the pressures used in this work. Measurements at three pressures on lines $3s-31p$ and $3s-32p$ yield:

Total pressure	$\lambda(n=31)$	$\lambda(n=32)$
18 mm	2418.881A	2418.435A
28 mm	2418.878A	2418.432A
43 mm	2418.883A	2418.435A

For larger values of n there was a small statistical trend towards longer wave-lengths for increased pressure, but in all these cases the observed fluctuation is within the errors of measurement, and we find a pressure shift of zero within ± 0.006 cm^{-1}/mm Hg.

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The Principal Series of Potassium, Rubidium, and Cesium in Absorption*

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The principal series of potassium, rubidium, and cesium in absorption have been measured. The doublet fine-structure has been resolved out to $17p$ in potassium, to $26p$ in rubidium, and to $21p$ in cesium; the doublet fine-structure interval varies in each spectrum inversely as the cube of the effective principal quantum number. In cesium, the doublet intensity ratio, instead of having a maximum, increases with increasing n as far as it can be followed. Higher series members, with their doublet fine-structure unresolved, have been measured to $79p$ in potassium, to $77p$ in rubidium, and to $73p$ in cesium. The series limits, calculated from the lowest hyperfine structure levels, are: K^{39} $4s\,{}^2S_{\frac{1}{2}}{}^1-\infty=35009.83$ cm^{-1}, Rb^{85} $5s\,{}^2S_{\frac{1}{2}}{}^2-\infty=33691.02$ cm^{-1}, Cs $6s\,{}^2S_{\frac{1}{2}}{}^3=31406.71$ cm^{-1}. The hyperfine structure of the ground level $6s\,{}^2S_{\frac{1}{2}}$ has been resolved in each member of the principal series of cesium.

INTRODUCTION

THE absorption spectra of the alkali metal atoms consist mainly of the principal series, corresponding to transitions from the normal $^2S_{\frac{1}{2}}$ level to the excited $np\,{}^2P_{1/2,\,3/2}$ levels.[1] The doublet interval $np\,{}^2P_{1/2}-np\,{}^2P_{3/2}$ increases with increasing atomic number and decreases with increasing principal quantum number n.

A considerable amount of work had previously been done on the absorption spectra of the alkali metal atoms, but since the early days of investigations of complex spectra, work on these simple spectra had been almost abandoned. The most extensive of the early work on the spectra of the alkali metal atoms is that of Wood and Fortrat[2] on sodium, in which they measured the doublet separations of the first seven members of the principal series and the higher members of the series, with the doublet structure unresolved, out to the 59th member.[3] Only the first member of the principal series of lithium has been resolved,[4] and 41 members measured.[5,6] Previous to this investigation, five members of the principal series of potassium,[7] six members of rubidium,[6] and nine members of cesium[6] had been resolved. Because of uncertainties in some of these wave-length measurements, and the relatively small numbers of doublets resolved, it seemed desirable to determine accurately the wave-lengths of the principal series as observed in absorption. In particular, it was the purpose of this investigation to measure the doublet separations of as many members of the principal series of potassium, rubidium, and cesium as possible, in order to determine accurately the variation of the doublet interval with the principal quantum number. The higher members of the principal series

* The experimental part of this paper was completed in 1942, having been begun at Wisconsin and continued at Princeton University. The cesium plates were measured after the war while the author was at Los Alamos.

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[1] Lines corresponding to forbidden transitions to $nd\,{}^2D_{3/2,\,5/2}$, $nf\,{}^2F_{5/2,\,7/2}$ and levels of even higher l were also observed on the same plates as the principal series. Measurements of these lines will be reported in a forthcoming paper by J. E. Mack.

[2] R. W. Wood and R. Fortrat, Astrophys. J. **43**, 73 (1916).

[3] Additional work on the absorption spectrum of sodium, carrying the measurements to $73p$, is reported by E. R. Thackeray, Phys. Rev. **75**, 1840 (1949).

[4] N. A. Kent, Astrophys. J. **40**, 337 (1914).

[5] Huppers, Zeits. f. Wiss. Phot. **13**, 46 (1914).

[6] P. V. Bevan, Proc. Roy. Soc. London **A83**, 421 (1910).

[7] S. Datta, Proc. Roy. Soc. London **A99**, 69 (1921).

of these spectra, with their doublet structure unresolved, were also measured.

EXPERIMENTAL

From considerations of the various causes of spectral line breadth, it can be seen to be necessary in order to produce absorption lines sharp enough for the resolution of close doublets, that: (a) the temperature and pressure of the absorbing vapor be sufficiently low, and (b) the pressure of any foreign gas be low. In order to have the pressure of the absorbing vapor low and at the same time have the number of atoms in the optical path necessary to produce absorption, a long optical path within the absorbing vapor is required.

