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THE FIRST SPARK SPECTRUM OF RUBIDIUM (Rb II)

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ABSTRACT

The resonance lines of Rb II have been photographed in the extreme ultraviolet region with the vacuum spectrograph. The mode of excitation was the hollow cathode discharge in helium, and in addition, the hot spark was employed with rubidium hydroxide in cored aluminum electrodes. The values of the wave-lengths of the ultraviolet lines for Rb II were obtained from third order measurements. The visible region was photographed with various glass and quartz spectrographs. With the separations of the resonance lines as guides, the classification scheme given by Reinheimmer was found to be correct, but incomplete. Some lines taken from Otsuka's data were fitted into the scheme. The coupling is of an intermediate type approaching that of (*jj*) form. Levels of the $4p^54d$, $4p^55s$, $4p^55p$, $4p^55d$, and $4p^56s$ configurations were identified. Their separations were compared with Kr I. It was also attempted to separate the $^3P_2$ and $^3P_1$ terms due to $4p^5(5s, 6s)$ from the $4p^5(4d, 5d)$ levels. The limit of excitation furnished by metastable helium falls exactly between the various levels caused by the $4p^55p$ configuration, thus providing a check on the interpretation of the classification. The ionizing potential of Rb II was calculated to be 27.3 volts.

I. EXPERIMENTAL PROCEDURE

A PRELIMINARY exposure of Rb II excited in the hollow cathode discharge in helium was photographed in the vacuum region with a 1 m vacuum spectrograph and the positions of the resonance lines were noted. Their intensities were not sufficient to give wave-length determinations from second and third order measurements hence the hot spark was employed for producing the excitation using rubidium hydroxide in cored aluminum electrodes.

An E_1 Hilger quartz prism spectrograph was used for the region λ2470 to λ4300 with an iron comparison spectrum as standards. Due to its higher dispersion, the E_1 glass prism spectrograph was used for the regions λ4100 to λ5800 with an iron comparison spectrum, and λ5800 to λ8000 with an argon comparison spectrum. The reductions of wave-lengths were made by means of a Hartmann formula.

II. ANALYSIS OF THE Rb II SPECTRUM

In Table I we give the spectral levels to be expected in Rb II for the two limiting cases of Russell-Saunders and of (*jj*) coupling. Rb II, however, belongs like many other spectra to an intermediate type where neither case is completely realized.

The positions of the levels due to various configurations are largely influenced by the principal quantum number of the valence electron and by the degree of ionization; i.e. according to whether we consider Kr I, Rb II, Sr III, the configurations will yield levels of different positions relative to each other. To illustrate this point a schematic Moseley diagram of the energy levels of Kr I and its isoelectronic analogues is given in Fig. 1.

TABLE I. *Electron configurations and theoretical terms of the Rb II spectrum.*

Electron configuration	Russell-Saunders						(*jj*)		Number of levels
$4p^5$	^2P						$^2P_{1\frac{1}{2}}$	$^2P_{\frac{1}{2}}$	
$4p^6$				$^1S_0$			0		(1)
$4p^55s$ $4p^56s$ $4p^57s$ —		$^1P_1$			$^3P_{210}$		12	01	(4)
$4p^55p$ $4p^56p$ $4p^57p$ —	$^1S_0$	$^1P_1$	$^1D_2$	$^3S_1$	$^3P_{210}$	$^3D_{321}$	12 0123	01 12	(10)
$4p^54d$ $4p^55d$ $4p^56d$ —	$^1P_1$	$^1D_2$	$^1F_3$	$^3P_{210}$	$^3D_{321}$	$^3F_{432}$	0123 1234	12 23	(12)
$4p^54f$ $4p^55f$ $4p^56f$ —	$^1D_2$	$^1F_3$	$^1G_4$	$^3D_{321}$	$^3F_{432}$	$^3G_{543}$	1234 2345	23 34	(12)

In this diagram the $(\nu/R)^{1/2}$ of the term values of the levels arising from one configuration and referred to $4p^5$ are represented by approximately straight lines as functions of the atomic number. Since we know the position of the levels in Kr I[1] and since for larger values of Z the slope of these Moseley curves approaches the value $1/n$ (n being the total quantum number of the valence electron) we are able to get a rough idea concerning the mutual position of the levels with respect to each other. It is seen that the Moseley lines of the configurations $4p^6$ and $4p^54d$ form a screening doublet because they involve valence electrons of the same principal quantum number 4. Similarly the configurations $4p^55s$ and $4p^55p$ form a screening doublet since their respective valence electrons have the same total quantum number 5. However, it is characteristic for this isoelectronic series that due to their higher total quantum number, the configurations $4p^55s$ and $4p^55p$ diverge from the Moseley line belonging to $4p^5$ and cross the Moseley line belonging to $4p^54d$. In the limit of high ionizations the configurations $4p^54d$ will be nearest to the ground level $4p^6$ while the configurations $4p^55s$ and $4p^55p$ are more and more removed from $4p^6$ an $4p^54d$. In Kr I the configuration $4p^55s$ is still nearest to

