frac{3}{2}[\frac{3}{2}]$	72% ^3P + 27% ^1D + 1% ^3D
	143 403	143 409	−6	1.12	1.177	100% $\frac{1}{2}[\frac{3}{2}]$	−46% ^3D − 34% ^1D + 20% ^3P
3	129 117	129 096	21	1.33	1.333	100% $\frac{3}{2}[\frac{5}{2}]$	100% ^3D

TABLE V. Lines used to establish the $5p^5 6d\,\frac{3}{2}[\frac{1}{2}]_0$, $\frac{3}{2}[\frac{7}{2}]_3$, and $\frac{3}{2}[\frac{7}{2}]_4$ levels. Wavelengths, intensities, and wave numbers taken from Sommer, Ref. 1; Zeeman data taken from Zelikina and Semenov, Ref. 6; components are given as displacements from center of pattern in Lorentz units.

λ (Å)	I	σ (cm^{-1})	Classification	Zeeman pattern
3974.239	6	25 154.96	$5p^5 6p\,\frac{3}{2}[\frac{1}{2}]_1$-$5p^5 6d\,\frac{3}{2}[\frac{1}{2}]_0$	(0)1.86 ± 0.03
4610.505	2	21 683.55	$\frac{3}{2}[\frac{3}{2}]_1$- $\frac{3}{2}[\frac{1}{2}]_0$	
4039.841	9	24 746.49	$5p^5 6p\,\frac{3}{2}[\frac{5}{2}]_2$-$5p^5 6d\,\frac{3}{2}[\frac{7}{2}]_3$	(0)1.02 ± 0.02
4213.129 [a]	6	23 728.67	$\frac{3}{2}[\frac{5}{2}]_3$- $\frac{3}{2}[\frac{7}{2}]_3$	
4264.675	10	23 441.87	$5p^5 6p\,\frac{3}{2}[\frac{5}{2}]_3$-$5p^5 6d\,\frac{3}{2}[\frac{7}{2}]_4$	(0)1.09 ± 0.03

[a] Previously classified as a transition to level 11^o_2 at 119 665.41 cm^{-1}, which has now been rejected.

the observed levels by a least-squares calculation are given in Tables II and IV. As shown in Table IV, the coupling is approximately $J_1 l$.

$5p^5(6d+7s)$ and higher odd configurations

These levels were interpreted by a procedure similar to that used for the $5p^5(5d+6s)$ levels, although configuration interaction was relatively unimportant for the $(6d+7s)$ group. The $5p^5(6d+7s)$ levels are plotted in Fig. 6, along with levels of the $5p^5 7d$ and $8s$ configurations. The $7s$ and $8s$ levels are shown as dashed lines. The predicted positions of the $7d\,\frac{3}{2}[\frac{1}{2}]_0$ and $7d\,\frac{3}{2}[\frac{7}{2}]_4$ levels are shown as thin lines.

The $5p^5 6d\,\frac{3}{2}[\frac{1}{2}]_0$, $\frac{3}{2}[\frac{7}{2}]_3$, and $\frac{3}{2}[\frac{7}{2}]_4$ levels were newly found here by using Sommer's line list and the Zeeman data of Zelikina and Semenov. The lines

TABLE VI. Calculated energy-level values in cm^{-1}, g values, and percentage compositions for the $5p^5(6d+7s)$ configurations of Cs II. Negative eigenvector components are preceded by a minus sign. States of $5p^5 7s$ are denoted by an asterisk. Mean error of level fit = 20 cm^{-1}.

