The Fifty-Three Electron Spectra of Caesium and Barium: Cs III and Ba IV

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The separations of the lowest levels $5s^2 5p^5\, ^2P$ of the Cs III and Ba IV spectra have been predicted and observed. In the case of Cs III, the prediction was made from the $s^2 p^5 p$ levels of Cs II by use of Shortley's equations. The separation as found is 13,870 cm^{-1} and several combinations of the terms with higher levels were located. The ^2P separation for Ba IV was estimated by the irregular doublet law and located from the data as 17,830 cm^{-1}.

New data were obtained for caesium by use of the vacuum spark, for barium by the vacuum spark and the condensed discharge in helium. The more complete data for barium enabled the location of a group of terms which combine both with the $(s^2 p^5)\, ^2P$ terms and also with a higher group of terms allowing the classification of about fifty lines in this spectrum.

INTRODUCTION

THE systems neutral iodine, singly ionized xenon, doubly ionized caesium and triply ionized barium are the first members of the isoelectronic sequence having fifty-three electrons outside of the nucleus. Although the spectrum of iodine I has been photographed from the ultraviolet, through the visible, into the infrared region, little advance has been made on the classification of the observed lines. The task of classifying the lines of this spectrum is particularly difficult. The multiplet separations of the levels are very large; consequently, lines belonging to the same series lie in widely separated regions of the spectrum. Turner[1] observed several pairs of lines in the violet which he attributed to the transitions to the normal state. Evans[2] and Deb[3] have attempted to classify the spectrum, but there is no agreement between the results of their work. The extrapolations made in this problem were based upon the results given by Evans. This was done for two reasons: it has been pointed out by Curtis[4] that of the one hundred sixty lines classified by Deb, sixty-four had been observed by Bloch[5] as spark lines; on the other hand, hyperfine structure data given by Tolansky[6] agree with assignments given by Evans. Although it is not entirely free from uncertainty, the scheme given by Evans is perhaps the most satisfactory that is available concerning the spectrum of neutral iodine.

Classifications for the spectra of both neutral and singly ionized xenon have been given by Meggers, deBruin and Humphreys.[7] The separation of the low ^2P terms of xenon II may be computed from the known values of the low terms in the xenon I spectra by the use of equations given by Shortley,[8] which will be discussed later, and which express the values of the levels of a rare gas like spectrum in terms of several parameters, one of which is $\frac{2}{3}$ the doublet separation of the once more ionized atom. Thus Shortley predicted 10,500 cm^{-1} for the Xe II separation, while Meggers, deBruin and Humphreys had found 10,540 cm^{-1}. We were thus encouraged to use the data on Cs II of Olthoff and Sawyer[9] to predict the fundamental separation of Cs III. In Ba IV this could not be done since no classification of Ba III has been carried out, although a list of lines attributed to Ba III has been published by Kimura and Nakamura.[10]

EXPERIMENTAL

A condensed discharge in helium was used to excite the Ba IV spectrum. Data obtained from this source were duplicated by a vacuum spark between electrodes made of a barium-aluminum alloy. The vacuum spark was also used to excite the Cs III spectrum, the electrodes being

[1] L. A. Turner, Phys. Rev. 27, 397 (1926).
[2] S. F. Evans, Proc. Roy. Soc. A133, 417 (1931).
[3] S. C. Deb, Proc. Roy. Soc. A139, 380 (1933).
[4] W. E. Curtis, Nature 131, 398 (1933).
[5] Leon and Eugene Bloch, Ann. d. Physik 11, 141 (1929).
[6] S. Tolansky, Proc. Roy. Soc. A136, 585 (1932).

[7] W. F. Meggers, T. L. deBruin, C. J. Humphreys, Bur. Stand. J. Research 3, 731 (1929); W. F. Meggers, T. L. deBruin, Science 68, 573 (1928); W. F. Meggers, T. L. deBruin, C. J. Humphreys, Bur. Stand. J. Research 6, 287 (1931).
[8] G. H. Shortley, Phys. Rev. 44, 666 (1933).
[9] J. Olthoff and R. A. Sawyer, Phys. Rev. 42, 766 (1932).
[10] M. Kimura and G. Nakamura, Jap. J. Phys. 3, 197 (1924).

aluminum cored with caesium alum. The ultra-violet region was photographed by a one meter vacuum spectrograph and the near violet by an E_2 Hilger quartz spectrograph.

