SERIES SPECTRA OF POTASSIUM AND CALCIUM

By I. S. Bowen

Abstract

Several of the strongest extreme ultra-violet lines in the K_{III}, K_{IV}, Ca_{IV}, and Ca_{V} spectra are given their series designtion. In K_{II} several lines are identified in addition to those found by DeBruin. The absolute value of the terms of K_{II} are determined thus fixing the ionization potential at 31.7 volts. 137 lines are classified in Ca_{III} and the term values of the levels involved are calculated. These correspond to an ionization potential of 51.0 volts.

I. *Six-Electron Systems.* Hopfield and Dieke[1] have called attention to a triplet PP' group which they traced from S_I to K_{IV}. Since this group follows the irregular doublet law it can be definitely identified as the PP'

TABLE I

Triplet PP′ groups in six-electron systems.

Ion	Int.	λI.A. Vac.	ν	Δν	Series designation
S_I			72380.		aP_2-bP_1
			72174.		aP_1-bP_0
			72019.		aP_2-bP_2
			71985.		aP_1-bP_1
			71805.		aP_0-bP_1
			71625.		aP_1-bP_2
				21348.9	
Cl_{II}	4	1063.77	94005.3		aP_2-bP_1
	4	1067.95	93637.4		aP_1-bP_0
	5	1071.03	93367.9		aP_2-bP_2
	3	1071.77	93304.0		aP_1-bP_1
	4	1075.22	93003.9		aP_0-bP_1
	3	1079.07	92672.7		aP_1-bP_2
				20426.1	
A_{III}		871.11	114796.		aP_2-bP_1
		875.56	114213.		aP_1-bP_0
		878.78	113794.		aP_2-bP_2
		879.62	113685.		aP_1-bP_1
		883.22	113222.		aP_0-bP_1
		887.45	112682.		aP_1-bP_2
				20387.	
K_{IV}	4	737.15	135658.		aP_2-bP_1
	4	741.94	134782.		aP_1-bP_0
	4	745.26	134181.		aP_2-bP_2
	3	746.39	133978.		aP_1-bP_1
	4	750.00	133333.		aP_0-bP_1
	4	754.66	132510.		aP_1-bP_2
				20497.	
Ca_V	4	637.89	156766.		aP_2-bP_1
	3	643.10	155497.		aP_1-bP_0
	5	646.51	154678.		aP_2-bP_2
	3	647.82	154364.		aP_1-bP_1
	4	651.49	153495.		aP_0-bP_1
	3	656.71	152275.		aP_1-bP_2

[1] Hopfield and Dieke, Phys. Rev. **27**, 638 (1926).

group to be expected on the return of a $3s$ electron that had been excited to a $3p$ orbit. The wave-lengths and frequencies of these groups along with the corresponding group in Ca_V are given in Table I. The frequencies for S_I were given by Hopfield and Dieke[1] while those for A_{III} were determined by Dorgelo and Abbink.[2] The data for Cl_{II}, K_{IV} and Ca_V represent new determinations.

II. *Seven-Electron Systems.* Turner[3] has given the wave-lengths of six lines in the extreme ultra-violet spectrum of Cl_I. Four of these can be arranged in a doublet PP' group, the position and separations of which are approximately those to be expected for the combination between the $4k^2P$ term of the $s^2p^4 \cdot s$ configuration and the a^2P term of the s^2p^5 configuration. A corresponding PP' group is found in the table of the "blue" argon spectrum in the extreme ultra-violet given by Dorgelo and Abbink. In this case the

TABLE II

Doublet lines in seven-electron systems.

Ion	Int.	λI. A. Vac.	ν	$\Delta\nu$	Series designation
Cl_I	2	1335.8	74863.		aP_2-4kP_1
	5	1347.2	74225.	884.	aP_2-4kP_2
	3	1351.7	73979.	883.	aP_1-4kP_1
	5	1363.5	73342.		aP_1-4kP_2
A_{II}		718.05	139266.		aP_2-4kP_1
		723.35	138246.	1436.	aP_2-4kP_2
		725.53	137830.	1430.	aP_1-4kP_1
		730.91	136816.		aP_1-4kP_2
K_{III}	2	466.78	214234.		aP_2-4kP_1
	3	470.08	212730.	2163.	aP_2-4kP_2
	2	471.54	212071.	2168.	aP_1-4kP_1
	2	474.92	210562.		aP_1-4kP_2
Ca_{IV}	2	335.36	298189.	3134.	aP_2-4kP_2
	2	338.92	295055.		aP_1-4kP_2
A_{II}		919.79	108720.	1431.	aP_2-bS
		932.06	107289.	21157.	aP_1-bS
K_{III}	5	765.65	130608.	2162.	aP_2-bS
	4	778.54	128446.	20875.	aP_1-bS
Ca_{IV}	6	665.96	152448.	3127.	aP_2-bS
	5	669.70	149321.		aP_1-bS