In this investigation, a long optical path was produced by repeated traversals of the length of a tube containing the alkali metal vapors.[8] The light beam was reflected at one end of the tube by a totally reflecting prism and at the other end by a spherical mirror whose radius of curvature was equal to the distance between the prism and the mirror. The absorption tube was a steel tube $13\frac{1}{2}$-feet long and 3 inches in diameter; each end of the tube was cooled by a water jacket. The optical parts were located beyond the water jackets at either end of this tube. The section of tube between the water jackets was heated by a d.c. current flowing in a winding of nickel ribbon. The temperature of this section of the tube was maintained constant to within ± 0.1°C by means of a balanced Wheatstone bridge circuit,[9] the nickel windings on the tube serving as one arm of the bridge circuit. The circuit was adjustable to any temperature between 100° and 500°C. The entire apparatus was mounted on a $2\frac{1}{2}\times 4$-inch steel I-beam to supply the rigidity necessary for accurate adjustment of the optical system. The optical system was designed for a total of twelve traversals of the absorption tube, but it was possible to adjust the system so that the twenty-traversal beam could be seen. Most of the absorption spectra were taken with from six to twelve traversals, giving an absorption path length of 24 to 48 meters. The light source was a General Electric, Type AH-6 water-cooled high-pressure mercury arc with a quartz water jacket. It had a fairly strong continuum throughout the wave-length region investigated. The alkali metals were prepared in a vacuum by reducing their chlorides with calcium metal.[10]

The procedure for filling the absorption tube with an alkali metal vapor was as follows: A bulb of the alkali metal was placed near the center of the tube,

[8] H. R. Kratz and J. E. Mack, J. Opt. Soc. Am. **32**, 457 (1942).

[9] H. S. Roberts, J. Opt. Soc. Am. **6**, 965 (1922).

[10] J. Strong, *Procedures in Experimental Physics* (Prentice Hall, Inc., New York, 1938), p. 531.

TABLE I. Principal series of potassium.

	λ(air)		ν(vacuum)		
n	$4s\ ^2S_{1/2}-np\ ^2P_{1/2}$	$4s\ ^2S_{1/2}-np\ ^2P_{3/2}$	$4s\ ^2S_{1/2}-np\ ^2P_{1/2}$	$4s\ ^2S_{1/2}-np\ ^2P_{3/2}$	$\Delta\nu_p$
4	7698.979*	7664.907*	12985.17	13042.89	57.72
5	4047.208	4044.136	24701.44	24720.20	18.76
6	3447.376	3446.376	28999.29	29007.70	8.41
7	3217.615	3217.151	31069.98	31074.46	4.48
8	3102.051	3101.791	32227.42	32230.12	2.70
9	3034.911	3034.751	32940.34	32942.08	1.74
10	2992.215	2992.108	33410.34	33411.54	1.20
11	2963.277	2963.203	33736.60	33737.44	0.84
12	2942.713	2942.661	33972.34	33972.94	0.60
13	2927.562	2927.521	34148.15	34148.63	0.48
14	2916.065	2916.033	34282.77	34283.15	0.38
15	2907.129	2907.103	34388.16	34388.46	0.30
16	2900.042	2900.021	34472.18	34472.43	0.25
17	2894.329	2894.311	34540.23	34540.44	0.21
18	2889.640		34596.27		
19	2885.760		34642.78		
20	2882.510		34681.84		
21	2879.758		34714.98		
22	2877.405		34743.37		
23	2875.384		34767.78		
24	2873.628±		34789.03		
25	2872.093		34807.62		
26	2870.756		34823.83		
27	2869.564±		34838.30		
28	2868.509		34851.11		
29	2867.570±		34862.52		
30	2866.733		34872.70		
31	2865.974		34881.94		
32	2865.295		34890.20		
33	2864.675		34897.75		
34	2864.115		34904.57		
35	2863.605		34910.79		
36	2863.136		34916.51		
37	2862.711		34921.69		
38	2862.319		34926.47		
39	2861.956		34930.91		
40	2861.623		34934.97		
41	2861.316		34938.72		
42	2861.031		34942.20		
43	2860.765		34945.45		
44	2860.517		34948.48		
45	2860.289		34951.26		
46	2860.077		34953.85		
47	2859.875		34956.32		
48	2859.688		34958.61		
49	2859.514		34960.73		
50	2859.342		34962.83		
51	2859.192		34964.67		
52	2859.046		34966.45		
53	2858.912		34968.09		
54	2858.781		34969.69		
55	2858.660		34971.17		
56	2858.546		34972.57		
57	2858.439		34973.88		
58	2858.335		34975.15		
59	2858.236		34976.36		
60	2858.143		34977.50		
61	2858.052		34978.62		
62	2857.972		34979.60		
63	2857.886		34980.65		
64	2857.810		34981.58		
65	2857.738		34982.47		
66	2857.672		34983.27		
67	2857.604		34984.10		
68	2857.545		34984.83		
69	2857.484		34985.57		
70	2857.429		34986.25		
71	2857.371		34986.96		
72	2857.324		34987.53		
73	2857.270		34988.19		
74	2857.216		34988.85		
75	2857.17		34989.4		
76	2857.13		34989.9		
77	2857.08		34990.5		
78	2857.05		34990.8		
79	2857.02		34991.2		
∞	2855.505		35009.82 ±0.03		