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[1] W. F. Meggers, T. L. de Bruin, C. J. Humphreys, Bureau of Standards, J. of Res. **3**, 731 (1929).

the ground level $4p^6$, but as is seen from the diagram it must be expected that in Rb II the configurations $4p^5 5s$ and $4p^5 4d$ will just be overlapping whereas for higher ionizations $4p^5 4d$ will lie below $4p^5 5s$. We shall see in the next chapter that indeed in Rb II, $4p^5 5s$ and $4p^5 4d$ overlap, thus complicating considerably the analysis of the spectrum. For the same reason, the configurations $4p^5 6s$ and $4p^5 5d$ overlap also.

The $4p^5 5p$ levels lie in a distinct group about in the middle between the lower $4p^5 5s$ and $4p^5 4d$ levels and the upper $4p^5 6s$ and $4p^5 5d$ levels.

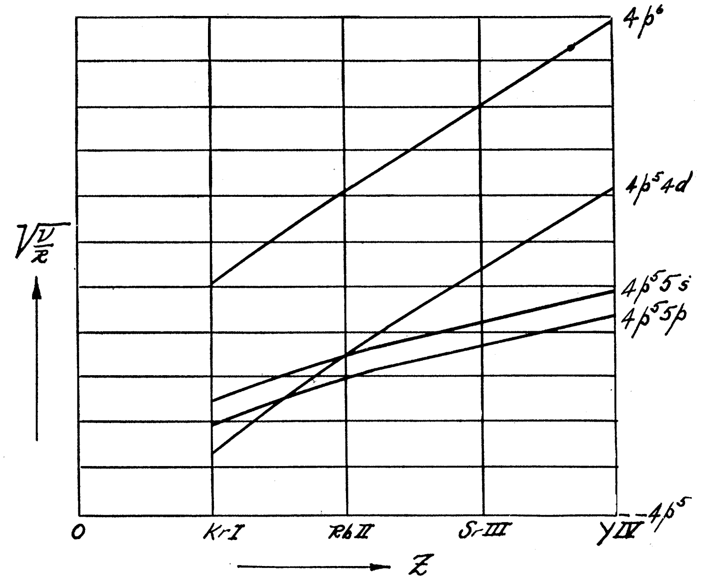

Fig. 1. Schematic Moseley diagram of "average" values of $(\nu/R)^{1/2}$ plotted against atomic number, Z.

III. IDENTIFICATION OF LEVELS AND CONFIGURATIONS IN Rb II

1. Using the separations of the resonance lines obtained in the extreme ultraviolet region as a guide, the classification was extended to the visible region and is presented in Table II.

The first and second columns contain the spectroscopic notations[2] of the levels arising from the $4p^5 4d$, $4p^5 5d$ and $4p^5 5s$, $4p^5 6s$ configurations respectively, while the third column contains the J values of these levels. The fourth column contains the relative term values of the levels of these configurations and are referred to the $4p^6\ {}^1S_0$ level. The heads of the remaining columns are designated with the spectroscopic notations[2] and relative term values (referred to $4p^6\ {}^1S_0$) of the levels due to the $4p^6$ and $4p^5 5p$ configurations. In the body of the table are the wave numbers of the spectral lines, followed in parenthesis by their intensities. Below each wave number is the discrepancy

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[2] Since it is impossible to assign L and S values to the levels, the levels were numbered according to their order, and the inner quantum number was given as lower index to this number. The odd configurations are indicated with a small zero as upper index.