identification is confirmed by the fact that the separation of the a^2P term is within 8 frequency units of the value predicted by Meissner[4] from the difference in the limits of the series of lines in A_I that are based on these

[2] Dorgelo and Abbink, Zeits. f. Physik **41**, 753 (1927).

[3] Turner, Phys. Rev. **27**, 397 (1926).

[4] Meissner, Zeits. f. Physik **39**, 172 (1926); **40**, 839 (1927).

two terms in the A_{II} ion. Assuming the identification of these two groups it is possible to predict the position and separations of the corresponding lines in K_{III} and Ca_{IV}. In K_{III} a strong PP' group is observed as predicted and in Ca_{IV} part of the group is found, the remainder being obscured by other strong lines.

Another group of lines that should be emitted by a seven-electron system is the combination of the a^2P term of the s^2p^5 configuration with the b^2S term of the sp^6 configuration. These pairs, having the same separation as that found in the PP' groups and following the irregular doublet law, have been traced from A_{II} to Ca_{IV}. These lines are among the strongest lines in the spectrum as would be expected from the fact that they are the resonance lines of these ions. The lines identified in these seven-electron systems are collected in Table II.

III. *Eight-Electron Systems.* Meissner[4] has made a very complete analysis of the A_I spectrum and DeBruin[5] has classified a large number of lines of the spark spectrum of potassium as due to jumps between various terms of K_{II}. More recently DeBruin[6] has been able to correlate about one-half of these terms with the corresponding terms of argon, as analyzed by the Meissner. On plates recently taken at this laboratory it has been possible to identify several very strong extreme ultra-violet lines as transitions between DeBruin's terms and the single ground term of the s^2p^6 configuration. These lines are given in Table III.

TABLE III

Series lines in K_{II}

Int.	λI. A. Vac.	ν	Series designation
5	600.75	166459.	$3p-4s_2$
5	607.90	164501.	$3p-3d_5$
4	612.61	163236.	$3p-4s_4$
2	615.40	162496.	$3p-4s_5$?

The series of s_2 and s_3 levels (Meissner's notation) in K_{II} are based on the a^2P_1 term of K_{III} while the s_4 and s_5 terms are based on the a^2P_2 term. Consequently for the higher members of these series the s_2, s_3 levels are separated from the corresponding s_4, s_5 levels by a frequency difference approximately equal to $a^2P_2-a^2P_1$. The identification, in Section II, of certain lines in the K_{III} spectrum fixes the separation in this a^2P term and therefore makes possible the approximate prediction of the separation between the $5s_2$, $5s_3$ terms and the $5s_4$, $5s_5$ terms. When this is done it is evident from the agreement in this separation as well as in the inner quantum numbers and position that DeBruin's Y_2, Y_3, Y_4 and Y_5 terms should be identified with these $5s_5$, $5s_4$, $5s_3$ and $5s_2$ terms respectively. Since DeBruin has already identified the $4s$ terms this fixes two successive members of a series from which the absolute term values can be calculated by the use of the Rydberg formula.

[5] DeBruin, Proc. R. S. Amsterdam, **29**, 713 (1926).

[6] DeBruin, Dissertation, Amsterdam, 1927.