* Wave-lengths for $n=4$ are from the vacuum arc measurements of C. W. Hetzler, R. W. Boreman, and K. Burns, Phys. Rev. **48**, 656 (1935).
± Measurement relatively uncertain (see text).

TABLE II. Principal series of rubidium.

	λ(air)		ν(vacuum)		
n	$5s\ ^2S_{1/2}-np\ ^2P_{1/2}$	$5s\ ^2S_{1/2}-np\ ^2P_{3/2}$	$5s\ ^2S_{1/2}-np\ ^2P_{1/2}$	$5s\ ^2S_{1/2}-np\ ^2P_{3/2}$	$\Delta\nu_p$
5	7947.60*	7800.227*	12578.96	12816.62	237.66
6	4215.524	4201.792	23715.19	23792.69	77.50
7	3591.572	3587.050	27835.05	27870.14	35.09
8	3350.812±	3348.696±	29834.96	29853.82	18.86
9	3229.156	3227.979	30958.94	30970.22	11.28
10	3158.259	3157.530	31653.88	31661.19	7.31
11	3113.047	3112.566	32113.58	32118.55	4.97
12	3082.340	3082.003	32433.50	32437.04	3.54
13	3060.491	3060.247	32665.03	32667.63	2.60
14	3044.368	3044.182	32838.02	32840.02	2.00
15	3032.120	3031.979	32970.66	32972.19	1.53
16	3022.591	3022.478	33074.59	33075.83	1.24
17	3015.029	3014.938	33157.54	33158.54	1.00
18	3008.923	3008.847	33224.83	33225.67	0.84
19	3003.923	3003.862	33280.13	33280.81	0.68
20	2999.776	2999.725	33326.13	33326.70	0.57
21	2996.299	2996.256	33364.81	33365.29	0.48
22	2993.352	2993.313	33397.66	33398.09	0.43
23	2990.835	2990.800	33425.76	33426.15	0.39
24	2988.665	2988.634	33450.03	33450.38	0.35
25	2986.782	2986.754	33471.11	33471.43	0.32
26	2985.140	2985.117	33489.53	33489.79	0.26
27	2983.679		33505.92		
28	2982.406		33520.22		
29	2981.278		33532.91		
30	2980.269		33544.26		
31	2979.362		33554.47		
32	2978.554		33563.57		
33	2977.819		33571.85		
34	2977.156		33579.34		
35	2976.555		33586.11		
36	2976.006		33592.31		
37	2975.505		33597.96		
38	2975.046		33603.14		
39	2974.620		33607.96		
40	2974.232		33612.34		
41	2973.874		33616.38		
42	2973.541		33620.15		
43	2973.236		33623.61		
44	2972.951		33626.83		
45	2972.688		33629.80		
46	2972.441		33632.60		
47	2972.210		33635.21		
48	2971.996		33637.63		
49	2971.796		33639.89		
50	2971.609		33642.01		
51	2971.431		33644.02		
52	2971.264		33645.96		
53	2971.105		33647.72		
54	2970.962		33649.33		
55	2970.819		33650.95		
56	2970.690		33652.41		
57	2970.568		33653.80		
58	2970.452		33655.11		
59	2970.339		33656.39		
60	2970.237		33657.55		
61	2970.136		33658.69		
62	2970.038		33659.80		
63	2969.948		33660.82		
64	2969.861		33661.81		
65	2969.779		33662.73		
66	2969.700		33663.63		
67	2969.625		33664.48		
68	2969.554		33665.28		
69	2969.487		33666.04		
70	2969.422		33666.78		
71	2969.359		33667.49		
72	2969.305		33668.11		
73	2969.245		33668.79		
74	2969.195		33669.36		
75	2969.138		33670.01		
76	2969.085		33670.61		
77	2969.045		33671.07		
∞	2967.226		33690.96±0.03		

* Wave-lengths for $n=5$ are from the vacuum arc measurements of C. W. Hetzler, R. W. Boreman, and K. Burns, Phys. Rev. **48**, 656 (1935).
± Measurement relatively uncertain (see text).

and the tube was evacuated and then filled to a pressure of 10 mm Hg with helium which had been dried by passing through a liquid air trap. The helium was introduced to prevent the alkali metal vapors from distilling too rapidly to the water jackets and to prevent the vapors from condensing on the optical parts. After the tube was filled with helium, the bulb of alkali metal was broken and the tube heated at the required temperature for a time sufficient to allow the section of tube between the water jackets to become completely filled with vapor.