J	E (obs)	E (calc)	obs − calc	g (obs)	g (calc)	Percent $J_1 l$	Percentage composition—LS
0	151 682	151 690	−8			99% $\frac{3}{2}[\frac{1}{2}]$	99% ^3P − 1% $^3P^*$
	163 034	163 023	11			99% $\frac{3}{2}[\frac{1}{2}]^*$	99% $^3P^*$ + 1% ^3P
1	149 614	149 610	4	1.18	1.183	98% $\frac{3}{2}[\frac{3}{2}]^*$	63% $^1P^*$ + 35% $^3P^*$ − 2% ^3P
	152 181	152 159	22	1.24	1.334	60% $\frac{3}{2}[\frac{1}{2}]$	82% ^3P − 15% ^3D + 2% $^1P^*$
	156 408	156 408	0	0.89	0.792	60% $\frac{3}{2}[\frac{3}{2}]$	−48% ^3D + 46% ^1P − 6% ^3P
	163 189	163 198	−9	1.38	1.326	99% $\frac{1}{2}[\frac{1}{2}]^*$	65% $^3P^*$ − 35% $^1P^*$
	169 192 [a]	169 101	91 [a]		0.866	96% $\frac{1}{2}[\frac{3}{2}]$	54% ^1P + 36% ^3D + 10% ^3P
2	149 221	149 226	−5	1.50	1.498	97% $\frac{3}{2}[\frac{3}{2}]^*$	97% $^3P^*$ − 2% ^3P
	152 800	152 815	−15	1.33	1.335	96% $\frac{3}{2}[\frac{3}{2}]$	54% ^3P − 33% ^3D + 11% ^1D
	153 311	153 310	1	0.97	0.959	98% $\frac{3}{2}[\frac{5}{2}]$	51% ^1D − 25% ^3F + 23% ^3D
	166 696 [a]	166 271	425 [a]		0.770	98% $\frac{1}{2}[\frac{5}{2}]$	−73% ^3F − 21% ^1D − 5% ^3D
	166 970 [a]	166 496	474 [a]	1.30	1.273	97% $\frac{1}{2}[\frac{3}{2}]$	43% ^3P + 39% ^3D − 17% ^1D
3	152 845	152 855	−10	1.07	1.087	84% $\frac{3}{2}[\frac{7}{2}]$	59% ^3F + 30% ^1F − 11% ^3D
	153 687	153 679	8	1.20	1.216	84% $\frac{3}{2}[\frac{5}{2}]$	65% ^3D + 35% ^1F
	167 025 [a]	166 797	228 [a]	1.10	1.114	100% $\frac{1}{2}[\frac{5}{2}]$	41% ^3F − 35% ^1F + 24% ^3D
4	152 558	152 560	−2	1.27	1.251	100% $\frac{3}{2}[\frac{7}{2}]$	100% ^3F

[a] Not included in least-squares fit.

TABLE VII. Calculated displacements of Cs II levels due to configuration interaction. A negative displacement indicates that the level has been displaced to lower energy.

Level (cm^{-1})	Designation	Displacement (cm^{-1})
107572	$5d\,^3P_0$	−376
107401	$6s\,\frac{3}{2}[\frac{3}{2}]_2$	−1000
107914	$5d\,^3P_1$	−1377
110954	$6s\,\frac{3}{2}[\frac{3}{2}]_1$	1144
112804	$5d\,^3P_2$	939
122374	$6s\,\frac{1}{2}[\frac{1}{2}]_0$	376
122874	$6s\,\frac{1}{2}[\frac{1}{2}]_1$	22
123645	$5d\,^3D_1$	208
149221	$7s\,\frac{3}{2}[\frac{3}{2}]_2$	−106
149614	$7s\,\frac{3}{2}[\frac{3}{2}]_1$	−70
163034	$7s\,\frac{1}{2}[\frac{1}{2}]_0$	50
163189	$7s\,\frac{1}{2}[\frac{1}{2}]_1$	44

used to establish these three levels are listed in Table V.

As shown in Fig. 6 the low part of the $5p^57d$ configuration lies just below the high part of the $5p^56d$ configuration. This causes the high part of the $5p^56d$ configuration to be displaced to higher energies by several hundred cm^{-1}. Because of these perturbations, the $5p^5(^2P_{1/2})6d$ levels were omitted from the least-squares fit for the $5p^5(6d+7s)$ levels given in Tables II and VI.

The high-lying experimental levels of odd parity that have been rejected all fall in regions where no levels are to be expected. For example, the levels listed in AEL at about 170000 cm^{-1} are too low to belong to either the high part of $5p^57d$ or to the low part of $5p^58d$, expected at about 172500 cm^{-1}. The levels 47^o_3 and 48^o_3 might possibly be part of $5p^58d$, but they do not appear to be well established and have not been retained.