Table IV gives the classification of 137 lines in the Ca_{III} spectrum. The wave-lengths above 2250A are taken from Anderson[7] while the remainder represent new determinations. The notation used in the present article follows that of Meissner for the s and p terms except that the preceding numeral is changed, in conformity with recent usage, to agree with the total quantum number of the excited electron. The correlation of the terms in

TABLE IV
Series lines in Ca_{III}

Int.	λI. A. Vac.	ν	Series designation	Int.	λI. A. Vac.	ν	Series designation
5	403.734	247688.	$3p-4s_2$	0*	1905.98	52466.4	$3D_5-4p_9$
5	409.948	243933.	$3p-4s_4$	2	1907.46	52425.7	$4p_7-5s_3$
2	490.56	203851.	$3p-3D_1$	4	1910.17	52351.4	$3D_7-4p_6$
2d	1270.54	78706.7	$3D_1-4p_2$	3*	1935.79	51658.5	$4p_6-5s_2$
2	1278.38	78224.0	$3D_1-4p_5$	4	1939.72	51553.8	$3D_6-4p_8$
2	1281.50	78033.6	$3D_1-4p_3$	6	1943.12	51463.6	$4p_{10}-4D_2$
3	1297.96	77044.0	$3D_2-4p_3$	5	1948.31	51326.5	$3D_8-4p_6$
1	1310.58	76302.1	$3D_2-4p_4$	3	1952.16	51225.3	$3D_7-4p_7$
2	1317.60	75895.6	$3D_1-4p_6$	4	1953.06	51201.74	$p_1-5s_4, 3D_6-4p_9$
3	1334.94	74909.7	$3D_2-4p_6$	2	1958.18	51067.8	$4p_9-4D_4$
1	1355.37	73780.6	$3D_2-4p_7$	5	1964.70	50898.4	$4p_9-5s_5$
1	1359.81	73539.7	$3D_1-4p_8$	5	1968.03	50812.2	$4p_{10}-4D_1$
2	1385.39	72181.8	$3D_2-4p_9$	1	1972.01	50709.7	$4p_8-4D_4$
3	1459.87	68499.2	$3D_3-4p_3$	3	1978.63	50540.0	$4p_8-5s_5$
4	1463.41	68333.5	$3D_1-4p_{10}$	2	1989.61	50261.1	$4p_4-5s_2$
2	1480.55	67542.5	$3D_4-4p_3$	4	2000.44	49989.0	$3D_7-4p_8$
4	1484.92	67343.7	$3D_2-4p_{10}$	4	2001.61	49959.8	$4p_7-5s_4$
2	1496.92	66803.8	$3D_4-4p_4$	3	2003.74	49906.7	$4p_4-5s_3$
3	1506.94	66359.6	$3D_3-4p_6$	1	2010.55	49737.6	$3D_9-4p_2$
0	1528.89	65406.9	$3D_4-4p_6$	3	2014.75	49633.9	$3D_7-4p_9$
4	1555.48	64288.8	$3D_4-4p_7$	4d	2019.42	49519.2	$4p_3-5s_2$
6	1562.50	64000.0	$3D_3-4p_8$	3	2021.48	49468.7	$4p_7-4D_4$
5	1571.31	63641.2	$3D_3-4p_9$	2	2027.34	49325.7	$4p_5-5s_2$
0*	1584.82	63098.6	$4p_{10}-4D_5$	2	2028.38	49300.4	$4p_7-5s_5$
4	1586.19	63044.1	$3D_4-4p_8$	1	2030.67	49244.8	$3D_9-4p_5$
1	1595.24	62686.5	$3D_4-4p_9$	4	2034.12	49161.3	$4p_9-4D_3$
1	1688.81	59213.3	$4p_{10}-5s_2$	3	2039.01	49043.4	$3D_9-4p_3$
1	1698.95	58859.9	$4p_{10}-5s_3$	4	2042.27	48965.1	$3D_8-4p_8$
1	1716.23	58267.2	$4p_9-4D_5$	4	2047.31	48844.6	$4p_6-5s_4$
1*	1726.88	57907.9	$4p_8-4D_5$	3	2047.80	48832.9	$4p_2-5s_2$
3	1738.56	57518.9	$3D_5-4p_5$	3	2049.02	48803.8	$4p_8-4D_3$
3	1744.61	57319.4	$3D_5-4p_3$	3	2057.30	48607.4	$3D_8-4p_9$
3	1762.14	56749.2	$3D_6-4p_2$	3*	2062.83	48477.1	$4p_2-5s_3$
3	1773.29	56392.4	$4p_{10}-5s_4$	2	2068.30	48348.9	$4p_6-4D_4$
0	1777.93	56245.2	$3D_6-4p_5$	2	2070.21	48304.3	$3D_9-4p_4$
4	1783.92	56056.3	$3D_6-4p_3$	2	2075.55	48180.0	$4p_6-5s_5$
4	1794.31	55731.7	$4p_{10}-5s_5$	5	2099.23	47636.5	$3D_5-4p_{10}$
4	1800.24	55548.1	$4p_6-4D_5$	6	2129.88	46951.0	$4p_4-4D_4$
5	1807.91	55312.5	$3D_6-4p_4$	3*	2132.17	46900.6	$3D_9-4p_6$
5	1812.17	55182.5	$3D_5-4p_6, 3D_7-4p_2$	6	2141.07	46705.6	$4p_3-5s_4$
1	1828.43	54691.7	$3D_7-4p_5$	1	2144.47	46631.6	$4p_9-4D_2$
2	1849.51	54068.4	$3D_5-4p_7$	6	2153.15	46443.6	$4p_6-4D_3$
6*	1854.72	53916.5	$3D_6-4p_6$	2	2161.07	46273.4	$4p_8-4D_2$
3	1860.50	53749.0	$3D_7-4p_4$	4	2164.18	46206.9	$4p_3-4D_4$
6	1870.28	53467.9	$3D_8-4p_3$	5	2172.27	46034.8	$4p_3-5s_5$
5	1872.39	53407.7	$4p_3-4D_5$	3	2183.98	45788.0	$3D_9-4p_7$
1*	1892.92	52828.4	$3D_5-4p_8$	2	2191.95	45621.5	$4p_8-4D_1$
3	1894.17	52793.6	$3D_6-4p_7$	3	2205.08	45349.8	$4p_2-5s_5$
0	1896.94	52716.5	$4p_2-4D_5$	2	2219.91	45046.9	$4p_4-4D_3$