The preliminary exposures to determine the optimum temperature of the absorption tube for different members of a series were taken with a Hilger E-1 quartz prism spectrograph. The plates on which the final measurements were made were taken with the 21-foot grating spectrograph at Princeton. This spectrograph had a nominal resolving power of approximately 300,000 in the second order. All the plates on which measurements were made were taken in the second order of the grating except those of wave-length greater than 4000A, for which the first order was used. The exposures at wave-lengths less than 3100A were taken on Eastman 33 spectrographic plates, and because of the shorter exposures required for longer wave-lengths, most of those at wave-lengths greater than 3100A were taken on Eastman Spectrum Analysis plates. The exposure times varied from two minutes, for the second member of the cesium series, to eight hours, for the higher members of the potassium series. Most of the exposure times, however, were between two and five hours.

The temperatures t, and the corresponding vapor pressures p,[11] that were required for resolving the doublet structure of the low members of the series and recording the unresolved higher members of the series are:

	Resolved Doublets	High Series Members
Potassium	$t=116°$ to 243°C $p=6\cdot10^{-5}$ to $4\cdot10^{-2}$ mm Hg	$t=303$°C $p=3\cdot10^{-1}$ mm Hg
Rubidium	$t=52°$ to 158°C $p=5\cdot10^{-6}$ to $6\cdot10^{-3}$ mm Hg	$t=270$°C $p=5\cdot10^{-1}$ mm Hg
Cesium	$t=37°$ to 248°C $p=4\cdot10^{-6}$ to $4\cdot10^{-1}$ mm Hg	$t=260$°C $p=6\cdot10^{-1}$ mm Hg

A different temperature, and hence a separate exposure, was required for nearly every resolved doublet in order to produce absorption lines of optimum sharpness. The relatively high vapor pressure of $4\cdot10^{-1}$ mm that was used for the highest series member of cesium whose doublet structure was resolved, was necessary because of the large intensity ratio of about 25:1 that exists between

[11] R. W. Ditchburn and J. C. Gilmour, Rev. Mod. Phys. **13**, 310 (1941).

TABLE III. Principal series of cesium.