TABLE II. *Classification of lines of Rb II.*

$4p^5(4d, 5s)$				$4p^6$	$4p^55p$									
d	s	J		$^1S_0$ $J=0$	1_1 $J=1$	2_2 2	3_3 3	4_1 1	5_2 2	6_0 0	7_2 1	8_2 2	9_1 1	10_0 0
			Rel. Term	0	154279.25	156742.20	156900.72	158156.66	158717.04	161205.13	163929.47	164972.81	165094.55	167367.30
1_1°		1	126453.53			30289.10*(13) .43		31703.10*(0) −.03	32263.90*(2) .39	34751.50*(2) −.10				
2_2°		2	128693.70		25585.57 (1) .24			29463.06 (7) .10	30023.60*(2) .26					
	$^3P_2^\circ$	2	133347.29		20932.20 (9) −.05	23395.24 (8) .33	23553.65 (10) .22	24809.60 (5) .23	25369.90 (10) .15			31625.30*(1) —.22	31747.20*(5) −.06	
	$^3P_1^\circ$	1	134875.14	134875.00(15) −.14	19404.19 (6) .08	21867.06 (10) 0		23281.81 (8) .29	23842.03 (9) .13	26330.36 (7) .37		30097.85 (0) .18	30219.30*(0) −.11	32762.00*(1) −.16
3_2°		2	136665.21								27264.20 (1) −.06	28307.70 (2) .10	28429.50*(2) .16	
4_0°		0	138799.56		15479.57 (6) −.05			19357.24 (2) .14			25129.87 (7)		26295.03 (5) .04	
5_1°		1	140615.18	140613.00 (9) −2.18	13663.97 (1) −.10	16126.94 (2) .08		17541.59 (6) .11	18101.78 (6) −.08	20590.06 (3) .11	23314.33 (8) −.04	24357.76 (8) .13	24479.35 (6) −.02	27022.13(4) .01
	$^3P_0^\circ$	0	141879.24								22050.27 (3) .04		23215.29 (2) −.02	
$6_{1,2}^\circ$		1,2	143027.39								20902.12 (7) .04		22067.14 (6) −.02	
	$^1P_1^\circ$	1	143467.00	143464.00 (5) −3.00				14689.64 (1) −.02	15249.87 (2) −.17	17738.19 (6) .06	20462.51 (5) .04	21506.03 (8) .22	21627.53 (5) −.02	24170.43 (7) .13
7°_2		2	143960.94					14195.70 (2) −.02	14755.95 (9) −.15			21012.03 (5) .16	21133.62 (5) .01	
$8_{1,2}^\circ$		1,2	145630.06					12526.30 (30) −.30	13087.10 (50) .12					
$4p^5(5d, 6s)$														
	$^3P_2^\circ$	2	179740.11		25460.86 (4) 0	22997.95 (4) .04	22839.52 (5) .13	21583.30 (2) −.15	21023.18 (5) .11					
	$^3P_1^\circ$	1	180173.33		25894.08 (2) .10	23431.17 (5) .04		22016.54 (5) −.13	21456.37 (4) .08	18968.24 (3) .04				
1_1°		1	184205.27		29926.12 (1) .20	27463.03 (1) −.04		26048.48 (1) −.13	25488.32 (3) .09	23000.14 (1) 0				
2_2°		2	184841.65		30562.60*(7)	28099.26 (0) −.19	27940.95 (1) .02	26684.87 (3) −.12	26124.74 (4) .13					
3_3°		3	185131.62			28389.40 (3) −.02	28230.85 (2) −.05		26414.60 (0) .02					
4_2°		2	185622.53		31343.70*(0) .42	28880.35 (2) −.02	28721.60*(3) −.21	27465.78 (4) −.09	26905.64 (1) .15					
5_3°		3	186010.87			29268.66 (6) −.04	29110.01 (0) −.14		27293.89 (4) .06					
6_1°		1	187340.37								23410.97 (4) .04	22367.53 (5) —.03	22245.92 (4) .10	19703.16 (0) .09
	$^1P_1^\circ$	1	188622.28					30465.30*(5) −.32		27417.12 (3) −.03	24692:70 (0) .07	23649.57 (0) .10	23527.88 (1) .15	
7_1°		1	189006.27			32263.90*(2) −.17			30289.10*(3) −.03	27801.5 (1) −.36				
$8_{1,2}^\circ$		1,2	192380.15								28450.50*(3) −.12	27407.39 (0) .05	27285.88 (4) .28	