ANALYSIS OF THE Cs III AND Ba IV SPECTRA

The normal state of the Cs III and Ba IV spectra is $5s^25p^5\,{}^2P_{3/2,\,1/2}$. If one of the $5s$ electrons is removed to a $5p$ orbit, the configuration becomes $5s5p^6$ yielding ${}^2S_{1/2}$. As one of the $5p$ electrons is removed from the system, it may pass into a $5d$, $6s$, $6p$, $6d$, $\cdots$ orbit. The resulting configurations and theoretical terms for Cs III and Ba IV are given in Table I.

In order to get some idea as to the region in which the transitions to the normal state might lie, extrapolations were made by means of a Moseley diagram. Since the configurations $5s^25p^5$ and $5s^25p^45d$ involve valence electrons of the same total quantum number 5, it would be expected that they should form a screening doublet and have parallel Moseley lines. The lines obtained from the available data on iodine I and Xe II are decidedly non-parallel and lead us to believe that there was some misassignment of terms in either or both of the iodine I and Xe II spectra. However, if the terms are real, even though wrongly assigned, a tentative prediction of the location of analogous transitions in Cs III and Ba IV may be made and gives for Cs III the region 114,000–139,000 cm^{-1} and for Ba IV, 144,000–178,000 cm^{-1}.

The search for Cs III doublets was aided by the prediction of the doublet separation by the use of Shortley's[8] equations which for low stages of ionization seem to give a better prediction than the irregular doublet law.

Shortley's equations for the s^2p^5p levels of a rare gas type spectrum are:

Upper levels

$$(2c) = -F_0 + \zeta' + \tfrac{1}{2}\zeta + 4G_2$$

$$(1c) = -F_0 + \zeta' + \tfrac{1}{2}\zeta$$

$$(1d) = -F_0 + \zeta' - \zeta$$

$$(0d) = -F_0 + \zeta' - \zeta + 2G_0$$

Lower levels

$$(3a) = -F_0 - \tfrac{1}{2}\zeta' + \tfrac{1}{2}\zeta - F_2$$

$$\left.\begin{matrix}2a\\2b\end{matrix}\right\} = -F_0 - \tfrac{1}{2}\zeta' - \tfrac{1}{4}\zeta + F_2 + 4G_2$$

$$\pm[(\tfrac{3}{4}\zeta + F_2)^2 + (2F_2 - 4G_2)^2]^{\frac{1}{2}}$$

$$\left.\begin{matrix}1a\\1b\end{matrix}\right\} = -F_0 - \tfrac{1}{2}\zeta' - \tfrac{1}{4}\zeta - \tfrac{1}{2}F_2$$

$$\pm[(\tfrac{3}{4}\zeta - \tfrac{1}{2}F_2)^2 + 20F^2]^{\frac{1}{2}}$$

$$(0a) = -F_0 - \tfrac{1}{2}\zeta' + \tfrac{1}{2}\zeta - 5F_2 + 4G_0.$$

The expression on the left-hand side of any one of the equations stands for the value of the level having j equal to the number which appears there. It is expressed in terms of parameters of which one is directly related to the ionic doublet

TABLE I. *Electron configurations and theoretical terms of the Cs III and Ba IV spectra.*

