

separation. The $2s^2 2p^4(^1D) 3d^2 G_{9/2}$ level has been omitted because the transition between it and the $2s^2 2p^4(^1D) 3p^2 F_{7/2}^0$ level could not be identified uniquely.

The classified lines by which the new levels were established are included in Table II. The intensities are visual estimates and are com-

parable only over short regions of the spectrum. Numerous intercombination lines between the doublet and quartet levels (limit 3P) have been observed.

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The Spectra of Rb III and Sr IV

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By applying Shortley's equations to the $4s^2 4p^5(^2P^0) 5p$ levels of Rb II, the separation of the ground levels $4s^2 4p^5(^2P^0)$ of Rb III has been computed, and experimentally observed to be 7380 cm^{-1} . In the case of Sr IV, the $^2P^0$ separation has been predicted from the regular doublet law and identified from the data as 9731 cm^{-1} . On the basis of transitions into the ground doublet certain $4s^2 4p^4 d$ and $4s^2 4p^4 s$ levels have been located.

AN analysis of the spectrum of Br I has been given by Kiess and de Bruin,¹ and the spectrum of Kr II has been investigated by de Bruin, Humphreys and Meggers.² The present investigation was undertaken to extend the Br I like sequence to Rb III and Sr IV. The essential features of the study presented here consist in predicting and locating the separation of the lowest levels and identifying certain transitions into the ground doublet.

EXPERIMENTAL

The condensed spark in vacuum was used to excite the spectra of Rb III and Sr IV. The region from 250 to 1200A was photographed with a vacuum spectrograph which was equipped with a grating having 30,000 lines per inch. The dispersion of the instrument was about 5.3A/mm. A kenetron rectifier (output potential 45 kv) supplied the high potential. The condenser had a capacitance of 0.18 μ f. In procuring the data for rubidium, aluminum electrodes cored with Rb₂SO₄ were employed. The rubidium lines were

duplicated when the discharge occurred between electrodes cored with Rb I. As a further aid in isolating the lines due to rubidium, a comparison spectrum of Rb₂SO₄ and Rb I was obtained. After eliminating the usual impurity lines of carbon, oxygen and aluminum, the remaining lines common to both spectra were regarded as belonging to rubidium. A similar procedure was followed in exciting the strontium spectrum, metallic strontium and strontium oxide serving as sources of strontium. Aluminum, carbon, and oxygen lines were used as standards in the reduction of the plates. The wave-lengths of the aluminum lines were taken from Ekefors,³ those of carbon and oxygen from Edlén's list.⁴

THE ANALYSIS OF THE SPECTRA

The normal $4s^2 4p^5$ electron configuration of Rb III and Sr IV gives rise to inverted $^2P^0$ terms. The terms which arise when one of the $4p$ electrons is raised to the $4d$, $5s$, $5p \dots$ states are given in Table I.

The starting point for the search of Rb III doublets was the prediction of the separation of

¹ Kiess and de Bruin, Nat. Bur. Stand. J. Research **4**, 667 (1930).

² de Bruin, Humphreys and Meggers, Nat. Bur. Stand. J. Research **11**, 409 (1933).

³ Ekefors, Zeits. f. Physik **51**, 471 (1928).

⁴ Edlén, Zeits. f. Physik, **85**, 85 (1933).

the ground levels. This separation was computed by the use of Shortley's⁵ equations. These relations apply to the ten s^2p^5p levels of a rare gas type spectrum and express the values of the levels involved in terms of a set of parameters one of which is related to the doublet separation of the next higher ion. Utilizing the term values for the $4s^24p^55p$ levels of Rb II, determined by Laporte, Miller and Sawyer⁶ one obtains 7550 cm^{-1} for the separation of the lowest doublet of Rb III. With this value as a guide, a careful examination of the Rb data yielded a score of pairs of lines having $\Delta\nu = 7380 \text{ cm}^{-1}$. This difference occurred more frequently than any other and included some of the strongest lines.

The next step was the determination of the separation of the lowest levels of Sr IV. Since no classification of Sr III has been carried out the previous procedure could not be used here. Recourse was therefore made to the regular doublet law given by

$$\Delta\nu = R\alpha^2(Z-s)^4/n^3(l+1)l.$$

The values of the screening constant s were calculated on the assumption $\Delta\nu = 7380 \text{ cm}^{-1}$ for Rb III and by the use of the known separations of the ground levels of Br I and Kr II. It is known that the screening constant plotted against the atomic number Z results in a smooth curve with diminishing slope as one passes on to the higher members in an isoelectronic sequence. There is also a progressive diminution in the values of s . Guided by these facts an extrapolated value of $\Delta\nu = 9825 \text{ cm}^{-1}$ was obtained for the $4s^24p^5 2P^0$ separation of Sr IV.

