CERTAIN MULTIPLETS IN THE SPECTRA OF Cb III AND Cb IV*

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Abstract

Relative positions of certain multiplets in two and three electron systems of the second long period with wave-lengths for Zr III, Cb IV and Cb III.—Applying the irregular doublet law to the data already known for the triad of multiplets ^3DF, $^3DD'$, and ^3DP, $(ds\text{-}dp)$ in the two electron systems of Sr I and Yt II, the corresponding multiplets for Zr III and Cb IV have been identified. Similarly the triad of multiplets $^4F'D'$, $^4F'F$, and $^4F'G'(d^2s\text{-}d^2p)$ in the three electron systems of Yt I and Zr II has been extended to Cb III and the stronger lines of the $^4F'G'$ multiplet of Mo IV. In passing successively from element to element in both of these iso-electronic systems the shift in the frequency of the radiated lines for each of these multiplets is approximately constant.

IT HAS been shown, for certain sequences of iso-electronic systems in the first long period of the periodic table, that when an electron in a $4p$ orbit jumps to a $4s$ orbit in the presence of 0, 1, 2, or 3, etc., $3d$ electrons the resulting radiated frequencies follow very closely the irregular doublet law.[1]

In the second long period one should expect similar relations to hold for the transition of an electron from a $5p$ orbit to a $5s$ orbit, in the presence of $4d$ electrons. This we have found for a certain triad of multiplets in the two-electron systems Sr I, Yt II, Zr III, and Cb IV, and the three-electron systems Yt I, Zr II, and Cb III.

For the two-electron systems the transition $4d5p$ to $4d5s$ gives rise to the triad of triplets, $^3D_{1,2,3}-{}^3P_{0,1,2}$, $^3D_{1,2,3}-{}^3D'_{1,2,3}$, and $^3D_{1,2,3}-{}^3F_{2,3,4}$ which were already known for Sr I and Yt II. A linear extrapolation of the strongest radiated frequencies in these two elements (the irregular doublet law) was sufficient to determine the corresponding triplets in first Zr III, and then Cb IV. The triplets of Zr III were first identified by C. C. Kiess, the relative term values being kindly sent to the authors before publication. The wave-lengths and intensities of these multiplets, given in Table I, are from our own measurements. The term values, taken with respect to the limit toward which these terms converge, are only extrapolations based upon known relations with term values of other elements.

Two of the corresponding multiplets of Cb IV are given in Table II, the third one lying just outside the region of air transmission.

In the three-electron systems the transition $4d^25p$ to $4d^25s$ gives rise chiefly to the triad of quartets $^4F'_{2,3,4,5}-{}^4G'_{3,4,5,6}$, $^4F'_{2,3,4,5}-{}^4F_{2,3,4,5}$, and

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[1] R. C. Gibbs and H. E. White, Phys. Rev. **29**, 426, 655 (1927).

TABLE I

*Zirconium III triplets**

$(ds-dp)$ λ(air)

Term values	$^3D_3$ 183123.0	(730.4)	$^3D_2$ 183853.4	(404.3)	$^3D_1$ 184257.7
	40		10		2
	2448.90		2405.82		2382.64
$^3P_2$ 142300.6	40822.4		41553.4		41957.4
659.0			20		15
			2444.60		2420.67
$^3P_1$ 142959.4			40894.0		41298.4
248.3					10
					2406.19
$^3P_0$ 142711.0					41546.7
	50		40		
	2643.79		2593.69		
$^3D_3'$ 145309.8	37813.2		38543.6		
911.1	12		40		30
	2709.06		2656.48		2628.25
$^3D_2'$ 146220.8	36902.2		37632.5		38036.8
821.7			14		30
			2715.79		2686.29
$^3D_1'$ 147042.5			36810.9		37215.0
	100				
	2620.57				
$^3F_4$ 144974.8	38148.2†				
1606.3	40		40		
	2735.78		2682.17		
$^3F_3$ 146581.1	36541.9		37272.2		
519.6	3		10		30
	2775.24		2720.08		2690.50
$^3F_2$ 147100.7	36022.3		36752.6		37156.7

* Identified by C. C. Kiess. Wave-lengths and term values by authors. (See text)
† Kiess selected $\nu = 37522.6$ for this line. (Indicated by a dotted line in Fig. 1.)

$^4F'_{2,3,4,5} - {}^4D'_{1,2,3,4}$. Again making a linear extrapolation of frequencies from these quartets already known for Yt I and Zr II, all three multiplets for Cb III, Table III, have been determined as well as several of the stronger lines of the $^4F'G'$ multiplet for Mo IV.