		$6s\ ^2S_{\frac{1}{2}}(F=3)-np\ ^2P_J$			$6s\ ^2S_{\frac{1}{2}}(F=4)-np\ ^2P_J$			
n	J	λ(air)	ν(vacuum)	$\Delta\nu_p$	λ(air)	ν(vacuum)	$\Delta\nu_p$	hfs $\Delta\nu$
6	1/2	8943.50*	11178.24	554.11	*			
	3/2	8521.10*	11732.35		*			
7	1/2	4593.114[ab]	21765.65	181.01	4593.193[ab]	21765.27	181.06	0.38
	3/2	4555.228[ab]	21946.66		4555.298[ab]	21946.33		0.33
8	1/2	3888.570[b]	25709.14	82.64	3888.613[b]	25708.85	82.63	0.29
	3/2	3876.109[b]	25791.78		3876.155[b]	25791.48		0.30
9	1/2	3617.271[b]	27637.29	44.67	3617.313[b]	27636.98	44.65	0.31
	3/2	3611.435[b]	27681.96		3611.478[b]	27681.63		0.33
10	1/2	3480.042[b]	28727.09	26.84	3480.080[b]	28726.77	26.87	0.32
	3/2	3476.794[b]	28753.93		3476.830[b]	28753.64		0.29
11	1/2	3399.963	29403.68	17.42	3399.999	29403.37	17.43	0.31
	3/2	3397.949	29421.10		3397.984	29420.80		0.30
12	1/2	3348.805	29852.85	11.87	3348.840	29852.54	11.86	0.31
	3/2	3347.474	29864.72		3347.510	29864.40		0.32
13	1/2	3314.040	30166.00	8.51	3314.074	30165.69	8.51	0.31
	3/2	3313.105	30174.51		3313.139	30174.20		0.31
14	1/2	3289.270	30393.16	6.33	3289.305	30392.84	6.33	0.32
	3/2	3288.585	30399.49		3288.620	30399.17		0.32
15	1/2	3270.962	30563.27	4.71	3270.995	30562.96	4.70	0.31
	3/2	3270.458	30567.98		3270.492	30567.66		0.32
16	1/2	3257.055	30693.76	3.76	3257.090	30693.43	3.76	0.33
	3/2	3256.656	30697.52		3256.691	30697.19		0.33
17	1/2	3246.220	30796.20	2.95	3246.255	30795.87	2.95	0.33
	3/2	3245.909	30799.15		3245.944	30798.82		0.33
18	1/2	3237.612	30878.07	2.34	3237.648	30877.73	2.37	0.34
	3/2	3237.367	30880.41		3237.400	30880.10		0.31
19	1/2	3230.663	30944.49	1.94	3230.699±	30944.15	1.96	0.34
	3/2	3230.460	30946.43		3230.494	30946.11		0.32
20	1/2	3224.967	30999.15	1.59	3225.000±	30998.83	1.58	0.32
	3/2	3224.801	31000.74		3224.836	31000.41		0.33
21	1/2	3220.242	31044.63	1.37	3220.276	31044.30	1.37	0.33
	3/2	3220.100	31046.00		3220.134	31045.67		0.33
22	1/2, 3/2	3216.155	31084.08		3216.188	31083.76		0.32
23		3212.814	31116.40		3212.849	31116.06		0.34
24		3209.954	31144.13		3209.984	31143.84		0.29
25		3207.491	31168.04		3207.524	31167.72		0.32
26		3205.349	31188.87		3205.380	31188.57		0.30
27		3203.480	31207.07		3203.512	31206.76		0.31
28		3201.836	31223.09		3201.870	31222.76		0.32
29		3200.385	31237.24		3200.418	31236.92		0.32
30		3199.097	31249.81		3199.131	31249.48		0.33
31		3197.948	31261.05		3197.983	31260.71		0.34
32		3196.917	31271.13		3196.949	31270.81		0.32
33		3195.993	31280.17		3196.028	31279.82		0.35
34		3195.157	31288.36		3195.189	31288.04		0.32
35		3194.401	31295.76		3194.434	31295.44		0.32
36		3193.712	31302.51		3193.743	31302.21		0.30
37		3193.090	31308.61		3193.123	31308.28		0.33
38		3192.518	31314.21		3192.550	31313.90		0.31
39		3191.990	31319.39		3192.024	31319.06		0.33
40		3191.510	31324.11		3191.543	31323.79		0.32

the components of this doublet. This high vapor pressure was required to bring out the weaker component of the doublet. At this pressure, however, the stronger component was very broad; it was this broadening of the stronger component that limited the number of cesium doublets that could be resolved. It was, therefore, necessary in the case of cesium to measure the components of some doublets separately on different plates taken at different temperatures.

The wave-lengths of the absorption lines were measured by comparing them with secondary and tertiary iron standards. A standard Pfund arc in air as specified by the International Astronomical Union[12] was used as the source of iron lines, the iron spectra being placed so that they partly overlapped the continuum of the absorption spectra. Each of the resolved doublets was measured on at least two plates except where the contrary is indicated, but several of the high series members

[12] Trans. Int. Astron. Union **2**, 18 (1925).

TABLE III—(*Cont.*).

n	J	$6s\ ^2S_{\frac{1}{2}}(F=3)-np\ ^2P_J$ λ(air)	ν(vacuum)	$\Delta\nu_p$	$6s\ ^2S_{\frac{1}{2}}(F=4)-np\ ^2P_J$ λ(air)	ν(vacuum)	$\Delta\nu_p$	hfs $\Delta\nu$
41		3191.066	31328.47		3191.096	31328.17		0.30
42		3190.658	31332.47		3190.690	31332.16		0.31
43		3190.279	31336.19		3190.309	31335.90		0.29
44		3189.925	31339.67		3189.957	31339.36		0.31
45		3189.602	31342.84		3189.634	31342.53		0.31
46		3189.301	31345.80		3189.334±	31345.48		0.32
47		3189.018±	31348.58		3189.052	31348.25		0.33
48		3188.754	31351.18		3188.786	31350.86		0.32
49		3188.510	31353.57		3188.543	31353.25		0.32
50		3188.279±	31355.85		3188.313	31355.51		0.34
51		3188.064	31357.96		3188.096	31357.64		0.32
52		3187.862	31359.95		3187.894	31359.63		0.32
53		3187.673	31361.80		3187.704	31361.50		0.30
54		3187.490	31363.60		3187.521	31363.30		0.30
55		3187.325	31365.23		3187.357	31364.91		0.32
56		3187.167	31366.78		3187.199	31366.47		0.31
57		3187.013	31368.31		3187.045	31367.99		0.32
58		3186.872	31369.69		3186.904	31369.38		0.31
59		3186.743	31370.96		3186.773	31370.67		0.29
60		3186.611	31372.26		3186.642	31371.96		0.30
61		3186.493	31373.43		3186.523	31373.13		0.30
62		3186.378	31374.56		3186.409	31374.25		0.31
63		3186.270	31375.62		3186.301	31375.31		0.31
64		3186.168	31376.62		3186.200	31376.31		0.31
65		3186.070	31377.59		3186.100	31377.29		0.30
66		3185.971	31378.56		3186.004	31378.24		0.32
67		3185.880	31379.46		3185.913	31379.13		0.33
68		3185.796	31380.29		3185.829	31379.96		0.33
69		3185.715	31381.08		3185.749	31380.74		0.34
70		3185.635	31381.87		3185.669	31381.54		0.33
71		3185.554	31382.67		3185.586	31382.36		0.31
72		3185.492	31383.28		3185.522	31382.99		0.29
73		3185.455	31383.65					
—		—	—		—	—		
∞		3183.115	31406.71		3183.146	31406.40		