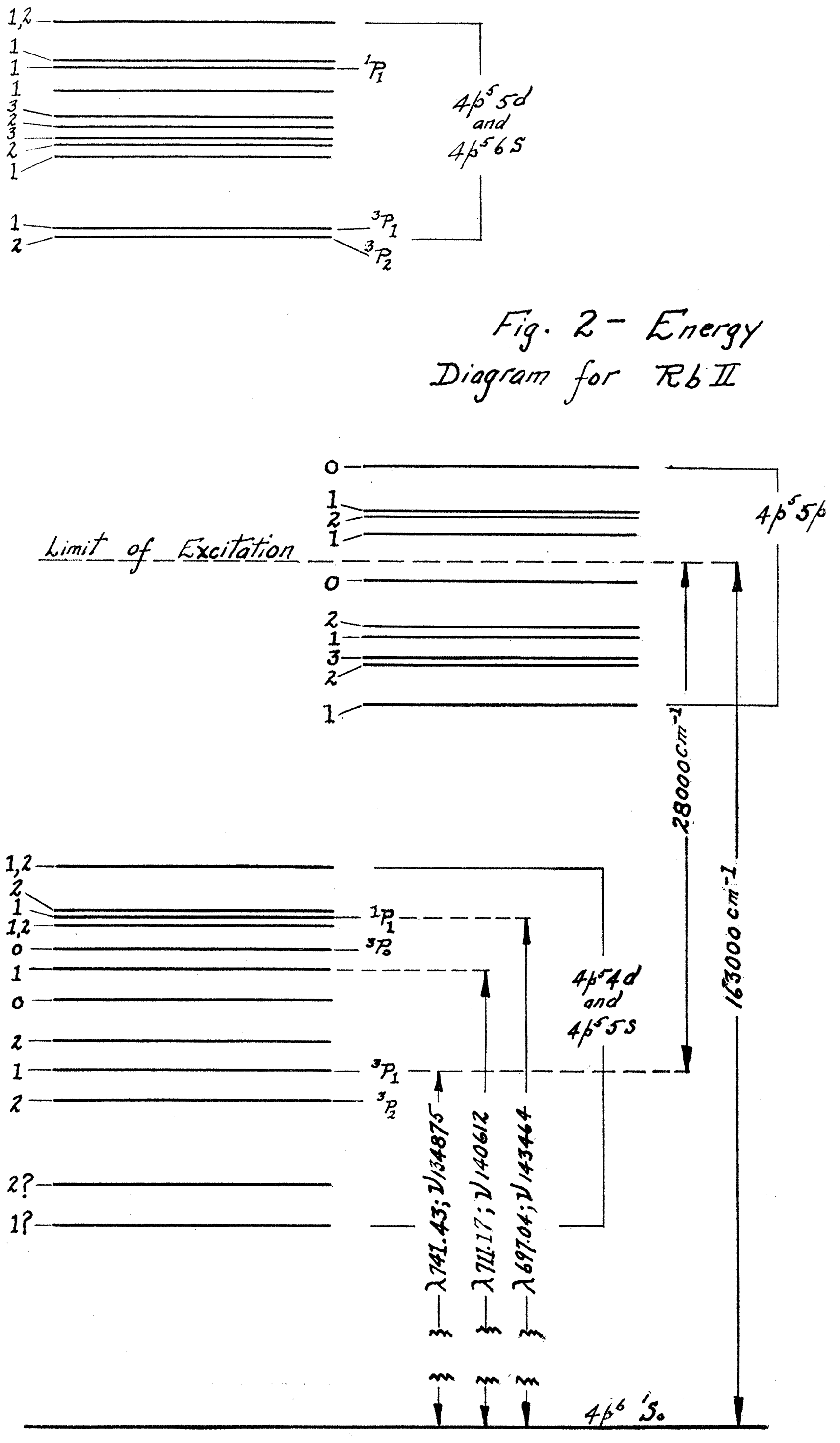

Fig. 2. Energy diagram for Rb II.

(observed value minus calculated value) between the observed wave number and the wave number calculated from the positions assigned to the levels. The scheme is essentially that of Reinheimmer's[3] with some additional lines (marked with an asterisk) taken from the tables of Otsuka[4] that fit very well into the classification.

2. The energy diagram of Rb II is represented by Fig. 2 and all levels are drawn to scale except the $4p^6\ ^1S_0$. The numerals on the left of the groups are the inner quantum numbers (J), while the term symbols to the right of the lower and upper groups designate the s levels. (See paragraph 5 below for identification of the s levels.) The three resonance lines representing transitions from the $4p^6$ to $4p^55s$ and $4p^54d$ levels are indicated. The limit of excitation of metastable helium falls about midway between the two groups of levels of the $4p^55p$ configuration.

3. Table III contains a list of Rb II lines classified in this investigation. In the first three columns are the intensities as obtained by the three investi-