The diagrams of Figs. 1 and 2 are drawn to show not only the linear progression of frequency with atomic number but also the relative intensities of the lines and the increase of the term separations in going from one element to the next. The exactness of this linearity of frequency with atomic number is more definitely shown by the differences appearing in the first, third, and fifth columns of Table IV. This linear relation, which constitutes the *irregular doublet law*, is to be expected whenever the transition of electrons involves a change in the azimuthal quantum number but no change in the total quantum number.

TABLE II

Columbium IV triplets
$(ds-dp)$ λ(air)

Term values	$^3D_3$ 290773.7	(1180.7)	$^3D_2$ 291954.4	(565.5)	$^3D_1$ 292519.9
	10		10		
	2084.06		2033.98		
$^3D_3'$ 242805.8	47967.9		49148.8		
1388.4	2		7		10
	2146.18		2093.12		2068.63
$^3D_2'$ 244194.2	46579.6		47760.3		48325.6
1397.9			5		7
			2156.24		2130.26
$^3D_1'$ 245592.1			46362.3		46927.8
	20				
	2032.49				
$^3F_4$ 241588.9	49184.8				
2609.2	10		10		
	2146.37		2093.29		
$^3F_3$ 244198.1	46575.6		47756.4		
661.4	3		5		3
	2177.29		2122.70		2097.51
$^3F_2$ 244859.5	45914.2		47094.9		47660.4

Using the interval rule Kiess selected for the transition $^3D_3-{}^3F_4$, in Zr III, the line at $\nu=37522.6$. This line gives for the intervals between the $^3F_{2,3,4}$ levels the ratio 981:520, the theoretical value being 4:3. Although the use

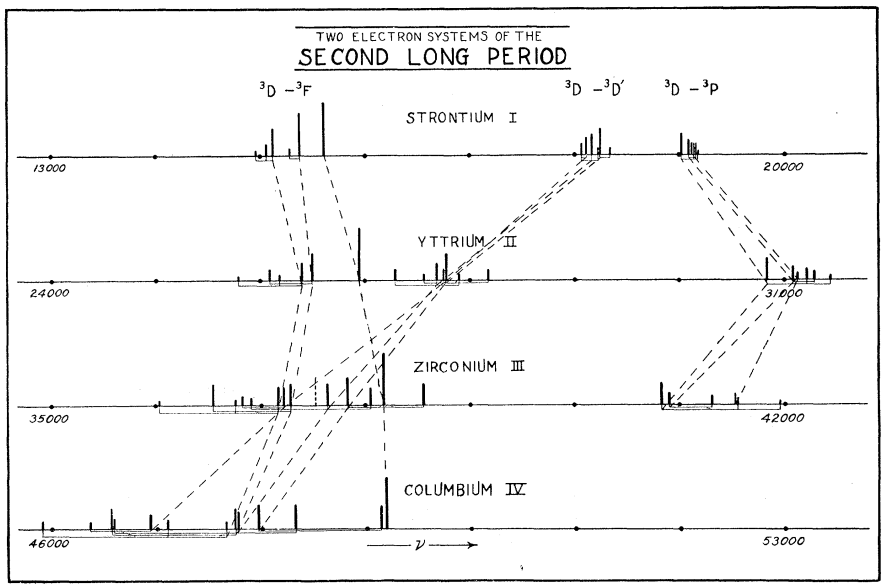


Fig. 1.

TABLE III

Columbium III quartets.
$(d^2s - d^2p)$ λ (air)

Term values	$^4F_5'$ 194142.9	(909.8)	$^4F_4'$ 195052.7	(728.4)	$^4F_3'$ 195781.1	(515.3)	$^4F_2'$ 196296.4
	100						
	2457.04						
$^4G_6'$ 153455.9	40687.0						
1605.2	30		80				
	2557.97		2499.77				
$^4G_5'$ 155061.1	39081.8		39991.6				
1449.4	2		25		70		
	2656.50		2593.78		2545.67		
$^4G_4'$ 156510.5	37632.4		38542.2		39270.6		
1319.7			2		15		60
			2685.75		2634.20		2598.91
$^4G_3'$ 157830.2			37222.5		37950.9		38466.2
	70		20				
	2413.96		2362.04				
$^4F_5$ 152729.8	41413.1		42323.0				
919.1	20		60		20		
	2468.75		2414.50		2372.75		
F_4 153648.9	40494.0		41403.8		42132.3		
773.6			40		50?		25
			2460.47		2417.13		2387.48
$^4F_3$ 154422.4			40630.3		41358.7		41872.4
595.6							60
					?		2421.93
$^4F_2$ 155019.6					40761.5		41276.8
	40		20		2		
	2313.39		2265.68		2228.89		
$^4D_4'$ 150929.6	43213.3		44123.1		44851.4		
307.3			25		15		2
			2281.56		2244.28		2218.61
$^4D_3'$ 151236.6			43816.1		44543.8		45059.1
606.4					25		10
					2275.26		2248.87
$^4D_2'$ 151843.7					43937.4		44452.8
490.1							20
							2273.95
$^4D_1'$ 152333.7							43962.7