* May be blend with impurity or high order line.

[7] Anderson, Astrophys. J. **59**, 76 (1924).

TABLE IV continued

Inf.	λI. A. Vac.	ν	Series designation	Int.	λI. A. Air	ν	Series designation
1	2220.56	45033.7	$4p_7-4D_2$	6	2704.87	36959.4	$4s_3-4p_2$
2	2245.01	44543.2	$3D_9-4p_8$	4	2771.27	36073.9	$4s_5-4p_7$
	I. A. Air			6	2791.63	35810.8	$4s_4-4p_6$
2	2252.65	44378.4	$4p_7-4D_1$	7	2813.88	35527.6	$4s_3-4p_4$
0	2256.33	44306.0	$4p_3-4D_3$	7	2866.57	34874.7	$4s_2-4p_2$
2	2276.54	43912.8	$4p_6-4D_2$	7	2869.95	34833.6	$4s_5-4p_8$
0	2310.87	43260.5	$4p_6-4D_1$	7	2881.80	34690.4	$4s_4-4p_7$
1	2351.40	42514.8	$4p_4-4D_2$	9	2899.78	34475.3	$4s_5-4p_9$
3	2393.20	41772.3	$4p_3-4D_2$	2	2907.90	34379.0	$4s_2-4p_5$
1	2431.08	41121.5	$4p_3-4D_1$	8	2924.33	34185.9	$4s_2-4p_3$
1	2442.54	40928.6	$4p_5-4D_1$	7	2988.61	33450.6	$4s_4-4p_8$
1	2472.52	40432.3	$4p_2-4D_1$	6	2989.30	33442.9	$4s_2-4p_4$
5	2497.67	40025.3	$4s_5-4p_2$	6	3028.66	33008.3	$4s_3-4p_7$
6	2541.49	39335.2	$4s_5-4p_3$	8	3119.66	32045.5	$4s_2-4p_6$
3	2587.09	38642.0	$4s_4-4p_2$	4	3233.02	30921.9	$4s_2-4p_7$
2	2590.34	38593.5	$4s_5-4p_4$	5	3367.81	29684.4	$4s_2-4p_8$
6	2620.82	38144.6	$4s_4-4p_5$	8	3372.68	29641.5	$4s_5-4p_{10}$
6	2634.17	37951.4	$4s_4-4p_3$	7	3537.75	28258.5	$4s_4-4p_{10}$
3	2686.73	37208.9	$4s_4-4p_4$	6	3761.62	26576.8	$4s_3-4p_{10}$
8	2687.78	37194.4	$4s_5-4p_6$	5	4081.74	24492.5	$4s_2-4p_{10}$

calcium arising from an excited d electron with the corresponding terms in argon is, in many cases, doubtful and therefore all of these terms are labeled with a D with subscripts numbered in the order of their term values.