	Russell-Saunders			$j-j$			Number of levels
$5s^25p^4$	${}^3P$	${}^1D$	${}^1S$	${}^3P$	${}^1D$	${}^1S$	
$5s^25p^45d$	${}^4F_{9/2\ 7/2\ 5/2\ 3/2}$ ${}^4D_{7/2\ 5/2\ 3/2\ 1/2}$ ${}^4P_{5/2\ 3/2\ 1/2}$ ${}^2F_{7/2\ 5/2}$ ${}^2D_{5/2\ 3/2}$ ${}^2P_{3/2\ 1/2}$	${}^2G_{9/2\ 7/2}$ ${}^2F_{7/2\ 5/2}$ ${}^2D_{5/2\ 3/2}$ ${}^2P_{3/2\ 1/2}$ ${}^2S_{1/2}$	${}^2D_{5/2\ 3/2}$	9/2 7/2 5/2 3/2 1/2 7/2 5/2 3/2 5/2 7/2 5/2 3/2 1/2 5/2 3/2 1/2 3/2	9/2 7/2 5/2 3/2 1/2 7/2 5/2 3/2 1/2	5/2 3/2	(28)
$5s^25p^46s$	${}^4P_{5/2\ 3/2\ 1/2}$ ${}^2P_{3/2\ 1/2}$	${}^2D_{5/2\ 3/2}$	${}^2S_{1/2}$	5/2 3/2 3/2 1/2 1/2	5/2 3/2	1/2	(8)
$5s^25p^46p$	${}^4D_{7/2\ 5/2\ 3/2\ 1/2}$ ${}^4P_{5/2\ 3/2\ 1/2}$ ${}^4S_{3/2}$ ${}^2D_{5/2\ 3/2}$ ${}^2P_{3/2\ 1/2}$ ${}^2S_{1/2}$	${}^2F_{7/2\ 5/2}$ ${}^2P_{3/2\ 1/2}$ ${}^2D_{5/2\ 3/2}$	${}^2P_{3/2\ 1/2}$	7/2 5/2 3/2 1/2 5/2 3/2 1/2 3/2 5/2 3/2 3/2 1/2 1/2	7/2 5/2 3/2 1/2 5/2 3/2	3/2 1/2	(21)

splitting $s^2p^5\ ^2P$. By using the term values for Cs II as given by Olthoff and Sawyer,[9] it was found that for caesium

$$3/2\zeta' = 13{,}840,$$

which from the definition of the parameters is the $s^2p^5\ ^2P$ separation. With this predicted separation as a guide, a search was made for doublets in the vacuum spark data for caesium. Several pairs of lines were found having $\Delta\nu = 13{,}870$ cm^{-1}, a value in good agreement with the predicted one. See Table II. These pairs are believed to repre-

TABLE II. *Possible resonance lines of Cs III.*

Int	ν	Int	ν	$\Delta\nu$
(3)	127779	(7)	113909	13870
(1)	136146	(1)	122262	13884
(2)	138458	(00)	124564	13894
(0)	145656	(1)	131770	13886
(4)	155041	(1)	141155	13886
(2)	167872	(0)	153988	13884
(2)	181759	(2)	167872	13887
(2)	182548	(0)	168659	13889
(0)	188789	(1)	174914	13875

sent transitions from higher terms to the low $s^2p^5\ ^2P$ of Cs III. The possible assignment of these higher levels will be discussed together with the treatment of the Ba IV spectrum.

The next problem was to find $\Delta\nu$ for Ba IV. By use of the Sommerfeld formula,

$$\Delta\nu = \frac{R\alpha^2(Z-s)^4}{n^3l(l-1)}$$

the values of s, the screening constant, were calculated for the first three members of the series. The results are shown in Table III. It

TABLE III. *Values of $\Delta\nu$ and Δs for Ba IV.*

Spectrum	$\Delta\nu$	$Z-s$	Z	s	Δs
I I	7600	23.90	53	29.10	
					1.04
Xe II	10540	25.94	54	28.06	
					.84
Cs III	13870	27.78	55	27.22	
					.80
Ba IV	17830	29.58	56	26.42	

has been observed that as we proceed through the members of an isoelectronic series, there is usually a progressive diminishing in the value of both s and Δs. Assuming that Δs from Cs III to

Ba IV might be 0.75, the calculated value of s for Ba IV would be 26.47 and the corresponding $\Delta\nu$ would be 17,695 cm^{-1}. The search for recurring frequency differences in the ultraviolet data yielded a group of lines having frequency separations of 17,830 cm^{-1}. This difference occurred more often than any other and between some of the most intense lines. Finally, it yielded terms which combine both with the $s^2p^5\ ^2P$ and with a higher group of terms. Lines in the near violet region led to the location of this upper group of terms. It seemed reasonable, therefore, to assume 17830 as the value of $\Delta\nu$ for Ba IV. On this assumption, the calculated value of s for Ba IV is 26.42 making the consecutive values of s as given in Table III.

