# The Absorption Spectrum of Atomic Sodium

E. R. THACKERAY*
*University of Wisconsin, Madison, Wisconsin*

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Using a long optical path attained by the method of Kratz and Mack, the wave-lengths of the principal series of sodium in absorption have been measured to $n=73$, and observed to $n=79$. The members to $n=9$ have been resolved. The series limit has been computed to be $41449.65\pm0.02$ cm$^{-1}$ from the center of gravity or $41449.69\pm0.02$ cm$^{-1}$ from the lower hyperfine structure component, of the $3s\,^2S_{1/2}$ term. Forbidden $3s\,^2S_{1/2}-nd\,^2D_{3/2,5/2}$ were found up to $n=13$. A critically compiled table to all known levels, including $np\,^2P_{1/2,3/2}$ to $n=73$ and $nd\,^2D_{3/2,5/2}$ to $n=13$, is given. The pressure shift from a foreign gas is less than reported by some earlier observers.

## EXPERIMENTAL

THE absorption spectrum of atomic sodium consists chiefly of the principal series, i.e., of transitions from the ground $3s\,^2S_{\frac{1}{2}}$ to the excited $np\,^2P_{\frac{1}{2},3/2}$ levels. Forbidden $3s\,^2S_{\frac{1}{2}}-nd\,^2D_{3/2,5/2}$ transitions occur with much lower intensity. In 1916 Wood and Fortrat[1] measured the principal series to $n=59$, resolving the first seven members. If their results are fitted to a Ritz formula the last three members show a marked discrepancy and the doublet separation of the last member resolved appears much too large. The present work has to do with the extension of the principal series and the forbidden $3s-nd$ series, and new measurements on the doublet separations.

In order to obtain absorption in a vapor at the low temperature and the low vapor pressure required to obtain sharp lines, it is necessary to have a long optical path. This was accomplished in this investigation by the use of the method and apparatus developed by H. R. Kratz and J. E. Mack,[2] in which the long optical path is achieved by repeated traversals between a concave spherical mirror and a totally reflecting prism. The absorption tube was maintained at a constant temperature to within $\pm0.5$°C by means of a balanced Wheatstone bridge circuit.[3] The furnace windings of the tube acted as one arm of the bridge. The galvanometer was replaced by a sensitive Weston 534 relay, which in turn was connected by means of a lock-in circuit of two Weston 712 relays to a power relay which controlled the heating circuit.

The sodium used was of ordinary chemical grade. It was placed at the center of the tube in an iron boat after a cleansing in water-free benzene. After the insertion of the sodium the tube was evacuated for 6 or 8 hours and then filled with helium to a pressure of about 1 or 2 mm.

The source of continuous radiation was a General Electric AH-6 mercury arc lamp. Chiefly because of the low reflectivity of the aluminum surface of the concave spherical mirror in the wave-length region in which most of the members of the principal series were found, the number of traversals was limited to six, yielding an absorption path of about 23 meters.

The spectrograms were made with a 21 foot, 15000 lines/inch grating 6-inches wide, in a Rowland mounting. Out to 2600A the third order, with a dispersion of about 0.88A/mm, was used, and beyond that, the fourth order, with a dispersion of 0.66A/mm. Suitable filters of bromine and chlorine vapor were used to prevent the overlapping of orders.

For the lower series members Eastman 103-O spectroscopic plates were used and exposure times ranged from 20 minutes to 1 hour. Beyond 2852A, the faintness of the continuum made it advisable to use 103a-O plates, with exposures of 10 to 20 hours. The wave-lengths of the absorption lines were found by comparing them with secondary standard and recommended iron lines[4] from a Pfund arc.[5] Except where the contrary is stated, each line was measured on at least two different plates. The last eight members of the principal series were measured on only the best plate.