A search for recurring differences of about this magnitude resulted in the location of pairs of

TABLE I. Term table for Br I like spectra.

CONFIGURATION	TERMS			
	$4s^24p^5$ $4s 4p^6$	$2P^0$ $2S$		
	Limit $4s^24p^4 3P$		Limit $4s^24p^4 1D$	Limit $4s^24p^4 1S$
$4s^24p^4ns$ ($n \geq 5$)	$4P$	$2P$	$2D$	$2S$
$4s^24p^4np$ ($n \geq 5$)	$4D^0 4P^0 4S^0$	$2D^0 2P^0 2S^0$	$2F^0 2D^0 2P^0$	$2P^0$
$4s^24p^4nd$ ($n \geq 4$)	$4F 4D 4P$	$2F 2D 2P$	$2G^2 2F^2 2D^2 2P^2 2S$	$2D$

⁵ Shortley, Phys. Rev. **44**, 666 (1933).

⁶ Laporte, Miller and Sawyer, Phys. Rev. **38**, 843 (1931).

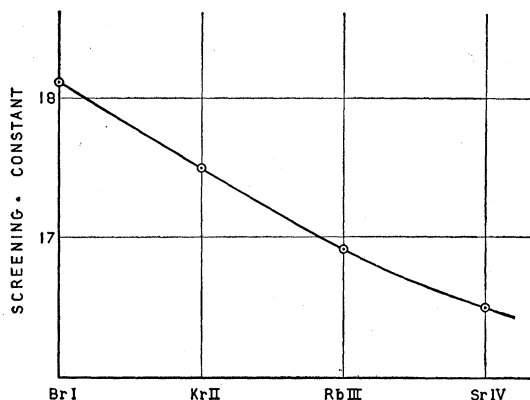


FIG. 1. Screening constant, configuration $4s^24p^5$.

lines having the separation $\Delta\nu = 9731 \text{ cm}^{-1}$. This was in good agreement with the predicted value and was assumed to be the separation of the ground doublet of Sr IV. The value of s for Sr IV was calculated by using this value of $\Delta\nu$. The results for the sequence are shown in Table II and the graph of the screening constant against the atomic number is given in Fig. 1.

ASSIGNMENT OF TERMS

The first lines to be identified were the transitions

$$4s^24p^5 2P^0 - 4s^24p^4(3P)5s 2P$$

$$" 2P^0 - " 4P_{3/2, 1/2}.$$

TABLE II. Configuration $4s^24p^5$. Separation of $2P^0$ levels and values of the screening constant.

SPECTRUM	$\Delta\nu$	$(Z-s)$	Z	s	Δs
Br I	3685	16.87	35	18.13	
Kr II	5371	18.54	36	17.46	0.67
Rb III	7380	20.07	37	16.93	0.53
Sr IV	9731	21.50	38	16.50	0.43

These four pairs of lines have their origin in the lowest levels belonging to the $5s$ electron configuration. Consequently they form a characteristic group of lines of high intensity. Their approximate positions had been predicted by the use of a Moseley diagram. The location of the observed lines agreed well with prediction. The $4s^24p^4(1D)5s 2D_{3/2}$ and $4s^24p^4(1S)5s 2S_{1/2}$ levels were also identified by extrapolations on a Moseley graph. These levels are well separated