ANALYSIS OF THE BARIUM DATA

The location of four pairs of lines in the ultraviolet region having a frequency difference of 17,830 units was the starting point in the analysis of the barium data. The frequencies of the lines fixed the position of an intermediate group of terms with respect to the ground levels. The spacings between the members of this intermediate group led to the identification of lines in the near violet which were interpreted as being transitions from a higher group of levels to the intermediate ones. With the spacings of this upper group as a guide, more lines were found. These lines proved to be transitions from the higher levels to levels in the intermediate group which due to Δj selection could not be located by pairs of resonance lines. Once the position of one of these additional intermediate levels was determined, a transition from it to one of the ground states could be estimated and verified by the data. All of the intermediate levels which combine with neither of the lowest levels, or with only one of them, were located in this manner. The arrangement of the lines in a quadratic scheme is shown in Table IV. Some of the expected lines are missing and there are remarkable differences in intensities among the observed lines. Both of these facts are also true of the observed lines in Xe II. The authors of the Xe II paper suggest that the majority of the missing lines are possible quartet-doublet inter combinations which might be expected to be very weak. Similar reasoning would hold in

TABLE IV. *Classification of lines of Ba IV.*

j	Relative term values	1/2 — 152963	5/2 — 154481	7/2 — 154631	3/2 or 1/2 — 156738	7/2 — 157656	1/2 — 157741	5/2 — 158170
3/2	0	152952 (5) −11	154493 (5) 12		156745 (2) 7		157731 (2) −10	158158 (2) −12
1/2	17830	135133 (5) 0			138918 (5) 10		139911 (2) 0	
5/2	196549			41918.0 (15) 0.0	39810.1 (15) 0.1	38893.4 (15) 0.4		
5/2	197504		43023.9 (20) 0.9		40765.2 (0) −0.8	39848.2 (10) 0.2		39332.9 (15) −1.1
7/2	197698		43218.5 (3) 1.5	43066.8 (2) −0.2		40041.8 (7) −0.2		39527.3 (1) −0.7
3/2	197711		43229.6 (6) −0.4					39542.1 (8) 1.1
3/2	198005	45042.0 (0) 0.0	43522.7 (10) −1.3		41266.9 (0) −0.1		40265.7 (4) 1.7	
5/2	198758		44277.2 (3) 0.2	44126.7 (0) −0.3		41100.7 (15) −1.3		40588.4 (5) 0.4
5/2	198889		44406.4 (1) −1.6	44258.8 (3) 0.8	42149.4 (8) −1.6			

j	Relative term values	5/2 — 158444	7/2 — 158750	5/2 — 158998	5/2 — 163254	3/2 — 175431	5/2 — 175926
3/2	0	158453 (2) 9		158990 (2) −8	163265 (1) 11	175423 (2) −8	
1/2	17830					157607 (0) 5	
5/2	196549						
5/2	197504	39058.4 (20) −1.6	38751.7 (7) −2.3				
7/2	197698	39255.9 (10) 1.9	38946.9 (10) −1.1			22266.9 (2) 0.1	21772.3 (5) 0.3
3/2	197711					22278.1 (8) −1.9	21783.2 (2) −1.8
3/2	198005			39005.7 (5) −1.3	34750.6 (7) −0.4		
5/2	198758	40314.8 (4) 0.8		39761.0 (0) 1.0	35502.6 (5) −1.4	23327.3 (3) 0.3	22831.8 (8) −0.2
5/2	198889						

the case of Ba IV. The irregular intensities indicate that the perturbations between the levels is probably very great.

