### THE SODIUM AND POTASSIUM ABSORPTION BANDS

BY W. R. FREDRICKSON AND WILLIAM W. WATSON

#### Abstract

Vibrational relations.—Formulas for the heads of the bands are:

Green Na<sub>2</sub>:  $\nu = 20301.62 + (123.84n' - 0.79n'^2) - (157.57n'' - 0.57n''^2)$ Red Na<sub>2</sub>:  $\nu = 15006.68 + (115.69n' - 0.427n'^2) - (157.81n'' - 0.538n''^2)$ Near red K<sub>2</sub>:  $\nu = 15368.63 + (74.58n' - 0.30n'^2) - (92.01n'' - 0.34n''^2)$ 

Since the coefficients of the n'' terms for the green and red Na<sub>2</sub> bands are the same, the two systems must have the same initial state (<sup>1</sup>S) in absorption. The similarity of the green Na<sub>2</sub> and the near red K<sub>2</sub> band systems is pointed out. The n' progressions are very large for small n'' values, especially in the red Na<sub>2</sub> system.

New potassium bands.—A new  $K_2$  band system has been discovered on the long wave-length side of the  $\lambda$ 7699, 7665 K doublet. This system bears a marked resemblance to the red Na<sub>2</sub> bands, and is no doubt due to the same electronic transition.

Fine-structure analysis.—The lines in the (1, 0), (1, 1), (0, 1) and (0, 2) green sodium bands have been assigned into branches by correlation with the fluorescence and magnetic rotation data of R. W. Wood. There are apparently two Q branches but only single P and R branches. An explanation of this is offered, together with the details of the agreements between Wood's data and the present analysis. The usual combination relations hold, except for a small P, Q, R "defect" which is to be expected. The K<sub>2</sub> bands show exactly the same structure, but no resonance series have been located with which to check our analysis. It is concluded that the green Na<sub>2</sub> and the near red K<sub>2</sub> bands are both  ${}^{1}S-{}^{1}P$  transitions. For the initial absorption state, the moment of inertia is  $7.20 \times 10^{-39}$  gm cm<sup>2</sup> for Na<sub>2</sub> and  $8.72 \times 10^{-39}$  gm cm<sup>2</sup> for K<sub>2</sub>.

### INTRODUCTION

A LTHOUGH some of the green sodium and near red potassium absorption bands have been arranged into branches by Smith,<sup>1</sup> no really satisfactory analysis of these bands with combination relations to verify the assignments has been available. Also it seemed necessary to have higher dispersion plates than those used previously since the band lines have such a close spacing. Judging by the character of the fluorescent spectra found in sodium vapor by Wood,<sup>2,3</sup> Mulliken<sup>4</sup> has recently concluded that these bands are due to a  ${}^{1}S - {}^{1}P$  transition in the Na<sub>2</sub> molecule, and that therefore the bands should consist of simple *P*, *Q*, *R* branches like the AlH bands. The presentation of the direct evidence as to the validity of this conclusion together with the report of the constants of the Na<sub>2</sub> and K<sub>2</sub> molecules are the objects of the present paper.

The vibrational relations in these band systems are first presented, and then the discussion of the fine-structure, using as a basis for the analysis

- <sup>1</sup> H. G. Smith, Proc. Roy. Soc. 106, 400 (1924).
- <sup>2</sup> R. W. Wood, Phil. Mag. (6), **15**, 581 (1908).
- <sup>8</sup> Wood and Hackett, Astrophys. J. 30, 339 (1909).
- <sup>4</sup> R. S. Mulliken, Phys. Rev. 28, 1216 (1926).

Wood's fluorescence and magnetic rotation data. We also include the vibrational data of the red system of sodium, but as yet the fine-structure of these bands has not been completely determined. The photographs were taken in the first and second orders of a Rowland concave grating giving a dispersion of 2.6 and 1.3A per mm respectively. The source was a 150-watt lamp and the vapor was kept in glass tubes 40 to 60 cm long, heated electrically.