The terms that have been identified in Ca_{III} are listed in the first column of Table V. The inner quantum number of the term, J, is given in the second column and the value of the term in the third column. In the fifth column the corresponding terms of K_{II} are listed using DeBruin's notation. The

TABLE V

Term values in eight-electron systems.

	Ca_{III}				K_{II}		A I
Term	J	Term value	$\Delta\nu$	DeBruin's Notation	Term value	$\Delta\nu$	Meissner's Notation
$4s_5$	2	170583.5		X_2	94130.0		$1s_5$
			1383.5			730.0	
$4s_4$	1	169200.0		X_3	93400.0		$1s_4$
			1681.4			1912.5	
$4s_3$	0	167518.6		X_7	91487.5		$1s_3$
			2085.0			1312.0	
$4s_2$	1	165433.6		X_8	90175.5		$1s_2$
$5s_5$	2	85210.0		Y_2	44061.5		$2s_5$
			663.4			417.4	
$5s_4$	1	84546.6		Y_3	43644.1		$2s_4$
			2462.3			1734.1	
$5s_3$	0	82084.3		Y_4	41910.0		$2s_3$
			355.9			291.8	
$5s_2$	1	81728.4		Y_5	41618.2		$2s_2$
$3p$	0	413127.			256637.		$1p_0$
$4p_{10}$	1	140941.6		P_1	73428.6		$2p_{10}$
			4833.4			3180.1	

TABLE V (*continued*)

Ca_{III}					K_{II}		A_I
Term	J	Term value	$\Delta\nu$	DeBruin's Notation	Term value	$\Delta\nu$	Meissner's Notation
$4p_9$	3	136108.2		P_2	70248.5		$2p_9$
			358.7			297.1	
$4p_8$	2	135749.5		P_3	69951.4		$2p_8$
			1239.2			845.5	
$4p_7$	1	134510.3		P_4	69105.9		$2p_7$
			1121.5			623.3	
$4p_6$	2	133388.8		P_5	68482.6		$2p_6$
			1398.1			1089.3	
$4p_4$	1	131990.7		P_6	67393.3		$2p_4$
			742.5			418.0	
$4p_3$	2	131248.2		P_7	66975.3		$2p_3$
			193.2			110.3	
$4p_5$	0	131055.0		P_8	66865.0		$2p_5$
			496.4			362.8	
$4p_2$	1	130558.6		P_9	66502.2		$2p_2$
						4641.3	
				P_{10}	61860.9		$2p_1$
				X_4	93200.7		$3d_6$
						1059.8	
$3D_1$	1	209281.9		X_5	92140.9		$3d_5$
			990.3			436.2	
$3D_2$	2	208291.6		X_6	91704.7		$3d_3$
			8542.9			5903.1	
$3D_3$	3	199748.7		X_9	85801.6		$3d_4$
			954.0			691.4	
$3D_4$	2	198794.7		X_{10}	85110.2		$3d_1''$
			10220.1				
$3D_5$	1	188574.6					$3d_2$
			1270.8				
$3D_6$	1–2	187303.8					$3s_1''''$
			1564.6				
$3D_7$	2	185739.2					$3s_1''$
			1023.8				
$3D_8$	3	184715.4					$3s_1'''$
			4419.8				
$3D_9$	1	180295.6					$3s_1'$
$4D_1$	1	90128.1		Y_6	41232.1		$4d_5$
			651.7			450.9	
$4D_2$	2	89476.4		Y_7	40781.2		$4d_3$
			2531.4			1210.5	
				Y_8	39570.7		
						660.1	
$4D_3$	3	86945.0		Y_9	38910.6		$4d_4$
			1904.5			1469.8	
$4D_4$	2	85040.5		Y_{10}	37440.8		$4d_1''$
			7199.4			3921.9	
$4D_5$	3?	77841.1					$4s_1'''$
				Y_{11}	33512.9		

sixth column gives the absolute value of these K_{II} terms as fixed by the method mentioned above. In the last column the corresponding levels of A_I are listed in Meissner's notation.

These term values fix the ionization potential of K_{II} as 31.7 volts and of Ca_{III} as 51.0 volts.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA.
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