* Wave-lengths for $n=6$ are from W. F. Meggers, Nat. Bur. Stand. J. Res. **10**, 669 (1933). The hyperfine structure was unresolved, so these values are for a mean of the $F=3$ and $F=4$ levels.

[a] The $6s-7p$ lines were not as sharp and could not be measured as accurately as the other lines. This may have been caused by structure in the $7p\ ^2P_{1/2,3/2}$ levels, although Granath and Stranathan, Phys. Rev. **48**, 725 (1935) report a value for the hyperfine structure interval of the $7p\ ^2P_{\frac{1}{2}}$ level of only 0.0033 cm^{-1}.

[b] Measured on one plate only.

± Measurement relatively uncertain (see text).

of potassium and rubidium were measured on only one plate.

RESULTS AND DISCUSSION

The wave-lengths of the principal series of potassium, rubidium, and cesium that were measured, and their reduction to wave-numbers, are given in Tables I, II, and III respectively. The wave-lengths are referred to air at 15°C and 760 mm pressure; the wave-numbers are reduced to vacuum by the use of the vacuum corrections given in Kayser's "Tabelle der Schwingungszahlen." Nearly all the wave-lengths that were measured on two or more plates agree to within ±0.003A, and all agree to within ±0.005A except those marked ± in the tables, which agree only to within ±0.006A. The doublet separations of 14 members of the principal series of potassium, 22 members of the rubidium series, and 16 members of the cesium series were measured. The higher members of the principal series, with their doublet fine-structure unresolved, were measured to the 76th member in potassium, the 73d member in rubidium, and the 68th member in cesium.

The series limits shown in Table IV, kindly calculated by J. G. Hirschberg and J. E. Mack, are from 2 to 4 cm^{-1} higher than those previously accepted. The values may be changed, within the limits of uncertainty listed, in a later investigation.

As shown in Table III, each component of the cesium fine-structure doublets is itself doubled by hyperfine structure. This structure results from the hyperfine structure of the ground level, $6s\ ^2S_{\frac{1}{2}}$; the hyperfine structure of the $np\ ^2P_{1/2,3/2}$ levels is too small to resolve. The hyperfine structure interval for each member of the series is recorded in

Table III, the values being generally in good agreement with the values 0.307 cm^{-1} reported by Granath and Stranathan[13] and 0.30665 cm^{-1} derived from a microwave experiment.[14] This hyperfine structure limited to 68 the number of higher series members that could be measured; beyond the 68th member the $F=3$ component of one member overlapped the $F=4$ component of the next higher member.

The doublet fine-structure in the spectra of the alkali metal atoms results from the electron spin-orbit interaction. Calculations of the spin-orbit interaction energy by quantum mechanical methods have been made by Pauli,[15] Darwin,[16] Dirac,[17] Gordon,[18] and others. These calculations lead to the following expression for the doublet fine-structure interval, if the screening effect of the electrons in the atomic core is neglected:

$$\Delta\nu=\frac{R\alpha^2Z^4}{n^3l(l+1)}\ \text{cm}^{-1} \qquad (1)$$

where R=Rydberg constant, α=fine structure constant, Z=atomic number, n=principal quantum number, and l=orbital angular momentum quantum number.