A different temperature was used for the optimum sharpness of each doublet resolved. For the higher series members many lines were found satisfactorily sharp on a single plate. The temperature, $t$, and the corresponding vapor pressure,[6] $p$, of sodium were as follows:

| | $t$ | $p$ |
|---|---|---|
| Resolved doublets | 130°C to 182°C | $10^{-6}$ to $4.5\cdot10^{-5}$ mm Hg |
| High series members | 326°C | $3.5\cdot10^{-2}$ mm Hg |
| Forbidden lines, $3s-nd$ | 218°C to 330°C | $3\cdot10^{-4}$ to $3\cdot10^{-2}$ mm Hg |

* Now at Regina College, Regina, Saskatchewan, Canada.
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Table I. Principal series of sodium in absorption.

| $n$ | λ (air) Angstrom units $3s\,^2S_{1/2}-np\,^2P_{1/2}$ | λ (air) Angstrom units $3s\,^2S_{1/2}-np\,^2P_{3/2}$ | ν (vacuum) cm$^{-1}$ $3s\,^2S_{1/2}-np\,^2P_{1/2}$ | ν (vacuum) cm$^{-1}$ $3s\,^2S_{1/2}-np\,^2P_{3/2}$ |
|---|---|---|---|---|
| 4 | 3302.987 | 3302.375 | 30266.94 | 30272.55 |
| 5 | 2853.023 | 2852.816 | 35040.27 | 35042.79 |
| 6 | 2680.421 | 2680.331 | 37296.51 | 37297.76 |
| 7 | —— | —— | —— | —— |
| 8 | —— | —— | —— | —— |
| 9 | 2512.149[b] | 2512.121[b] | 39794.53 | 39795.00 |
| 10 | 2490.701± | | 40137.23 | |
| 11 | 2475.532 | | 40383.16 | |
| 12 | 2464.371 | | 40566.03 | |
| 13 | 2455.916 | | 40705.68 | |
| 14 | 2449.369 | | 40814.47 | |
| 15 | 2444.180 | | 40901.11 | |
| 16 | 2440.001 | | 40971.16 | |
| 17 | 2436.580 | | 41028.68 | |
| 18 | 2433.751 | | 41076.37 | |
| 19 | 2431.388 | | 41116.28 | |
| 20 | 2429.373 | | 41150.39 | |
| 21 | 2427.672 | | 41179.22 | |
| 22 | 2426.195 | | 41204.28 | |
| 23 | 2424.918 | | 41225.88 | |
| 24 | 2423.813 | | 41244.77 | |
| 25 | 2422.835 | | 41261.42 | |
| 26 | 2421.973 | | 41276.11 | |
| 27 | 2421.207 | | 41289.16 | |
| 28 | 2420.528 | | 41300.74 | |
| 29 | 2419.922 | | 41311.09 | |
| 30 | 2419.380 | | 41320.34 | |
| 31 | 2418.881 | | 41328.87 | |
| 32 | 2418.434 | | 41336.50 | |
| 33 | 2418.025 | | 41343.49 | |
| 34 | 2417.662 | | 41349.70 | |
| 35 | 2417.323 | | 41355.50 | |
| 36 | 2417.012 | | 41360.82 | |
| 37 | 2416.729 | | 41365.66 | |
| 38 | 2416.469 | | 41370.11 | |
| 39 | 2416.226 | | 41374.27 | |
| 40 | 2416.006 | | 41378.04 | |
| 41 | 2415.801 | | 41381.55 | |
| 42 | 2415.609 | | 41384.84 | |
| 43 | 2415.430 | | 41387.91 | |
| 44 | 2415.265 | | 41390.73 | |
| 45 | 2415.113 | | 41393.34 | |
| 46 | 2414.971 | | 41395.77 | |
| 47 | 2414.835 | | 41398.10 | |
| 48 | 2414.708 | | 41400.28 | |
| 49 | 2414.593 | | 41402.25 | |
| 50 | 2414.481 | | 41404.18 | |
| 51 | 2414.373 | | 41406.03 | |
| 52 | 2414.276 | | 41407.69 | |
| 53 | 2414.182 | | 41409.30 | |
| 54 | 2414.094 | | 41410.81 | |
| 55 | 2414.013 | | 41412.20 | |
| 56 | 2413.932 | | 41413.59 | |
| 57 | 2413.856 | | 41414.89 | |
| 58 | 2413.788 | | 41416.06 | |
| 59 | 2413.722 | | 41417.18 | |
| 60 | 2413.660 | | 41418.26 | |
| 61 | 2413.599 | | 41419.30 | |
| 62 | 2413.539 | | 41420.33 | |
| 63 | 2413.485 | | 41421.26 | |
| 64 | 2413.434 | | 41422.13 | |
| 65 | 2413.382 | | 41423.03 | |
| 66 | 2413.337[b] | | 41423.80 | |
| 67 | 2413.291[b] | | 41424.59 | |
| 68 | 2413.248[b] | | 41425.32 | |
| 69 | 2413.208[b] | | 41426.01 | |
| 70 | 2413.170[b] | | 41426.66 | |
| 71 | 2413.136[b] | | 41427.25 | |
| 72 | 2413.102[b] | | 41427.83 | |
| 73 | 2413.069[b] | | 41428.40 | |
| 74 | (2413.035) | | (41428.98) | |
| 75 | (2413.003) | | (41429.53) | |
| 76 | (2412.971) | | (41430.07) | |
| 77 | (2412.942) | | (41430.58) | |
| 78 | (2412.913) | | (41431.07) | |
| 79 | (2412.885) | | (41431.55) | |
| ∞ | (2411.832) | | (41449.65±0.02) | |