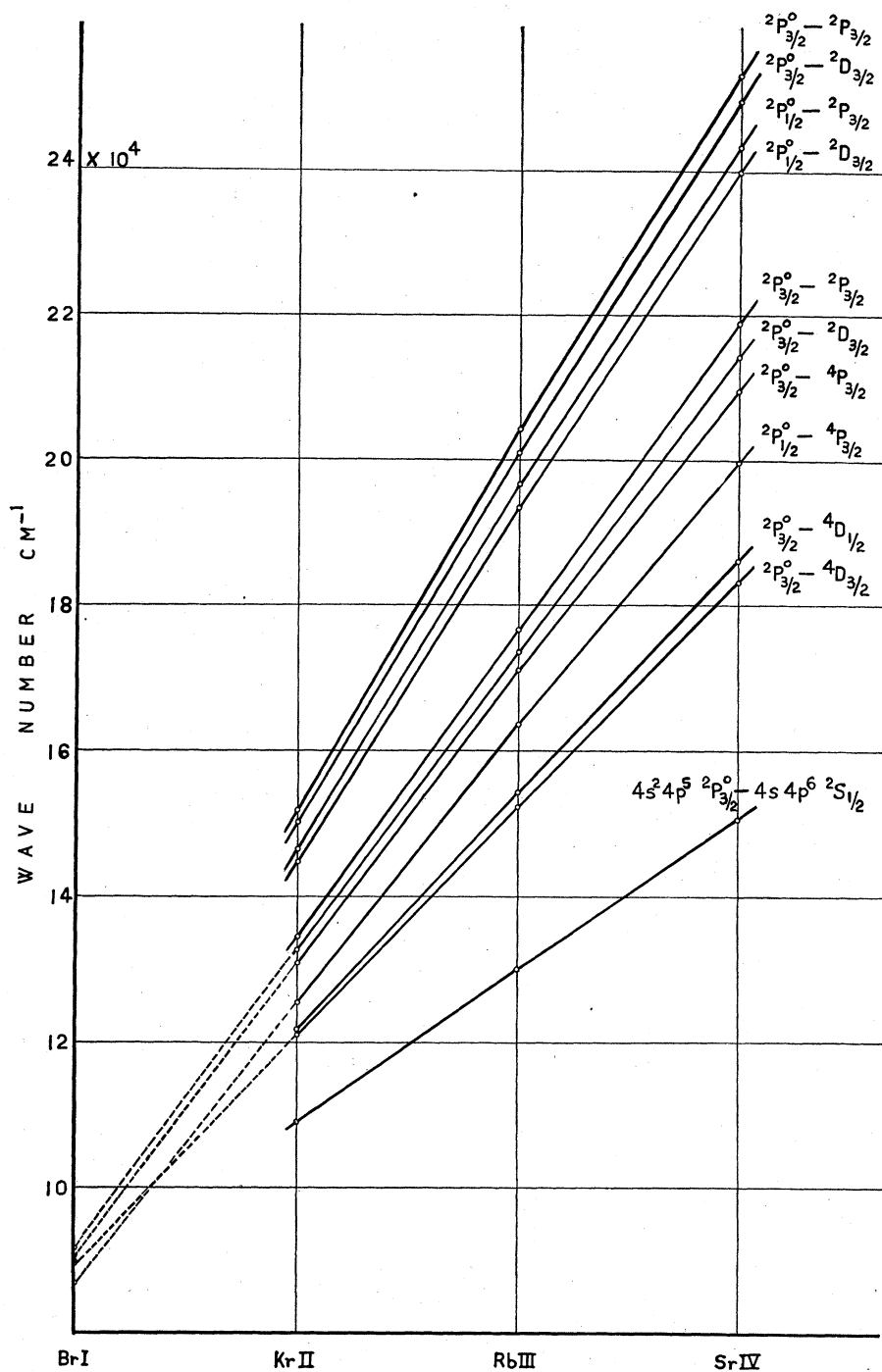


FIG. 2. Linear displacement of wave number. Transitions $4p^5-4p^4d$ and $4p^5-4s4p^6$.

and lie much higher than the $5s$ states built on the 3P limit. The remaining $5s$ levels, namely $4s^24p^4(^1D)5s^2D_{5/2}$ and $4s^24p^4(^3P)5s^4P_{5/2}$ could

not be identified with certainty since they combine only with the $4s^24p^5^2P_{3/2}^0$ level.

The $4p-4d$ transitions do not involve a

TABLE III. Square roots of certain terms.

CONFIGURATION	TERM	Br I	$\Delta(T)^{1/2}$	Kr II	$\Delta(T)^{1/2}$	Rb III	$\Delta(T)^{1/2}$	Sr IV
$4s^24p^5$	$^2P^0_{3/2}$	309.1	136.1	445.2	119.8	565.0*	113.2	678.2*
$4s4p^6$	$^2S_{1/2}$	—	—	298.6	137.2	435.8	120.5	556.3
$4s^24p^4(^3P)5s$	$^4P_{3/2}$	175.1	113.1	288.2	106.1	394.3	94.4	488.7
	$^2P_{3/2}$	168.4	113.9	282.3	102.4	384.7	91.8	476.5
$4s^24p^4(^1D)5s$	$^2D_{3/2}$	135.1	130.6	265.7	104.5	370.2	90.6	460.8
$4s^24p^4(^3P)4d$	$^4D_{3/2}$	75.4	202.4	277.8	131.6	409.4*	116.6	526.0*
	$^2P_{3/2}$	—	—	252.1	125.9	378.0	112.9	490.9
$4s^24p^4(^1D)4d$	$^2D_{3/2}$	—	—	219.0	126.1	345.1	113.5	458.6
$4s^24p^4(^1S)5s$	$^2S_{1/2}$	140.2	88.6	228.8	106.9	335.7	98.1	433.8