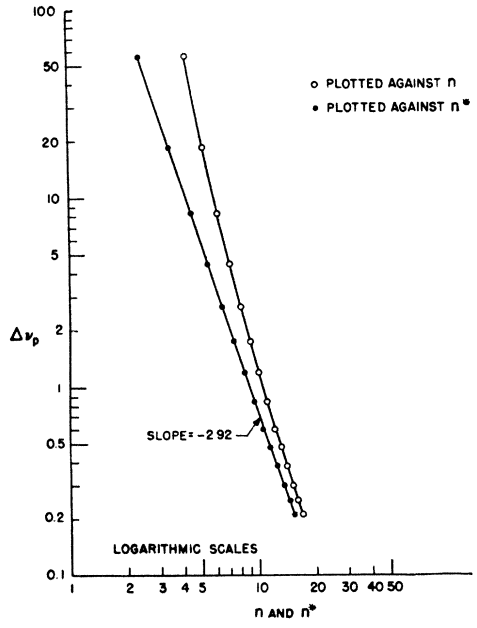

FIG. 1. Variation of $\Delta\nu_p$ with n and n^* in the principal series of potassium.

[13] L. P. Granath and R. K. Stranathan, Phys. Rev. **48**, 725 (1935).
[14] S. Millman and P. Kusch, Phys. Rev. **60**, 91 (1941).
[15] W. Pauli, Zeits. f. Physik **43**, 601 (1929).
[16] C. G. Darwin, Proc. Roy. Soc. London **A116**, 227 (1927); **A118**, 654 (1928).
[17] P. A. M. Dirac, Proc. Roy. Soc. London **A117**, 610 (1927); **A118**, 351 (1928).
[18] W. Gordon. Zeits. f. Physik **48**, 11 (1929).

TABLE IV. Series limits and ionization potentials.

	K	Rb	Cs
n (ground level)	4	5	6
Centroid of ns hfs pattern:			
$ns\ ^2S_{\frac{1}{2}}-\infty$ (cm^{-1})	35009.82 ±0.03	33690.96 ±0.03	31406.54 ±0.03
Predominant isotope	39	85	133
F (lowest sublevel)	1	2	3
$ns\ ^2S_{\frac{1}{2}}{}^F-\infty$ (cm^{-1})	35009.83 ±0.03	33691.02 ±0.03	31406.71 ±0.03
Ionization potential (volts) basis: 8068.2 cm^{-1}=1 volt	4.3392	4.1758	3.8926
Fowler report (1922)	35005.88	33689.1	31404.6
Edlén [Zeits. f. Physik **98**, 445 (1933)]	35009.08		
MMHO (see note at end of this paper)			31406.32

For principal series doublets, Eq. (1) reduces to

$$\Delta\nu_p=np\ ^2P_{1/2}-np\ ^2P_{3/2}=R\alpha^2Z^4/2n^3. \qquad (2)$$

In view of the influence of the screening upon the roles of Z and n, this expression could not be expected to predict accurately the magnitudes of the doublet fine-structure intervals. In the modified

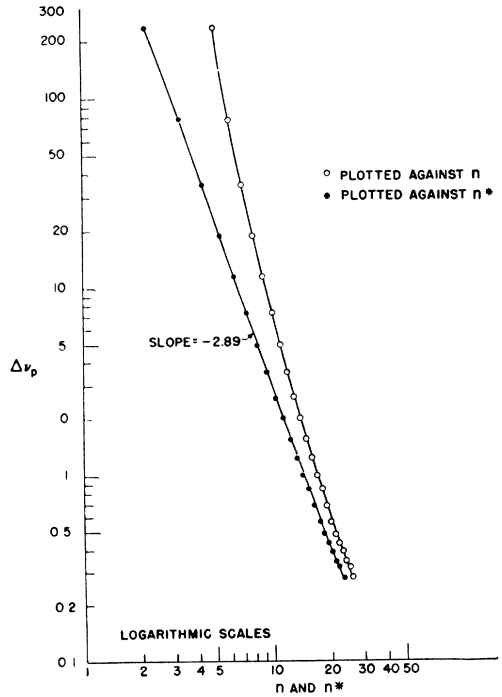

FIG. 2. Variation of $\Delta\nu_p$ with n and n^* in the principal series of rubidium.