# VIBRATIONAL DATA

The band heads of the green and red systems of sodium and the near red system of potassium can be expressed by the following formulas: Green Na<sub>2</sub>  $\nu = 20301.62 + (123.84n' - 0.79n'^2) - (157.57n'' - 0.57n''^2)$ Red Na<sub>2</sub>  $\nu = 15006.68 + (115.69n' - 0.427n'^2) - (157.81n'' - 0.538n''^2)$ Red K<sub>2</sub>  $\nu = 15368.63 + (74.58n' - 0.30n'^2) - (92.01n'' - 0.34n''^2)$ An inspection of Tables I and II discloses the fact that the intensity distri-

An inspection of Tables I and II discloses the fact that the intensity distribution among the green  $Na_2$  and the  $K_2$  bands is practically identical. An

	TAI	BLE	Ι
Green	$Na_2$	band	system.

n'	n'' = 0	1	2	3	4	5	6	7	8
0	20301.62	20144.40	19988.77 (5)	19834.18	19678.63 (4)	19527.92 (2)			
1	20425.40	20267.56 (6)			19803.44 (4)	19652.08	19502.47 (1)		
2	20546.98	(-)		20078.47 (3)	( )		19624.02	19474.40	
3	20667.12		20352.48	20200.61		19893,29 (3)	(-)	19593.74	19447.77 (1)
4	20785.53	20627.23	20471.95	(-)		(0)		(-)	(/
5	20901.76	20743.38	(0)						
6	21016.00	23858.53							
7	(1)	20972.71							
8		21084.04	20926.19						
9	21351.17	21196.74	(1)						
10	(1)	21303.70	21147.10						
11		21409.32	21253.91						

TABLE II Near red K2 band system

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n'	$n^{\prime\prime}=0$	1	2	3	4	5	6	7	8	9	10		
0	15368.63	15277.08	15186.32	15095.92	15005.86	14916.55	-						
1	15442.88	15351.28 (5)			15079.75 (5)	14991.85 (3)	14902.94 (2)	14814.97 (0)					
2	15516.71	.,	15337.75 (2)	15242.33	. ,		14975.84 (1)	14887.92 (2)	14800.92 (1)				
3	15590.15 (7)		15407.36 (3)						14874.97	14787.39 (2)	14702.68 (0)		
4	15661.14 (5)	15569.61 (3)								14859.34	14773.93		
5	15733.35 (3)	15641.12 (4)		15461.35 (2)									
6	15805.38 (2)	15712.19 (4)											
7	15875.58 (2)	15782.47 (3)	15691.43 (3)										
8		15851.29 (2)	15760.72 (3)										
9			15829.18	•		<u>.</u>	•						

	Red Na <sub>2</sub> band system.												
n'	<i>n''</i> =0	1	2	3	. 4	5	6	7	8	9			
0	15006.68	14850.60	14691.34										
1	15122.33	14966.61	14807.95	14655.14				14045.21	14893.89	13744.23			
2	15236.35	15078.50	14921.66	14767.18	14614.15	14465.41	14308.27	14156.88	(1)	(1)			
3	15349.23	15191.97	(4)	(4)	(3)	14573.25	(2) 14422.45	(1)		13972.20			
4	15461.83	x(3)				(2)	(2)			(1)			
5	(5) 15575.87	15421.36											
6	(5) 15683,82	(4)											
7	(5) 15796.92												
8	(3) 15904.00				•								
9	x(4) 16011.67	15851.80											
10	(3) 16120,44	(4) 15962,95											
11	(2) 16232.60	x(3) 16070.39											
12	x(2) 16333.59	(2) 16177_04											
13	(3)	(3)											
14	(2)	(2)				•							
15	x(1)	(2)											
15	(1)	(2)											
10		(1)											

TABLE III

Bands indicated by x are difficult to measure accurately.

eye estimate of the intensity of each band is given by the number below the frequency of the head. The (0,0) band in each system is weak, but is definitely there. In each system the (2, 1), (3, 1), (1, 2), and (1, 3) bands are missing, and if a line were drawn through the squares of the most intense bands, we would have a parabola which is rather wide.<sup>5</sup> The similarity of these two systems is very marked, and, as will be shown later, is even more evident when the fine-structure is considered.