* Used in determining the approximate absolute term values.

change in the total quantum number. Hence a plot of the wave numbers of analogous transitions against the atomic number should result in nearly straight lines. Accordingly several $4d$ levels which combine with the ground doublet were established on the basis of the irregular doublet law. Fig. 2 represents certain $4p-4d$ transitions for Br I like spectra.

In an isoelectronic sequence when the square roots of corresponding term values are plotted against the atomic number, smooth curves are obtained. Such curves tend to become approximately linear as one progresses to higher members of a sequence. Furthermore, as a consequence of the irregular doublet law, the difference between the square roots of the term values of levels approaching the same limit and having the same total quantum number should be independent of the atomic number, i.e., $\Delta\sqrt{T} = \text{const}$. The absolute term values were approximated by the application of these two regularities. On a Moseley diagram (see Fig. 3 and Table III) the lines representing the $4s^24p^5\ ^2P^0_{3/2}$ and

$4s^24p^4(^3P)4d\ ^4D_{3/2}$ levels were extended to Rb III and Sr IV so as to keep $\Delta\sqrt{T}$ nearly constant and at the same time the ordinates were chosen so that the difference between their squares was equal to the wave number of the $4s^24p^5\ ^2P^0_{3/2} - 4s^24p^4(^3P)4d\ ^4D_{3/2}$ transition. In this manner the approximate absolute term value of the $4s^24p^5\ ^2P^0_{3/2}$ level in Rb III was found to be 320,000 cm^{-1} below the 3P ionization limit. The corresponding level in Sr IV was estimated to be 460,000 cm^{-1} with respect to the 3P states of Sr V.

In the data for strontium, the most intense pair of lines having the separation of the ground levels, yielded a level nearest to normal state. Since the $4s4p^6\ ^2S_{1/2}$ level is expected to lie closest to the ground state, these lines were thought to be the transitions

$$4s^24p^5\ ^2P^0_{3/2, 1/2} - 4s4p^6\ ^2S_{1/2}.$$

Since these transitions would have to follow the

TABLE IV. Term values for Rb III.

TERM SYMBOL	APPROXIMATE ABSOLUTE TERM VALUE (CM^{-1})
$4s^24p^5\ ^2P^0_{3/2}$	320,000
$4s^24p^5\ ^2P^0_{1/2}$	312,620
$4s\ 4p^6\ ^2S_{1/2}$	189,964
$4s^24p^4(^3P)4d\ ^4D_{3/2}$	167,647
$4s^24p^4(^3P)4d\ ^4D_{1/2}$	165,597
$4s^24p^4(^3P)5s\ ^4P_{3/2}$	155,493
$4s^24p^4(^3P)5s\ ^4P_{1/2}$	151,915
$4s^24p^4(^3P)4d\ ^4P_{1/2}$	149,577
$4s^24p^4(^3P)4d\ ^4P_{3/2}$	149,153
$4s^24p^4(^3P)5s\ ^2P_{3/2}$	147,955
$4s^24p^4(^3P)4d\ ^2D_{3/2}$	146,525
$4s^24p^4(^3P)5s\ ^2P_{1/2}$	144,604
$4s^24p^4(^3P)4d\ ^2P_{3/2}$	142,956
$4s^24p^4(^1D)5s\ ^2D_{3/2}$	137,037
$4s^24p^4(^1D)4d\ ^2D_{3/2}$	119,117
$4s^24p^4(^1D)4d\ ^2P_{3/2}$	115,896
$4s^24p^4(^1S)5s\ ^2S_{1/2}$	112,723

TABLE V. Term values for Sr IV.