$5p^57p$ and nf configurations

Several of the levels Wheatley and Sawyer designated as $5p^57p$ have been included in Table I, although confirmation of their reality is definitely needed. The levels in AEL designated as $5p^5nf$ all lie above the ionization limit and have been dropped. The $5p^5(^2P_{3/2})4f$ levels are expected to lie at about 152000 cm^{-1}, the $5p^5(^2P_{1/2})4f$ levels at about 166000 cm^{-1}.

IONIZATION ENERGY

The revised value of Ref. 7 for the ionization energy of Cs II, 186900 cm^{-1}, was obtained by calculating the limit of the series of $J=1$ levels, $5p^5(^2P_{3/2})ns$, $n=6$, 7, 8, and the limit of the series of $J=1$ levels, $5p^5(^2P_{1/2})ns$, $n=6$, 7, assuming that $\Delta n^*(7s-6s)=1.050\pm0.005$. The uncertainty of ±300 cm^{-1} was intended to allow for possible displacements of the $5p^56s$ levels owing to interaction with levels of $5p^55d$.

The present calculations show that these displacements are indeed significant, and that the ionization energy should be further revised downward. The calculated displacements of the relevant levels owing to configuration interaction are listed in Table VII. The effect of these calculated displacements on the series limits is shown in Table VIII. According to these results we adopt a value for the ionization energy of Cs II of 186600 ±150 cm^{-1} (23.14 ± 0.02 eV).

TABLE VIII. Limits of $5p^5ns$ series of Cs II calculated with configuration interaction taken into account. Limits for series based on $^2P_{1/2}$ core calculated assuming $\Delta n^*(7s-6s)=1.050\pm0.005$.

Series		Limit using observed levels (cm^{-1})	Limit with configuration interaction taken into account (cm^{-1})
$5p^5ns\,\frac{3}{2}[\frac{3}{2}]_1$	$n=6$–8	186937	186684
$\frac{3}{2}[\frac{3}{2}]_2$	6–8	186571	186535
$\frac{3}{2}[\frac{3}{2}]_{1,2}$ – c.g.	6–8	186699	186590
$\frac{1}{2}[\frac{1}{2}]_1$	$n=6$, 7	186720	186662
$\frac{1}{2}[\frac{1}{2}]_0$	6, 7	186732	186846
$\frac{1}{2}[\frac{1}{2}]_{0,1}$ – c.g.	6, 7	186723	186708

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[18]The use of Zeeman data to help establish the term dependence of Slater parameters is not new; G. W. King and J. H. Van Vleck [Phys. Rev. 56, 464 (1939)] used term-dependent radial wave functions to account for relative intensities of ns^2-$nsnp$ transitions in several spectra, and their treatment has been much used to interpret sp levels, including Landé g values. For more complex configurations see, for example, the work on As II by H. Li and K. L. Andrew, J. Opt. Soc. Am. 62, 255 (1972) and the work on P II by H. Li, J. Opt. Soc. Am. 62, 1476 (1972).
[19]*Note added in proof.* In addition to the HF calculation for the $5p^55d$ configuration as a whole, given in Table II, HF calculations have been carried out specifically for the $5d\,^1P$ and ^3P terms. The results are similar to those given for Rb II by Hansen, Ref. 16. For Cs II the mean radius of the $5d$ electron is 5.45 a.u. when the atom is in a ^1P state compared to 3.17 a.u. when in a ^3P state. The mean radius of the $5p$ electron is approximately 2.05 a.u. The overlap between the $5d$ and $5p$ wave functions thus differs greatly for the ^1P and ^3P terms, leading to the need for term-dependent parameters. The $^1P - {}^3P$ energy difference given by the difference between the total atom energies in the term-dependent calculations is 29 200 cm^{-1} compared to a difference of 47 700 cm^{-1} found by diagonalizing the energy matrix with the average-energy HF parameters of Table II. The observed difference is 28 700 cm^{-1}, after displacements due to configuration interaction are taken into account.
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