TABLE III. *Wave-length list of Rb II lines.*

Intensity			λ air I.A.	ν vac.	Classification
M	O	R			
5			697.04 (vac.)	143464	$4p^{6\,1}S_0-5s^1P_1^\circ$
9			711.17 (vac.)	140613	$4p^{6\,1}S^\circ-4d5_1^\circ$
15			741.43 (vac.)	134875	$4p^{6\,1}S_0-5s^3P_1^\circ$
	2		2876.73	34751.5	$4d1_1^\circ-5p6_0$
	1		3051.43	32762.0	$5s^3P_1^\circ-5p10_0$
	2		3098.55	32263.9	$4d1_1^\circ-5p5_2\ (5p2_2-5d7_1^\circ)$
	5		3148.98	31747.2	$5s^3P_2^\circ-5p9_1$
	0		3153.36	31703.1	$4d1_1^\circ-5p4_2$
	1		3161.11	31625.3	$5s^3P_2^\circ-5p8_2$
	0		3185.51	31343.7	$5p1_1-5d4_2^\circ$
	7		3271.03	30562.6	$5p1_1-5d2_2^\circ$
	5		3281.49	30465.3	$5p4_1-6s^1P_1^\circ$
2	3		3300.73	30289.1	$4d1_1^\circ-5p2_2\ (5p5_2-5d7_1^\circ)$
	0		3308.20	30219.2	$5s^3P_1^\circ-5p9_1$
2	8	0	3321.545	30097.85	$5s^3P_1^\circ-5p8_2$
	2		3329.91	30023.6	$4d2_2^\circ-5p5_2$
		1	3340.605	29926.12	$5p1_1-5d1_1^\circ$
1	7	2	3393.111	29463.06	$4d2_2^\circ-5p4_2$
		0	3415.648	29268.66	$5p2_2-5d5_3^\circ$
		0	3434.263	29110.01	$5p3_3-5d5_3^\circ$
		2	3461.574	28880.35	$5p2_2-5d4_2^\circ$
	3		3480.71	28721.6	$5p3_3-5d4_2^\circ$
	3		3513.88	28450.5	$5p7_1-5d8_{1,2}^\circ$
	2		3516.53	28429.50	$4d3_2^\circ-5p9_1$
		3	3521.439	28389.40	$5p2_2-5d3_3^\circ$
0	9	2	3531.602	28307.70	$4d3_2^\circ-5p8_2$
		2	3541.216	28230.85	$5p3_3-5d3_3^\circ$
		0	3557.800	28099.26	$5p2_2-5d2_2^\circ$
		1	3577.959	27940.95	$5p3_3-5d2_2^\circ$
	1		3595.91	27801.5	$5p6_0-5d7_1^\circ$
		4	3639.860	27465.78	$5p4_1-5d4_2^\circ$
		1	3640.225	27463.03	$5p2_2-5d1_1^\circ$
		3	3646.321	27417.12	$5p6_0-6s^1P_1^\circ$
		0	3647.616	27407.39	$5p8_2-5d8_{1,2}^\circ$
		4	3662.784	27293.89	$5p5_2-5d5_3^\circ$
		4	3663.859	27285.88	$5p9_1-5d8_{1,2}^\circ$

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[3] H. Reinheimmer, Ann. d. Physik **71,** 162 (1923).

[4] O. Otsuka, Zeits. f. Physik **36,** 786 (1926).

TABLE III (*Continued*).

Intensity			λ air I.A.	ν vac.	Classification
M	O	R			
		1	3666.774	27264.20	$4d3_2^\circ-5p7_1$
		4	3669.622	27022.13	$4d5_1^\circ-5p10_0$
		1	3715.640	26905.64	$5p5_2-5d4_2^\circ$
		3	3746.381	26684.87	$5p4_1-5d2_2^\circ$
		0	3784.714	26414.60	$5p5_2-5d3_3^\circ$
		1	3796.393	26333.34	$5s^3P_1^\circ-5p6_0$
50		7	3796.823	26330.36	
		1	3797.170	26327.96	
		1	3797.276	26327.23	
		5	3801.925	26295.03	$4d4_0^\circ-5p9_1$
		4	3826.708	26124.74	$5p5_2-5d2_2^\circ$
		1	3837.910	26048.48	$4p4_1-5d1_1^\circ$
4		2	3860.796	25894.08	$5p1_1-6s^3P_1^\circ$
		1	3907.350	25585.57	$4d2_2^\circ-5p1_1$
		3	3922.259	25488.32	$5p5_2-5d1_1^\circ$
2		4	3926.489	25460.86	$5p1_1-6s^3P_2^\circ$
50		10	3940.568	25369.90	$5s^3P_2^\circ-5p5_2$
		1	3940.915	25367.67	
		1	3941.099	25366.48	
2		7	3978.207	25129.87	$4d4_0^\circ-5p7_1$
7		5	4029.562	24809.60	$5s^3P_2^\circ-5p4_1$
		0	4048.640	24692.70	$5p7_1-6s\ P_1^\circ$
3		6	4083.927	24479.35	$4d5_1^\circ-5p9_1$
6		8	4104.313	24357.76	$4d5_1^\circ-5p8_2$
2		7	4136.125	24170.43	$5s^1P_1^\circ-5p10_0$
		1	4192.566	23845.05	$5s^3P_1^\circ-5p5_2$
20		9	4193.097	23842.03	
		1	4193.467	23839.93	
		1	4193.612	23839.10	
		0	4227.222	23649.57	$5p8_2-6s^1P_1^\circ$
		1	4243.888	23556.69	$5s^3P_2^\circ-5p3_3$
25		10	4244.436	23553.65	
		1	4244.800	23551.63	
		1	4244.981	23550.62	
		1	4249.085	23527.88	$5p9_1-6s^1P_1^\circ$
		5	4266.622	23431.17	$5p2_2-6s^3P_1^\circ$
		4	4270.303	23410.97	$5p7_1-5d6_1^\circ$
		1	4272.640	23398.17	$5s^3P_2^\circ-5p2_2$
20		8	4273.176	23395.24	
		1	4273.524	23393.33	
		1	4273.703	23392.35	
0		8	4288.005	23314.33	$4d5_1^\circ-5p7_1$
		1	4293.484	23284.58	$5s^3P_1^\circ-5p4_1$
20		8	4293.994	23281.81	
		1	4294.362	23279.82	
		1	4294.567	23278.71	
		2	4306.299	23215.29	$5s^3P_0^\circ-5p9_1$
		1	4346.582	23000.14	$5p6_0-5d1_1^\circ$
		4	4346.996	22997.95	$5p2_2-6s^3P_2^\circ$
3		5	4377.150	22839.52	$5p3_3-6s^3P_2^\circ$
		5	4469.516	22367.53	$5p8_2-5d6_1^\circ$
		4	4493.949	22245.92	$5p9_1-5d6_1^\circ$
1		6	4530.358	22067.14	$4d6_{1,2}^\circ-5p9_1$
		3	4533.824	22050.27	$5s^3P_0^\circ-5p7_1$
		5	4540.771	22016.54	$5p4_1-6s^3P_1^\circ$
15		10	4571.790	21867.16	$5s^3P_1^\circ-5p2_2$
		1	4572.162	21865.38	
1		5	4622.447	21627.53	$5s^1P_1^\circ-5p9_1$
		2	4631.918	21583.30	$5p4_1-6s^3P_2^\circ$
5		8	4648.562	21506.03	$5s^1P_1^\circ-5p8_2$
		4	4659.320	21456.37	$5p5_2-6s^3P_1^\circ$
1		5	4730.479	21133.62	$4d7_2^\circ-5p9_1$
		5	4755.329	21023.18	$5p5_2-6s^3P_2^\circ$