TERM SYMBOL	APPROXIMATE ABSOLUTE TERM VALUES (CM^{-1})
$4s^24p^5\ ^2P^0_{3/2}$	460,000
$4s^24p^5\ ^2P^0_{1/2}$	450,269
$4s\ 4p^6\ ^2S_{1/2}$	309,495
$4s^24p^4(^3P)4d\ ^4D_{3/2}$	276,695
$4s^24p^4(^3P)4d\ ^4D_{1/2}$	273,935
$4s^24p^4(^3P)4d\ ^4P_{1/2}$	250,786
$4s^24p^4(^3P)4d\ ^4P_{3/2}$	250,471
$4s^24p^4(^3P)4d\ ^2D_{3/2}$	245,655
$4s^24p^4(^3P)4d\ ^2P_{3/2}$	241,061
$4s^24p^4(^3P)5s\ ^4P_{3/2}$	238,851
$4s^24p^4(^3P)5s\ ^4P_{1/2}$	234,147
$4s^24p^4(^3P)5s\ ^2P_{3/2}$	227,030
$4s^24p^4(^3P)5s\ ^2P_{1/2}$	221,797
$4s^24p^4(^1D)5s\ ^2D_{3/2}$	212,384
$4s^24p^4(^1D)4d\ ^2D_{3/2}$	210,354
$4s^24p^4(^1D)4d\ ^2P_{3/2}$	206,767
$4s^24p^4(^1S)5s\ ^2S_{1/2}$	188,226

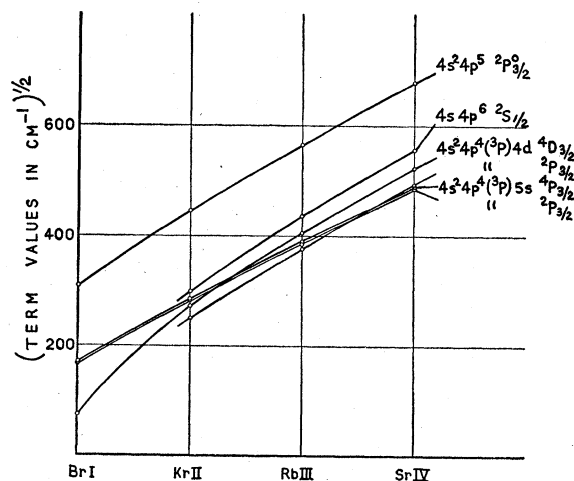


FIG. 3. Moseley diagram.

TABLE VI. *Classified lines of Rb III.*

INT.	λ/ν (VAC.)	λ/ν CM ⁻¹	CLASSIFICATION	INT.	λ/ν (VAC.)	λ/ν CM ⁻¹	CLASSIFICATION
18	815.27	122,658	$4s^2 4p^5 \ ^2P_{01/2} - 4s^2 4p^6 \ ^2S_{1/2}$	25	589.42	169,658	$4s^2 4p^5 \ ^2P_{01/2} - 4s^2 4p^4 (3P) 4d \ ^2P_{3/2}$
25	769.03	130,034	" $\ ^2P_{3/2} - \ ^2S_{1/2}$	20	586.78	170,422	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 4d \ ^4P_{1/2}$
12	689.80	144,969	$4s^2 4p^5 \ ^2P_{01/2} - 4s^2 4p^4 (3P) 4d \ ^4D_{3/2}$	d8	585.29	170,855	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 4d \ ^4P_{3/2}$
10	680.16	147,024	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^4D_{1/2}$	30	581.26	172,040	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 5s \ ^2P_{3/2}$
15	656.34	152,360	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 4d \ ^4D_{3/2}$	25	576.43	173,482	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 4d \ ^2D_{3/2}$
15	647.66	154,402	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 4d \ ^4D_{1/2}$	20	570.14	175,396	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 5s \ ^2P_{1/2}$
3	636.42	157,129	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^4P_{3/2}$	5	569.53	175,583	$4s^2 4p^5 \ ^2P_{01/2} - 4s^2 4p^4 (1D) 5s \ ^2D_{3/2}$
18	622.26	160,704	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^4P_{1/2}$	10	564.81	177,051	" $\ ^2P_{3/2} - 4s^2 4p^4 (3P) 4d \ ^2P_{3/2}$
6	613.33	163,044	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^4P_{1/2}$	25	546.56	182,963	" $\ ^2P_{3/2} - 4s^2 4p^4 (1D) 5s \ ^2D_{3/2}$
30	611.77	163,460	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^4P_{3/2}$	30	516.78	193,506	" $\ ^2P_{1/2} - \ ^2P_{3/2} - 4d \ ^2P_{3/2}$
15	607.88	164,506	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 5s \ ^4P_{3/2}$	8	508.33	196,723	" $\ ^2P_{1/2} - \ ^2P_{3/2} - 4d \ ^2P_{3/2}$
15	607.28	164,669	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^2P_{3/2}$	30	500.25	199,900	" $\ ^2P_{1/2} - 4s^2 4p^4 (1S) 5s \ ^2S_{1/2}$
40	602.09	166,088	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^2D_{3/2}$	20	497.81	200,880	" $\ ^2P_{3/2} - 4s^2 4p^4 (1D) 4d \ ^2D_{3/2}$
15	595.18	168,016	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^2P_{1/2}$	25	489.95	204,103	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 4d \ ^2P_{3/2}$
25	594.93	168,087	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 5s \ ^4P_{1/2}$	30	482.45	207,275	" $\ ^2P_{3/2} - 4s^2 4p^4 (1S) 5s \ ^2S_{1/2}$