[b] Measurement from one plate only.
± For the unresolved $10p$ line, the readings on two plates differed by 0.007A.
( ) Extrapolated limit, or interpolated value of observed but unmeasured line.

The maximum variations of the temperature and pressure in the grating room for long exposures were 0.3°C and 6 mm, respectively. These variations, together with the line width, appear to have been the limiting factor in the number of members resolved near the series limit.

In the course of an exposure of 10 hours or longer, the pressure of the foreign gas increased as much as 55 mm at the higher operating temperatures. Since pumping was not feasible during an exposure the pressure was observed and found to range from about 6 to 55 mm for the different plates. The nature of the foreign gas was not investigated.

TABLE II. Forbidden transitions $3s\,^2S_{\frac{1}{2}}-nd\,^2D$ in sodium.

| $n$ | λ (air) Angstrom units $3s\,^2S_{1/2}-nd\,^2D$ | ν (vacuum) cm$^{-1}$ $3s\,^2S_{1/2}-nd\,^2D$ |
|---|---|---|
| 3 | 3426.858 | 29172.92 |
| 4 | 2893.619 | 34548.70 |
| 5 | 2699.217[b] | 37036.81 |
| 6 | | |
| 7 | | |
| 8 | 2516.296 | 39729.00 |
| 9 | 2493.600 | 40090.57 |
| 10 | 2477.617 | 40349.17 |
| 11 | 2465.932 | 40540.35 |
| 12 | 2457.11± | 40685.9 |
| 13 | 2450.31[b] | 40798.8 |

[b] Measurement from one plate only. The $3s-5d$ and $3s-13d$ lines were faint.
± The readings on two plates differed by 0.02A.

TABLE III. Energy levels of neutral sodium, NaI ($cm^{-1}$).