of the stronger line at $\nu = 38148.2$ gives a still greater interval ratio it appears to fit into the frequency diagram of Fig. 1 much better than the dotted line at $\nu = 37522.6$.

Starting with the data for the stripped atoms of Sr, Yt, and Zr,[2] Table IV, it is seen that the screening effect due to the addition of first one and then a second $4d$ electron is to shift the spectral lines toward the longer wave-

[2] R. C. Gibbs and H. E. White, Proc. Nat. Acad. Sci., **12**, 551 (1926).

lengths by very nearly the same frequency interval, $\Delta\nu$ second and fourth columns, and at the same time to increase the multiplicity.

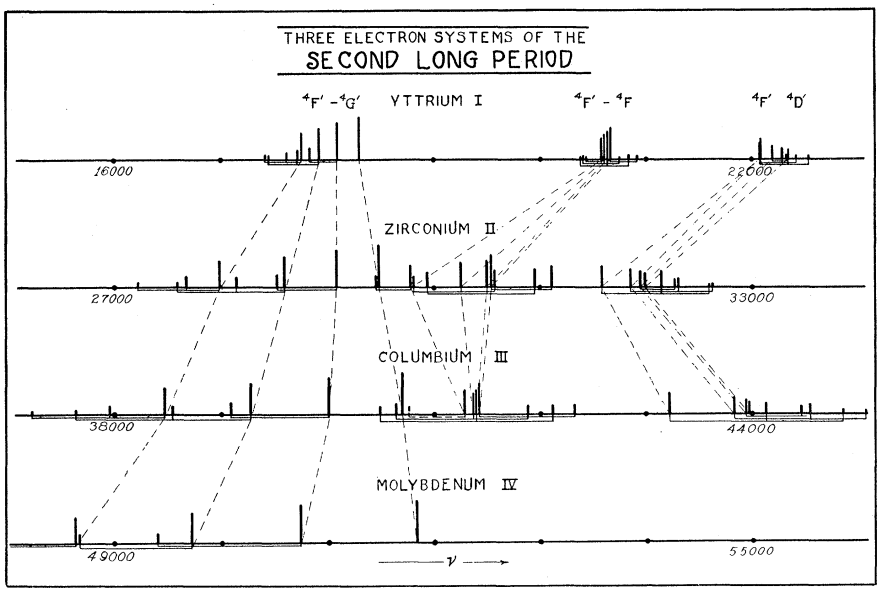


Fig. 2.

Since the known term values for Rb I, Sr I, and Sr II are nearly the same as those for the corresponding terms for K I, Ca I, and Ca II, we may reasonably expect the term values of Yt I, II, Zr II, III, Cb III, IV, and Mo

TABLE IV

Screening due to successive addition of "4d" electrons.

ν	$\Delta\nu$	ν	$\Delta\nu$	ν
$^2S_1-{}^2P_2$ $s-p$	*Screening*	$^3D_3-{}^3F_4$ $ds-dp$	*Screening*	$^4F_5'-{}^4G_6'$ d^2s-d^2p
Sr II		Sr I		
24516.7	8912.4	**15604.3**		
10971.3		11340.1		
Yt III		Yt II		Yt I
35488.0	8543.6	**26944.4**	8656.1	**18288.3**
10713.5		11203.8		11184.8
Zr IV		Zr III		Zr II
46201.5	8053.3	**38148.2**†	8675.1	**29473.1**
		11036.6		11213.9
		Cb IV		Cb III
—	—	**49184.8**	8497.8	**40687.0**