TABLE VII. *Classified lines of Sr IV.*

INT.	λ/ν (VAC.)	λ/ν CM ⁻¹	CLASSIFICATION	INT.	λ/ν (VAC.)	λ/ν CM ⁻¹	CLASSIFICATION
45	710.35	140,776	$4s^2 4p^5 \ ^2P_{01/2} - 4s^2 4p^6 \ ^2S_{1/2}$	20	456.76	218,933	$4s^2 4p^5 \ ^2P_{03/2} - 4s^2 4p^4 (3P) 4d \ ^2P_{3/2}$
70	664.43	150,504	" $\ ^2P_{3/2} - \ ^2S_{1/2}$	12	452.18	221,151	" $\ ^2P_{3/2} - \ ^2P_{3/2} - 5s \ ^4P_{3/2}$
25	576.10	173,580	" $\ ^2P_{01/2} - 4s^2 4p^4 (3P) 4d \ ^4D_{3/2}$	6	447.95	223,239	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^2P_{3/2}$
30	567.11	176,333	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^4D_{1/2}$	25	442.77	225,851	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 5s \ ^4P_{1/2}$
35	545.55	183,301	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 4d \ ^4D_{3/2}$	8	437.69	228,472	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^2P_{1/2}$
15	537.44	186,067	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 4d \ ^4D_{1/2}$	15	429.24	232,970	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 5s \ ^2P_{3/2}$
d2	501.29	199,485	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^4P_{1/2}$	3	420.37	237,886	" $\ ^2P_{01/2} - 4s^2 4p^4 (1D) 5s \ ^2D_{3/2}$
50	500.51	199,796	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^4P_{3/2}$	25	419.81	238,203	$4s^2 4p^5 \ ^2P_{03/2} - 4s^2 4p^4 (3P) 5s \ ^2P_{1/2}$
30	488.74	204,608	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^2D_{3/2}$	1	416.82	239,912	" $\ ^2P_{01/2} - 4s^2 4p^4 (1D) 4d \ ^2D_{3/2}$
5	477.98	209,214	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^2P_{3/2}$	8	410.67	243,505	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 4d \ ^2P_{3/2}$
			" $\ ^2P_{03/2} - \ ^2P_{3/2} - 4d \ ^4P_{1/2}$	25	403.85	247,616	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 5s \ ^2D_{3/2}$
20	477.26	209,530	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 4d \ ^4P_{3/2}$	d3	400.56	249,651	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 4d \ ^2D_{3/2}$
8	473.00	211,416	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^4P_{3/2}$	20	394.90	253,229	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 4d \ ^2P_{3/2}$
20	466.52	214,353	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 4d \ ^2D_{3/2}$	12	381.62	262,041	" $\ ^2P_{01/2} - 4s^2 4p^4 (1S) 5s \ ^2S_{1/2}$
25	462.70	216,123	" $\ ^2P_{01/2} - \ ^2P_{3/2} - 5s \ ^4P_{1/2}$	10	367.95	271,776	" $\ ^2P_{03/2} - \ ^2P_{3/2} - 5s \ ^2S_{1/2}$

irregular doublet law, a corresponding pair of lines in Rb III were located readily by extrapolating backwards from Sr IV to Kr II. The $4s^2 4p^6 \ ^2S$ level is not known in Br I.

The intermediate term structure presented here is of necessity incomplete. Since the analysis is based on transitions to the ground doublet, it has been possible to establish only even levels with J values equal to $\frac{3}{2}$ to $\frac{1}{2}$. The assignments are therefore considered subject to correction

until the important odd $5p$ levels are located. It is hoped that with new data the analysis can be extended to the classification of the $5s-5p$ transitions. The term values and the classified lines of Rb III and Sr IV are included in Tables IV to VII.

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