| $n$ | $ns^2S_{1/2}$ | $np^2P_{1/2}$ | $np^2P_{3/2}$ | $\Delta\nu(^2P)$ | $nd^2D_{3/2}$ | $nd^2D_{5/2}$ | $\Delta\nu(^2D)$ | $nf^2F_{5/2,7/2}$ |
|---|---|---|---|---|---|---|---|---|
| 3 | 41449.6500ah | 24493.4672hm | 24476.2709hm | 17.1963hm | 12276.746m | 12276.795m | −0.0494m | |
| 4 | 15709.78m | 11182.77g | 11177.14g | 5.63g | 6900.861m | 6900.896m | −0.0346m | 6861.0p |
| 5 | 8248.954m | 6409.38 | 6406.86 | 2.52 | 4412.845m | 4412.869m | −0.0230m | 4392.0r |
| 6 | 5077.004m | 4153.14 | 4151.89 | 1.25 | 3062.350m | 3062.363m | −0.0124m | 3049.5r |
| 7 | 3437.576m | (2909.25) | (2908.51) | (0.74) | 2248.688m | | | 2240.4r |
| 8 | (2481.03)d | (2151.11) | (2150.64) | (0.47) | 1720.65 | | | 1715.6r |
| 9 | (1874.67)d | 1655.12b | 1654.65b | 0.47 | 1359.08 | | | 1356.4r |
| 10 | (1466.24)d | 1312.42± | | | 1100.48 | | | (1097.9)s |
| 11 | (1178.096)z | 1066.49 | | | 909.30 | | | (907.3)s |
| 12 | (967.246)z | 883.62 | | | 763.8 | | | |
| 13 | (808.327)z | 743.97 | | | 650.8b | | | |
| 14 | (685.586)z | 635.18 | | | (561.15)z | | | |
| 15 | | 548.54 | | | (488.75)z | | | |
| 16 | | 478.49 | | | | | | |
| 17 | | 420.97 | | | | | | |
| 18 | | 373.28 | | | | | | |
| 19 | | 333.37 | | | | | | |
| 20 | | 299.26 | | | | | | |
| 21 | | 270.43 | | | | | | |
| 22 | | 245.37 | | | | | | |
| 23 | | 223.77 | | | | | | |
| 24 | | 204.88 | | | | | | |
| 25 | | 188.23 | | | | | | |
| 26 | | 173.54 | | | | | | |
| 27 | | 160.49 | | | | | | |
| 28 | | 148.91 | | | | | | |
| 29 | | 138.56 | | | | | | |
| 30 | | 129.31 | | | | | | |
| 31 | | 120.78 | | | | | | |
| 32 | | 113.15 | | | | | | |
| 33 | | 106.16 | | | | | | |
| 34 | | 99.95 | | | | | | |
| 35 | | 94.15 | | | | | | |
| 36 | | 88.83 | | | | | | |
| 37 | | 83.99 | | | | | | |
| 38 | | 79.54 | | | | | | |
| 39 | | 75.38 | | | | | | |
| 40 | | 71.61 | | | | | | |
| 41 | | 68.10 | | | | | | |
| 42 | | 64.81 | | | | | | |
| 43 | | 61.74 | | | | | | |
| 44 | | 58.92 | | | | | | |
| 45 | | 56.31 | | | | | | |
| 46 | | 53.88 | | | | | | |
| 47 | | 51.55 | | | | | | |
| 48 | | 49.37 | | | | | | |
| 49 | | 47.40 | | | | | | |
| 50 | | 45.47 | | | | | | |
| 51 | | 43.62 | | | | | | |
| 52 | | 41.96 | | | | | | |
| 53 | | 40.35 | | | | | | |
| 54 | | 38.84 | | | | | | |
| 55 | | 37.45 | | | | | | |
| 56 | | 36.06 | | | | | | |
| 57 | | 34.76 | | | | | | |
| 58 | | 33.59 | | | | | | |
| 59 | | 32.47 | | | | | | |
| 60 | | 31.39 | | | | | | |
| 61 | | 30.35 | | | | | | |
| 62 | | 29.32 | | | | | | |
| 63 | | 28.39 | | | | | | |
| 64 | | 27.52 | | | | | | |
| 65 | | 26.62 | | | | | | |
| 66 | | 25.85b | | | | | | |
| 67 | | 25.06b | | | | | | |
| 68 | | 24.33b | | | | | | |
| 69 | | 23.64b | | | | | | |
| 70 | | 22.99b | | | | | | |
| 71 | | 22.40b | | | | | | |
| 72 | | 21.82b | | | | | | |
| 73 | | 21.25b | | | | | | |
| 74 | | (20.67) | | | | | | |
| 75 | | (20.12) | | | | | | |
| 76 | | (19.58) | | | | | | |
| 77 | | (19.07) | | | | | | |
| 78 | | (18.58) | | | | | | |
| 79 | | (18.10) | | | | | | |