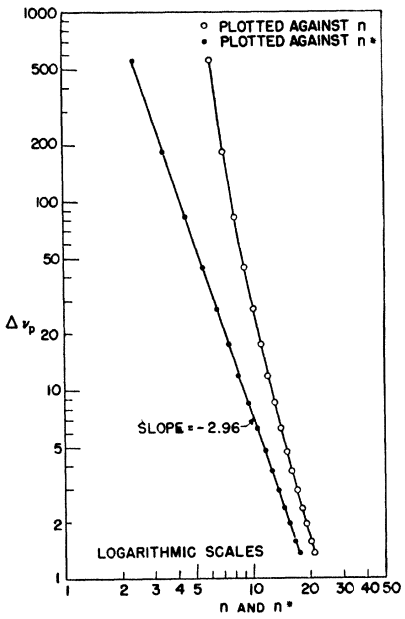

FIG. 3. Variation of $\Delta\nu_p$ with n and n^* in the principal series of cesium.

expressions

$$\Delta\nu_p=\frac{R\alpha^2Z^4_{\text{eff}}}{2n^3_{\text{eff}}} \quad \text{or} \quad \frac{R\alpha^2Z_{\text{outer}}{}^2Z_{\text{inner}}{}^2}{2n^3_{\text{eff}}} \tag{3}$$

where Z_{eff} and n_{eff} stand for Z and n respectively, corrected for the core effect, the accurate calculation of Z_{eff} and n_{eff} presents difficulties.

Let us assume Z_{eff}, or Z_{outer} and Z_{inner}, to be independent of n, and n_{eff} to be the same as n^* in the Rydberg expression

$$n^*=[R/(\text{term value})]^{\frac{1}{2}}. \tag{4}$$

If these assumptions are valid, we get by taking the logarithm of each side of Eq. (3)

$$\log\Delta\nu_p=\text{constant}-3\log n^*. \tag{5}$$

This is the equation of a straight line with a slope of -3. Plots of $\Delta\nu_p$ against n^* and n on logarithmic scales are given in Figs. 1, 2, and 3 for potassium, rubidium, and cesium respectively. In each case the plot against n^* is a straight line with a slope of almost exactly -3, whereas the plot against n is not a straight line.

Sambursky[19] has made quantitative measurements of the intensity ratios in the first eight members of the principal series of cesium. He found the intensity ratio to increase from 2 in the first member to 25 in the fifth member, and then to decrease to 4.5 in the eighth member. Although no quantitative measurements of these intensity ratios were made in this investigation, an inspection of the cesium plates shows, not the decrease observed by Sambursky, but rather an increase in the ratios, perhaps to an asymptotic value, with increasing principal quantum number. It was the large intensity ratios of the cesium doublets which limited to 16 the number that could be resolved.

[19] S. Sambursky, Zeits. f. Physik **49**, 731 (1928).

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It is a pleasure for the author to acknowledge his appreciation to Professor J. E. Mack, under whose direction this work was done, for his constant encouragement and considerable assistance. The author is also indebted to Princeton University, where the latter part of the experimental work was done, for cooperation during his stay there.

Note added February 16, 1949: Dr. McNally has kindly sent me, through Professor Mack, the galley proof of the paper by J. R. McNally, J. P. Molnar, W. J. Hitchcock, and N. F. Oliver, J. Opt. Soc. Am. **39**, 57 (1949), on cesium. The results of that investigation are qualitatively in agreement with those in this paper. The principal difference, aside from their failure to resolve the hyperfine structure, is a general discrepancy of between 0.1 and 0.2 cm^{-1} in wave number. This discrepancy can probably be attributed to the higher cesium pressure necessary in their investigation as a consequence of their shorter path length. Dr. McNally remarks that the line breadths are of the order of the expected hyperfine structure, and I agree with him that, in the face of the theoretical resolution of more than 10^5 in their grating, their lack of actual resolution must probably be accounted for by a combination of instrumental and source broadening. Their lines lie consistently to the red of mine by an amount shown in the following table, which gives the average of the quantity ν(Kratz, $J=3/2$ or unresolved fine structure, hfs centroid) $-\nu$(MMHO) for principal quantum numbers taken in groups of five:

$n=11$ to 15	0.18 cm^{-1}
16 to 20	0.15
21 to 25	0.18
26 to 30	0.19
31 to 35	0.18
36 to 40	0.15
41 to 45	0.16
46 to 50	0.12
51 to 55	0.13
56 to 60	0.1
61 to 62	0.1

In this Table I have neglected their value for the $26p$ line; I was able to obtain the values given in Table III for the $26p$ and $32p$ lines, in spite of the Fe lines at 3205.400 and 3196.930A, only by reading them relative to neighboring lines in the series, in a strip free of iron lines.

Possibly the trend toward agreement with increasing n results from my use of plates with a Cs pressure of almost 1 mm for the highest members of the series. Unfortunately, the pressure used in the other investigation is not reported. In view of that trend, however, the discrepancy of 0.22 cm^{-1} in the series limits is not easy to account for wholly in terms of pressure shift. Mack and Hirschberg assign an uncertainty of 0.03 cm^{-1} to their series limit value (neglecting any possible error in Kayser's values for the index of air) and state that a change as great as 0.05 cm^{-1} from the value given in Table IV would cause an egregious trend in the quantum defects.