An attempt to assign the terms either of this spectrum or of that of Cs III to possible configurations does not seem to offer much promise of success. It may be said that since the ^1S and ^1D states of the next ion probably lie much higher than the ^3P, the terms found here are believed to be built on ^3P. In his extension of Houston's and Slater's multiplet relations, Goudsmit[11] has derived a set of expressions giving the change in positions of the energy levels of the configuration ^3P+s with change in electron coupling. Neither the assignments in iodine I nor in Xe II satisfy these expressions. This fact together with the non-parallelism of the Moseley diagram lines, mentioned above, leads to the belief the reassignments need to be made in the first members of this isoelectronic series.

Since the transition $5s^25p^5 \leftarrow 5s5p^6$ would have to follow the irregular doublet law, it should be possible to locate the level $5s5p^6\,^2S_{1/2}$. Our data, however, yielded no levels that would form a sequence involving the level assigned to this configuration in Xe II. Because it seemed probable that $5s5p^6\,^2S_{1/2}$ would lie nearest to the normal state, the levels 127,779 above the normal state in Cs III and 152,963 in Ba IV were thought to be $5s5p^6\,^2S_{1/2}$. Extrapolating backwards from Cs III and Ba IV would place $5s5p^6\,^2S_{1/2}$ at about 102,700 in Xe II. Meggers gives a level in Xe II at 102,798 which he has assigned to $5s^25p^46s\,^2P$. Although the assignments in iodine I and Xe II are doubtful, the levels are probably real. Extrapolating from them led to the discovery of a set of levels for Ba IV which we believe are also real but assignments of which are sugject to considerable uncertainty. The terms near 156,000 are too closely grouped to belong wholly to any one configuration, but some of them are probably due to $5s^25p^45d$. The

[11] S. Goudsmit, Phys. Rev. **35**, 1325 (1930).

TABLE V. *Wave-length list of Cs III lines.*

Int.	λ vac.	ν vac.	Int.	λ vac.	ν vac.
0	529.7	188789	1	708.4	141155
2	547.8	182548	2	722.2	138458
2	550.2	181759	1	734.5	136146
1	571.7	174914	1	758.9	131770
0	592.9	168659	3	782.6	127779
2	595.7	167872	00	802.8	124564
4	645.0	155041	1	817.9	122262
0	649.4	153988	7	877.9	113909
0	686.5	145656			

TABLE VI. *Wave-length list of Ba IV lines.*

Int.	λ in air	ν vac.	Int.	λ in air	ν vac.
2 vac.	570.1	175423	15	2432.31	41100.7
1 "	612.5	163265	0	2452.43	40765.2
2 "	629.0	158990	5	2463.01	40588.4
2 "	631.1	158453	4	2479.78	40314.8
2 "	632.3	158158	4	2482.75	40265.7
2 "	634.0	157731	7	2496.64	40041.8
0 "	634.5	157607	10	2508.77	39848.2
2 "	638.0	156745	15	2512.17	39810.1
5 "	647.3	154493	0	2514.27	39761.0
5 "	653.8	152952	8	2528.19	39542.1
2 "	714.7	139911	1	2529.14	39527.3
5 "	719.9	138918	15	2541.62	39332.9
5 "	740.0	135133	10	2546.62	39255.9
0	2220.15	45042.0	20	2559.50	39058.4
1	2251.23	44406.4	5	2562.96	39005.7
3	2257.80	44277.2	10	2566.83	38946.9
3	2258.74	44258.8	15	2570.36	38893.4
0	2265.50	44126.7	2	2576.01	38808.1
10	2296.84	43522.7	7	2579.76	38751.7
6	2312.52	43229.6	5	2815 86	35502.6
3	2313.36	43218.5	7	2876.80	34750.6
2	2321.26	43066.8	3	4285.62	23327.3
20	2323.57	43023.9	8	4378.62	22831.8
8	2371.79	42149.4	8	4487.46	22278.1
15	2384.88	41918.0	2	4489.70	22266.9
0	2422.51	41266.9	2	4589.40	21783.2
			5	4591.72	21772.3

two highest of the even levels are separated from the remainder of the group by about 12,000 units. It may be that they are the beginning of the levels due to $5s^25p^46s$. The group of upper terms must come from the addition of a p electron to $5s^25p^4$. They too are very closely grouped. Some of them may be due to $5s^25p^46p$.

The classified lines of caesium are listed in Table V, and those of barium in Table VI.