a In this number, the last two digits (zeros), which have no significance for the absolute value of the term, have been arbitrarily added for convenience in expressing certain accurately known differences. The probable error in the value of the term, estimated from the series limit, is about $\pm 0.02$ $cm^{-1}$. In the term values given elsewhere to 2 digits after the decimal point (except $10p$), the uncertainty is about $\pm 0.04$ $cm^{-1}$. These estimates depend upon our acceptance of Kayser's values for the index of air; i.e., the terms ought to be recalculated when new values are available for the refractive index of air.

b Measurement for one plate only.

d Experimental values of Datta[1] corrected for the ground state are:

$8s = 2481.28$
$9s = 1875.14$
$10s = 1466.6$

g Mean between this work and unpublished values from the infra-red solar absorption transition $4s-4p$, kindly supplied by L. Goldberg. The separate values are:

$4p^2\,P_{1/2}$—This work, 11182.71; Goldberg (22083.9A), 11182.83.
$4p^2\,P_{3/2}$—This work, 11177.10; Goldberg (22056.4A), 11177.19.

h Center of gravity of hyperfine structure. The following is a critical estimate of the hyperfine structure of sodium, kindly supplied by Hack Arroe. $\Delta\nu(3s^2S_{1/2})$ is from the radiofrequency measurements of Millman and Kusch.[2] The values assigned to $\Delta\nu(3p^2P_{1/2})$ and $\Delta\nu(3p^2P_{3/2})$ agree with the experimental results of Meissner and Puft (reference 9), Jackson and Kuhn,[3] and Arroe[4] within the limits of experimental error.

$3s^2S_{1/2}{}^1 = 41449.6869$
$3s^2S_{1/2}{}^2 = 41449.6278$ $\qquad \Delta\nu(3s^2S_{1/2}) = 0.059103 \pm 0.000002$
$3p^2P_{1/2}{}^1 = 24493.4706$
$3p^2P_{1/2}{}^2 = 24493.4652$ $\qquad \Delta\nu(3p^2P_{1/2}) = 0.0054 \pm 0.0002$
$3p^2P_{3/2}{}^{0\text{ to }3} = 24476.2729$ to 24476.2697 $\qquad \Delta\nu(3p^2P_{3/2},\text{ total}) = 0.0032 \pm 0.0002$

m Meissner and Luft, reference 9, interferometric values, corrected for the ground state found in this work. This work, which yields less accurate differences, would independently give the following center-of-gravity values:

$3d = 12276.73$
$4d = 6900.95$
$5d = 4412.84$

p Experimental value of Paschen[5] corrected for the ground state.

r Experimental value of Rood and Sawyer[6] corrected for the ground state.

s Experimental values of Rood and Sawyer[6] yield

$10f = 1098.7$
$11f = 911.0$

z Experimental values of Zickendraht[7] corrected for the ground state are:

$11s = 1176.2$ $\qquad 14d = 559.7$
$12s = 966.8$ $\qquad 15d = 491.0$
$13s = 805.1$
$14s = 680.1$

± This value is uncertain by about ±0.06.

( ) Interpolated value supplied by J. E. Mack.


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## RESULTS

The wave-lengths of the principal series and of the forbidden $3s\,^2S_{\frac{1}{2}}-nd\,^2D_{3/2,5/2}$ transitions, referred to air at 15°C and 760 mm, are recorded in Tables I and II, respectively. These wave-lengths have been reduced to vacuum wave numbers by use of the corrections given in Kayser's "Tabelle der Schwingungszahlen." The wave-lengths as measured on different plates agree in almost all cases to 0.003A, and all agree to within 0.005A with two exceptions marked ± in the tables. In the $3s-10p$ line evidently the unresolved doublet separation was enough to make the reading unreliable. The random error in the wave numbers does not exceed about $\pm 0.04$ cm$^{-1}$, except where indicated. The ± estimates on the wave numbers do not take into account the uncertainty in the dispersion of air.