TABLE III (*Continued*).

Intensity			λ air I.A.	ν vac.	Classification
M	O	R			
3		5	4757.853	21012.03	$4d7_2^\circ-5p8_2$
20		9	4775.998	20932.20	$5s^3P_2^\circ-5p1_1$
		1	4776.410	20930.39	
0		7	4782.871	20902.12	$4d6_{1,2}^\circ-5p7_1$
10		3	4855.361	20590.16	$4d5_1^\circ-5p6_0$
		5	4885.627	20462.51	$5s^1P_1^\circ-5p7_1$
		0	5073.919	19703.16	$5p10_0-5d6_1^\circ$
10		6	5152.094	19404.19	$5s^3P_1^\circ-5p1_1$
0		2	5164.592	19357.24	$4d4_0^\circ-5p4_1$
		3	5270.508	18968.24	$5p6_0-6s^3P_1^\circ$
20		6	5522.789	18101.78	$4d5_1^\circ-5p5_2$
15		6	5635.994	17738.91	$5s^1P_1^\circ-5p6_0$
5		6	5699.159	17541.59	$4d5_1^\circ-5p4_1$
		2	6199.093	16126.94	$4d5_1^\circ-5p2_2$
8		6	6458.347	15479.57	$4d4_0^\circ-5p1_1$
2		2	6555.625	15249.87	$5s^1P_1^\circ-5p5_2$
15		9	6775.062	14755.95	$4d7_2^\circ-5p5_2$
		1	6805.646	14689.64	$5s^1P_1^\circ-5p4_1$
		2	7042.450	14195.70	$4d7_2^\circ-5p4_1$
8		1	7316.505	13663.97	$4d5_1^\circ-5p1_1$
50			7664.43	13087.10	$4d8_{1,2}^\circ-5p5_2$
30			7698.57	12526.30	$4d8_{1,2}^\circ-5p4_1$

gators; in the fourth column are the frequencies in vacuum; the last column contains the classification. ($4p^5$) is omitted in the classification since it is common to all configurations lying above the $4p^6\ {}^1S_0$ ground state. The odd configurations are indicated by an upper index^0.

4. As far as the identification of the levels whose term values are written down at the top of Table II is concerned, there seems to be no ambiguity to assign them to the configuration $4p^55p$. Not only does their number (namely 10) agree with what is to be expected theoretically, but also the individual inner quantum numbers are exactly those which the configuration is to yield (compare Table I) In addition to that, a very convincing argument in favor of the present identification is given by a consideration of the change of separation when going from Kr I to Rb II

In the following figure (Fig. 3), the relative term values of the ten p terms of Kr I are drawn referred to their center of gravity, and analogously the relative term values of the ten p terms of Rb II are plotted referred to the center of gravity but reduced in scale to the magnitude of the relativisitic doublet p^5 of Kr I by multiplication with 5220/8500. This method is the same as that used by Mack, Laporte, and Lang.[5] As may be seen from this diagram, there is a very good correspondence between the two respective groups of levels. It is interesting to note that the two crossings-over which occur take place between levels which in both spectra have very small separations between them. It is also interesting to note the beginning of (jj) coupling since in both spectra, the largest separation divides the ten p levels into two groups of four and six levels each with the inner quantum numbers 011223 and 0112 respectively. This division is exactly the one required by (jj) cou-

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[5] J. E. Mack, O. Laporte, and R. J. Lang, Phys. Rev. **31**, 748 (1928).

pling as is seen from Table I. In the limit of very high ionization, the levels will be arranged in four groups, namely 12, 0123, 01, 12.