TABLE V

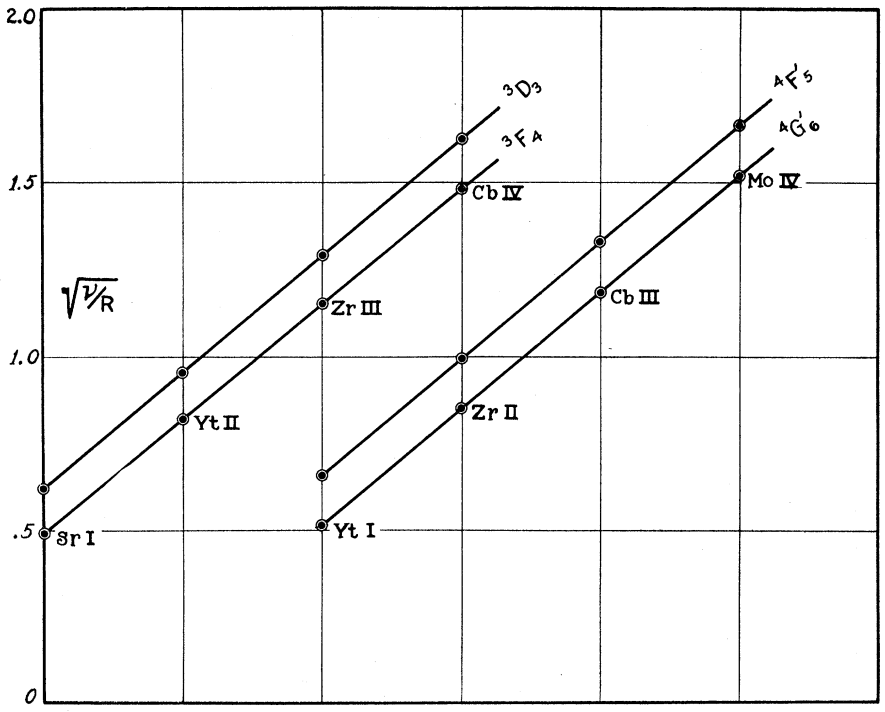
Values of $(\nu/R)^{1/2}$. *Two electron systems.*

Terms	Sr I	Diff.	Yt II	Diff.	Zr III	Diff.	Cb IV
$^3P_2$	0.4592	0.3361	0.7953	0.3434	1.1387		
$^3D_3'$	.4668	.3459	.8127	.3380	1.1507	0.3368	1.4875
$^3F_4$	.4919	.3254	.8173	.3320	1.1493	.3344	1.4837
$^3D_3$	.6198	.3360	.9558	.3360	1.2918	.3360	1.6278

Values of $(\nu/R)^{1/2}$. *Three electron systems.*

Terms	Yt I	Diff.	Zr II	Diff.	Cb III	Diff.	Mo IV
$^4D_4'$	0.4801	0.3562	0.8363	0.3364	1.1727		
$^4F_5$	.4935	.3485	.8420	.3377	1.1797		
$^4G_6'$	.5149	.3328	.8477	.3348	1.1825	0.3358	1.5183
$^4F_4'$	.6571	.3365	.9936	.3365	1.3301	.3365	1.6666

IV to be nearly the same as those for Sc I, II, Ti II, III, V III, IV, and Cr IV respectively. The method used in computing the $(\nu/R)^{1/2}$ values given



MOSELEY DIAGRAM

Fig. 3.

in Table V and Fig. 3 is the same as was used for some of the corresponding elements in the first long period.[3]

Taking the value of $(\nu/R)^{1/2}$ for the $^3D_3$ level of Sr I, which is known, and being guided by the slope of the $5p$ and $5s$ lines on the Moseley Diagram for the one-electron systems for these elements, values of $(\nu/R)^{1/2}$ are assumed for the $^3D_3$ level of Yt II and Zr III, from which the term values of the $^3D_3$ levels are computed. The corresponding term values for the $^3F_4$ levels are then obtained by the subtraction of the radiated frequencies in these elements. The values of $(\nu/R)^{1/2}$ can now be determined for the $^3F_4$ levels and the $\Delta(\nu/R)^{1/2}$ for the two terms thus obtained for each element should be almost the same as the corresponding difference for the same terms in Sr I. If such is not the case slightly different values of $(\nu/R)^{1/2}$ for the $^3D_3$ levels are taken and the process is repeated until suitable values of $\Delta(\nu/R)^{1/2}$ are obtained. The $^3P_2$ and $^3D_3'$ terms are then determined directly from the observed radiated frequencies. The same method was followed in determining the $(\nu/R)^{1/2}$ values shown in Table V for the three electron systems.

CORNELL UNIVERSITY,
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[3] R. C. Gibbs and H. E. White, Proc. Nat. Acad. Sci. **13**, 525 (1927).