In Table III the values of the $S$, $P$, $D$ and $F$ levels are recorded. For completeness the values of other observers are included for levels unobserved in this work or measured more accurately by others. The limit of the principal series, computed in collaboration with Mr. J. G. Hirschberg, Jr., by the method of Shenstone and Russell,[7] was found to be $41449.65\pm 0.02$ cm$^{-1}$ from the center of gravity of the ground term or $41449.69\pm 0.02$ cm$^{-1}$ from the lower hyperfine structure level $3s\,^2S_{\frac{1}{2}}$,[1] the ionization potential is thus $5.138\pm 0.001$ volts, the uncertainty in the ionization potential lying principally in the value of the electron volt.[8] The smallness of the uncertainty as to the length of the series may be credited to the closeness of the approach to the series limit. Other low levels, including the separations of the $3p\,^2P$ and the $nd\,^2D$ terms up to $6d$, are from the definitive work of Meissner and Luft,[9] corrected to the ground level value found in this work. Values for the hyperfine structure of the $3s\,^2S_{\frac{1}{2}}$ and $3p\,^2P_{\frac{1}{2},3/2}$ levels were kindly supplied by Mr. Hack Arroe.

The $3s-7p$ and $3s-8p$ lines were not observed, for they fell in a gap in the continuum. The $7p$ and $8p$ term values have been computed by use of a Ritz formula.

A microphotometer traced of the higher members of the principal series of sodium is shown in Fig. 1. It shows the presence of lines to $n=79$, or approximately 1 angstrom unit from the series limit. [*Note added in Proof:* New microphotometer traces clearly show the presence of lines to $n=82$.] Although the present work does not include any intensity measurements, it can be stated that microphotometer traces traversing the series limit do not show the sudden change in absorption at the series limit that has been reported by some, but not all, previous observers.[10–13] Our failure to find the discontinuity may have been a result of our careful limitation of the pressure to avoid unnecessary line breadth.

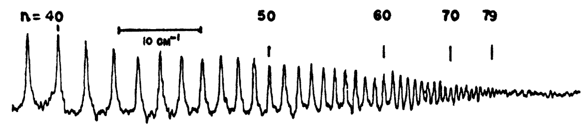


FIG. 1. A microphotometer trace of the higher members of the principal series of sodium showing the presence of lines to $n=79$.

## DISCUSSION OF RESULTS

The principal series has been measured for values of $n$ to 73 and observed to 79. This is 14 to 20 members beyond the observations of Wood and Fortrat. The wave-lengths found are in general slightly shorter than those of Wood and Fortrat. The energy levels found, as measured from the series limit, are both larger and smaller.

The number of doublets resolved was not increased but the separation of 0.028A found for $n=9$ was much smaller than that of Wood and Fortrat, who reported 0.082A. Although there was some difficulty in resolving this doublet, there is no doubt that the separation obtained here is much nearer the true one than is that of Wood and Fortrat: the over-all width of the line pair measured only 0.06A. A calculation, assuming an $n_{\text{eff}}^{-3}$ law of $\Delta\nu$, yields 0.019A. When the possible experimental error is considered in the measurement of the barely resolved components, the observed value is in fair agreement.

The forbidden $3s\,^2S_{\frac{1}{2}}-nd\,^2D_{3/2,5/2}$ transitions were found up to $n=13$, since the absorption occurred in a field-free region, it ought undoubtedly to be attributed principally to electric quadrupole absorption. These $3s-nd$ transitions to $n=20$ have been previously observed in the presence of an electric field by Ny Tsi-Ze and Weng Wen-Po.[14] The expected pressure shift,[15] due to foreign gas, was not found. A shift of the order of magnitude found in the sodium $D$ lines by Kleman and Lindholm[16] would have been too small for detection at

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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 $\pm 0.006$ cm$^{-1}$/mm Hg.

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

H. R. KRATZ**
*University of Wisconsin, Madison, Wisconsin*
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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

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** Now at the Research Laboratory, General Electric Company, Schenectady, New York.

[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.

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