5. So far the discussion has been confined to the even levels. The odd levels offer the singular problem of separating the levels due to $4p^5 5s$ from those due to $4p^5 4d$. To be sure, this is impossible from a strictly theoretical point of view due to the complete overlapping of the two configurations, just as it is impossible to assign L or S values unless there is decided Russell-Saunders coupling. In our case we were guided by the three resonance lines, two of which would have to involve the difference ${}^3P_1 - {}^1P_1$. For fairly pronounced (*jj*) coupling, this difference could be expected to be equal to${}^3P_2 - {}^3P_0$ which distance was estimated to be in the neighborhood of 7500 cm^{-1}. The nearest approach to this were the two resonance lines $\nu\nu$134875, 143646 with $\Delta\nu = 8589$ cm^{-1}. Thus the levels 134875 cm^{-1} and 143467 cm^{-1} were decided on as ${}^3P_1$ and ${}^1P_1$. After that, the levels 133347 cm^{-1} and 141879 cm^{-1} immediately suggested themselves as ${}^3P_2$ and ${}^3P_0$. A confirmation of this identification is the fact that according to Reinheimmer[3] the levels ${}^3P_2$ and ${}^3P_1$ show a characteristic hyperfine structure. It must nevertheless be admitted that the identification of the level 141879 cm^{-1} as ${}^3P_0$ is not very certain and rests

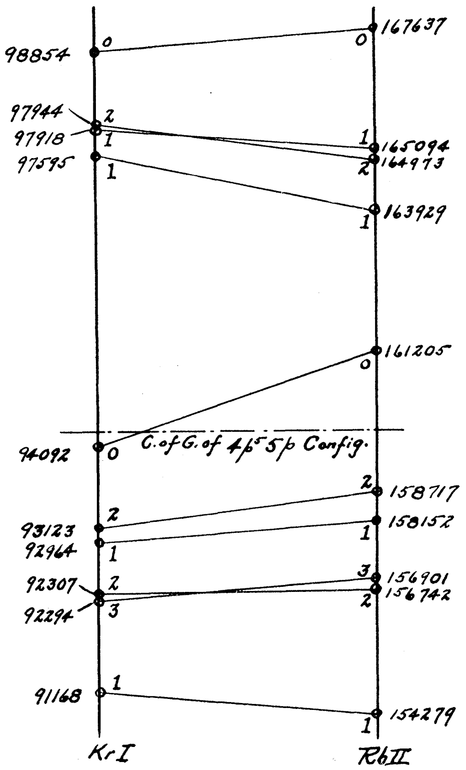

Fig. 3. The $4p^5 5p$ configurations of Kr I and Rb II referred to the center of gravity and reduced to the same magnitude of the relativistic doublet $4p^5$.

mainly upon an order of magnitude agreement with Houston's formula.[6]

Exact agreement with Houston's formula cannot be expected, since the p^5s overlap with p^5d. Compare Laporte and Inglis[7] for disagreement in case of K II where the analogous situation occurs.

After the identification of the $4p^55s$ levels, we are left with eight levels with the following inner quantum numbers: 0; 1?; 2?; 1; 2; 2; 1, 2; 1, 2. A question mark following two of the levels means that while there is a sufficient number of combinations of these levels to fix the quantum numbers unambiguously, the reality of the levels as such, is somewhat doubtful due to the fact that their combinations do not appear strongly enough in the hollow cathode discharge. On the other hand, the notation 1, 2 means that due to an insufficient number of combinations of these levels, their inner quantum number cannot be determined completely, while nevertheless the levels seem real. On the whole the result of Table I is not unsatisfactory. Counting one of the 1, 2 levels as having $J=1$, and the other as having $J=2$, we get: one level with $J=0$, three levels with $J=1$, and four levels with $J=2$ which is indeed the required number for $4p^54d$ according to Table I. Although a thorough search for levels with $J=3$ was made, none could be established satisfactorily, at least not with the present data. Their combinations appear not to lie within our region of observation.

