STRIPPED YTTRIUM (Y_{III}) AND ZIRCONIUM (Zr_{IV})

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Abstract

Hot spark spectra of yttrium and zirconium.—Using aluminum electrodes, first with yttrium oxalate and borax fused into their cores, and second with zirconium hydroxide replacing the yttrium oxalate, the hot spark spectra of Y_{III} and Zr_{IV} have been identified and the series relationships and term values analyzed. The results are tabulated. In these stripped atoms the normal position of the electron is in a $4d$ orbit rather than in a $5s$.

In preceding work we have presented the spectral relationships of the stripped atoms of the elements contained in the first two rows of the periodic table, and in this laboratory with the aid of our apparatus, J. A. Carroll[1] has extended this sort of analysis to some of the elements in each of the three rows beginning with copper, silver, and gold, respectively.

In the present paper we extend the same process to the row beginning with rubidium, taking the appropriate data from the literature for

Table I

Series lines of Y_{III}

Int.	λ(I. A. Vac.)	ν	Δν		Term	values
1	989.21	101090.8	726.5	$4d_2-4f$	$5s$	157822.9
2	996.37	100364.3		$4d_1-4f$	$6s$	78572.6
1	2128.66	46977.9	1553.1	$5p_2-5d_2$	$5p_1$	122335.0
2	2191.84	45623.8	199.0	$5p_1-5d_1$	$5p_2$	123888.7
1	2201.44	45424.8		$5p_1-5d_2$	$4d_1$	164565.8
1	2206.73	45315.9	1553.2	$5p_2-6s$	$4d_2$	165289.2
1	2285.05	43762.7		$5p_1-6s$	$5d_1$	76711.4
5*	2328.06	42954.2	723.4	$4d_2-5p_1$	$5d_2$	76910.4
20*	2367.94	42230.8	1553.7	$4d_1-5p_1$	$4f$	64200.0
15*	2415.43	41400.5		$4d_2-5p_2$		
30*	2817.86	35487.9	1553.8	$5s-5p_1$		
20*	2946.89	33934.1		$5s-5p_2$		

* The intensities and wave-lengths of these lines were taken from Exner and Haschek.

[1] Carroll, Phil. Trans. Roy. Soc. **225,** 357 (1926).

rubidium and strontium and, for the first time presenting, with the aid of our own work, the spectral relationships of the stripped atoms of yttrium and zirconium.

Taking new hot spark spectra, first, when the aluminum electrodes have had a mixture of yttrium oxalate and borax fused into their cores, and, second, when zirconium hydroxide has replaced the yttrium oxalate and using the general method of procedure which we have fully explained in preceding articles we have obtained the results shown in the following Tables I and II, and again summarized in very condensed form in Table III.

TABLE II

Series lines of Zr_{IV}

Int.	λ(I. A. Vac.)	ν	Δν		Term values	
1	628.65	159071.0	1235.2	$4d_2-4f$	$5s$	238545.9
2	633.57	157835.8		$4d_1-4f$	$6s$	124291.1
2	1183.97	84461.6	1253.8	$4d_2-5p_1$	$5p_1$	192344.4
4	1201.81	83207.8	2486.3	$4d_1-5p_1$	$5p_2$	194827.4
4	1219.88	81975.3		$4d_2-5p_2$	$4d_1$	275553.3
0	1417.66	70538.8	1488.0	$5p_2-6s$	$4d_2$	276803.5
1	1469.49	68050.8		$5p_1-6s$	$4f$	117725.0
2*	2164.43	46201.5	2483.0	$5s-5p_1$		
2*	2287.36	43718.5		$5s-5p_2$		

TABLE III

Comparison of term values

	$N=$ $R/N^2=$	4 6858.44	5 4389.40	6 3048.19
s	Rb		33689.1	13557.9
	Sr/4		22238.1	10304.0
	Y/9		17535.9	8730.3
	Zr/16		14909.1	7768.2
p_2	Rb		21110.2	9974.1
	Sr/4		16309.3	
	Y/9		13765.4	
	Zr/16		12176.7	
d_2	Rb	14334.3	7988.9	5002.4
	Sr/4	18598.9	8916.6	5357.5
	Y/9	18365.5	8545.6	
	Zr/16	17300.2		
f	Rb	6897.6	4418.2	3068.0
	Sr/4	6990.1	4474.0	3103.0
	Y/9	7133.3		
	Zr/16	7357.8		

The plotting of the atomic number against the $\sqrt{\nu/R}$ values corresponding to the *s*, *p*, *d*, and *f* terms in the case of these four elements yields the Moseley diagram shown in Fig. 1. This is like the other Moseley diagrams which we have presented in the field of optical spectra save in two particulars, namely:

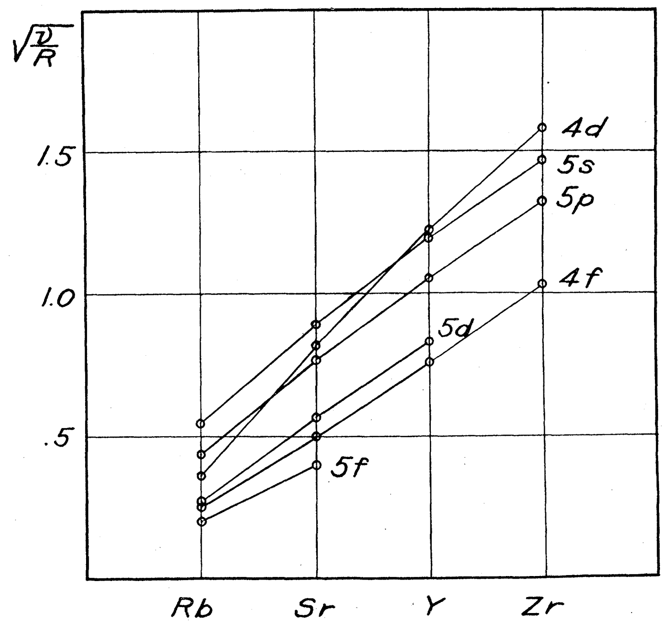

Fig. 1. Moseley's law in the field of optics.

(1) the lines corresponding to the 4*d* and 4*f* terms are seen in Fig. 1 to be no longer parallel, and hence they appear to violate the irregular doublet law,[2] and

(2) the 4*d* line starts at rubidium below the 5*s* and 5*p* lines and rises above these lines in progressing from rubidium to zirconium. This obviously means that while an electron is less tightly bound in rubidium in the 4*d* level than in the 5*s* or 5*p* levels, in yttrium and zirconium these relations are reversed and an electron is most tightly bound in the 4*d* level. *In other words, in yttrium and zirconium the normal position is in a 4d orbit rather than a 5s orbit. This is the first time that a stripped atom has been observed in which the lowest level, and hence the rest position, of the electron has not been an s orbit.*

The lack of parallelism in Fig. 1 between the 4*d* and 4*f* lines, i.e., the failure of the irregular doublet law, is explained as follows. This law

[2] Bowen and Millikan, Phys. Rev. **24,** 209 (1924).

should hold only when the screening constant σ for each of the two orbits involved is the same for atoms of adjacent atomic number. Such a change in the screening constant as must occur when with increasing atomic number the $4d$ level changes from a non-penetrating to a penetrating orbit of course destroys at once the irregular doublet law.

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