At our instigation, C. H. Hsü has very recently looked for and found a new potassium absorption band system in the region around 8000A. This system is situated with respect to the first doublet in the principal series of  $K(\lambda 7699.3 \text{ and } 7665.6)$  as is the red sodium band system with respect to the *D* lines of Na. No doubt an investigation of the structure of these two systems will reveal their likeness, since they are undoubtedly produced by the same electronic transition.

Particularly in the red sodium bands, the n' progressions are very large for small n''(i.e., n''=0, 1). This is perhaps solely a temperature effect showing that at the temperature of the absorbing gas most molecules are in a low vibrational quantum state, and thus on the basis of probability should give the distribution observed.

An interesting fact is that the coefficients of the n'' terms in the red and green bands of sodium have practically the same values:

<sup>5</sup> See R. T. Birge's discussion in Bulletin No. 57 of the National Research Council.

Green Na<sub>2</sub>  $(157.57n'' - 0.57n''^2)$ Red Na<sub>2</sub>  $(157.81n'' - 0.538n''^2)$ 

This shows that the final states in emission (the initial states in absorption) are the same in both systems, in agreement with Mulliken's prediction that the two band systems arise from the same electronic state. However from the data we find that we have too few bands with high quantum numbers to be able accurately to determine the energies of dissociation and thus the exact energy and state of each atom. We observe, though, that the bands appear only when the D lines are very broad which suggests that the sodium molecule may be due to the joining of a normal atom with an excited one in a P state. This combination, as well as the union of two normal atoms, will give a  ${}^{1}S$  molecular state.

### FINE-STRUCTURE ANALYSIS

Green sodium bands. Four bands—(1, 0), (1, 1), (0, 1), (0, 2)—have been analyzed. At high dispersion the bands display a great number of lines, and therefore due to the closeness of the lines at the head and the possible overlapping of another band, it was found that we could not with any degree of accuracy carry the branches within six or eight wave-numbers of the head. However, in each case studied the following band in the same sequence was missing or so weak that we could measure a sufficient number of lines in the band and make the assignments by correlation of our data with the fluorescence and magnetic rotation data.

Wood and Hackett<sup>2,3</sup> have obtained fluorescent spectra of sodium using various lines as the exciting source. Two of the lines, silver  $\lambda$ 5209 and cadmium  $\lambda$ 4800 give rise to singlet fluorescent series, while the two lines cadmium  $\lambda$ 5086 and lead  $\lambda$ 5006.1 excite doublet series. A number of other lines were also used as sources; barium  $\lambda$ 4934 (or  $\lambda$ 4900), lithium  $\lambda$ 4972, 4603—, magnesium green triplet, copper triplet, but their fluorescent lines show no such regularity as that mentioned above. For example, in the bands analyzed the fluorescent lines due to one of the mentioned sources may be single, double, or triple, and they do not appear at corresponding distances from the heads. Therefore, the doublets of cadmium and lead were used as the only safe clue for making the assignments.

We find that these doublets appear only in the bands with zero initial vibrational state. It seems, then, that the molecules excited by cadmium  $\lambda 5086$  and lead  $\lambda 5006.1$  pass to an excited zero vibrational state and emit the doublet lines in returning to the various vibrational levels in the unexcited state. According to the theory as developed by Kemble and Witmer,<sup>6</sup> and Loomis,<sup>7</sup> we should expect one component of the doublet to lie on the R branch and the other on the P branch with the  $\Delta j$  between the lines equal to 2. Also, we should expect the R(j) and P(j) to be the same for all the doublets due to the same source.

<sup>6</sup> E. C. Kemble and E. E. Witmer, Phys. Rev. 28, 633 (1926).

<sup>7</sup> F. W. Loomis, Phys. Rev. 29, 112 (1927).