6. We come now to a corresponding discussion of the levels due to $4p^56s$ and $4p^55d$ configurations. Since from the previous discussion we have a fairly accurate estimate of the $4p^5\ {}^2P$ separation, namely:

$$4p^55s({}^3P_2 - {}^3P_0) = 8532 \text{ cm}^{-1}$$

$$4p^55s({}^3P_1 - {}^1P_1) = 8592 \text{ cm}^{-1},$$

we now have to search for two $J=1$ levels which should show the same separation, with the lower one of the two having $J=2$ level nearby. The levels with relative term values 180173.33 cm^{-1} and 188622.28 cm^{-1} were chosen as ${}^3P_1$ and ${}^1P_1$ respectively. They show the separation $4p^56s\ ({}^3P_1-{}^1P_1)=8448.85$ cm^{-1}. This choice also fixes the level 179740.11 cm^{-1} as being ${}^3P_2$. A search for the level ${}^3P_0$ which ought to lie a little below ${}^1P_1$ has been unsuccessful. This is not surprising since even the combinations with ${}^1P_1$ are rather weak.

Having thus selected the levels belonging to $4p^56s$, there remain for the configuration $4p^55d$ eight levels with inner quantum numbers: 1; 2; 3; 1; 2; 3; 1; 1, 2 while the theory leads one to expect one level with $J=0$, three levels with $J=1$, four levels with $J=2$, three levels with $J=3$, and one level with $J=4$.

It is seen by comparison that level "1, 2" with relative term value 192380.15 cm^{-1}, the inner quantum number of which cannot be decided from its combinations (compare Table I), must be given $J=2$. This leaves one more level with $J=2$ and one level with $J=3$ undiscovered. Needless to say the level $J=4$ cannot be established from its one combination with the $4p^55p$ group.

[6] W. V. Houston, Phys. Rev. **33**, 297 (1929).

[7] O. Laporte and D. R. Inglis, Phys. Rev. **35**, 1337 (1930).

7. The separations between the first and second series members of $^3P_2$ and $^3P_1$ are found to be equal to 46393 cm^{-1} and 45298 cm^{-1} respectively. Using the Rydberg term tables for spark spectra,[8] these differences were each fitted into a Rydberg sequence thus giving two independent determinations of the absolute scale:

$$\begin{array}{rl|rl} 5s^3P_2 - 6s^3P_2 & = 46393\ \text{cm}^{-1} & 5s^3P_1 - 6s^3P_1 & = 45298 \\ ^3P_2 & = 88556 & ^3P_1 & = 86926\ \text{cm}^{-1} \\ 5s(^3P_2 - {}^3P_1) & = \underline{\ 1528\ } & & \\ ^3P_1 & = 87028\ \text{cm}^{-1} & & \end{array}$$

The agreement is very good; we take as average value $^3P_1 = 86977$. By adding the frequency of the resonance line $\lambda 741.43$, $\nu 134875\ \text{cm}^{-1}$ $(^1S_0 - {}^3P_1)$ to the $^3P_1$ term value, we obtain

$$^1S_0 = 221852\ \text{cm}^{-1}$$

as the calculated term of the normal rubidium ion and corresponds to an ionizing potential of 27.3 volts. Mohler[9] gives 25.2 volts.

8. The available energy of metastable helium atoms is about[10] 163000 cm^{-1}. Since 134875 cm^{-1} are expended in exciting the first resonance line, then only the remaining energy of about 28000 cm^{-1} will be available to excite additional levels. Thus the limit of excitation falls between level 161205 and level 163929 cm^{-1}.

This is in complete agreement with the experimental facts. Numerous strong lines given by Reinheimmer[3] which represent transitions from $4p^55p$ towards $4p^55s$ do not appear in the hollow cathode discharge in helium because they come from one of the ten $4p^55p$ levels which lies beyond the just mentioned limit of excitation. (For example, the line representing the transition $4p^55s\ ^3P_2{}^0 - 4p^55p\ 9_1 = 31747.2$ does not appear in this investigation.) On the other hand many of Reinheimmer's lines appear strongly on our plates also because they involve a $4p^55p$ level that lies inside the limit of excitation (for example, the line $4p^55s\ ^1P_1{}^0 - 4p^55p\ 6_0 = 17738.19$ has intensity 6 in Reinheimmer's data, and appears with an intensity of 15 in the hollow cathode discharge in helium). To be sure, a few lines whose initial levels lie beyond the excitation limit appear weakly in the hollow cathode discharge also because there is always a small number of ionized helium atoms present to furnish a much higher energy of excitation of Rb^+.

A corresponding analysis of Cs II is being made at the present time[11] and will be published in the near future.

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[8] F. Paschen, J.O.S.A. and R.S.I. **16,** 231 (1928).

[9] F. L. Mohler, Phys. Rev. **28,** 46 (1928).

[10] For convenience in spectroscopic discussion, the energy is given in ν units. It may be converted to equivalent volts by multiplying by 1.2345×10^{-4}.

[11] See preliminary communication, Phys. Rev. **37,** 845 (1931).