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With the above as a guide, we find that each band is composed of four branches, on two of which the lines of the singlet resonance series lie. These two branches are apparently, then, Q, type. A possible explanation of this will be given later. The magnetic rotation data of Wood and Hackett also serve as a guide since the lines which are rotated negatively should appear on R branches, while those positively rotated should lie on P branches. The wave-numbers of the lines of the branches in each of the four bands are given in Table IV.

### TABLE IV Sodium bands.

			~ .		•	_	-	
j	R	QR	QP	Р	R	QR	QP	Р
63 73 83 93 103	20421.30 19.78 17.90 15.60 12.90	(1,0 20413.70 10.80 07.69	) band 20417.70CuLi 20 15.40Ba 12.70 09.34 06.19	0414.80 11.99x 08.99 05.50 02.32	20262.70 61.07Ba 59.27 57.08 54.80	(1,1)	band 20252.00 49.20	20255.87 53.59 51.00 48.09Ba 44.87
$   \begin{array}{r}     11\frac{1}{2} \\     12\frac{1}{2} \\     13\frac{1}{2} \\     14\frac{1}{2} \\     15\frac{1}{2}   \end{array} $	10.08 07.01 03.75x 00.56Ba 396.86	04.55 01.50 397.54 93.40 89.37	02.90 399.54Ba 95.37 91.73 87.32Cu	398.70x 94.47 90.08 85.90 81.34	52.30 49.80 46.67x 43.22 40.08	$20241.95 \\ 38.47 \\ 34.60$	46.30 42.81 39.40 35.75 31.89	41.15 37.47 33.80 29.77x 25.20
$   \begin{array}{r} 16\frac{1}{2} \\     17\frac{1}{2} \\     18\frac{1}{2} \\     19\frac{1}{2} \\     20\frac{1}{2} \\   \end{array} $	92.90 88.51 83.82 78.92 73.70	84.47 79.32	82.75 77.63	76.40 70.86	$\begin{array}{r} 36.46\\ 32.73\\ 28.60\\ 24.10\\ 19.83\end{array}$	30.57 26.29 22.11 17.47Cd 12.42	27.50 23.18 18.57 13.27 08.67Mg	21.05 16.23Cd 11.00 06.00 00.00
$21\frac{1}{2}$ $22\frac{1}{2}$	68.20 62.34				$\begin{array}{r}14.80\\10.06\end{array}$	07.01Ag 01.90Cu	03.21	
51 61 7 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2	20139.15 37.60Pb 36.10 34.50 32.50 30.30	(0, 1)	) band 2 20132.00 29.80CuMg 27.25 24.50	0133.50 31.00x 28.45 25.70Pb 22.70 19.60	19982.45x 80.67Pb 79.20 77.47 75.40 73.20	(0,2)	band 19970.40 67.40Li	19974.20 71.60 68.86xPb 65.70x 62.50
$ \begin{array}{c} 11\frac{1}{2}\\ 12\frac{1}{2}\\ 13\frac{1}{2}\\ 14\frac{1}{2}\\ 15\frac{1}{2}\\ \end{array} $	27.70 25.00 22.10 19.00Cd 15.40	23.44 20.46 17.02 13.72 09.78	21.70 18.11 14.63 10.80 06.82Li	16.10 12.45 08.50x 04.40Ba 00.21	70.66 68.12 65.20 62.20xCc 58.20	19965.70Ba 62.80 60.02 56.35 52.32Cu	64.15 61.00 57.60 54.40BaC 50.00	59.16 55.59 51.40 u 47.70Ba 43.20
$16\frac{1}{2}$ $17\frac{1}{2}$ $18\frac{1}{2}$ $19\frac{1}{2}$ $20\frac{1}{2}$ $21\frac{1}{2}$ $22\frac{1}{2}$	11.50 07.50 03.30Ba	05.68 01.30 96.74	02.60 098.25 • 93.30	95.40Cd 90.80 85.60	55.10 50.80Li 46.60 42.40 37.80 32.75 27.70	49.00Li 45.00 40.60 36.10 31.20 26.25 20.89	45.80 41.40 37.00 31.95 27.00 21.75 15.44Cd	39.30Cd 34.55 29.37Cu 24.80 19.30 13.70

The magnetic rotation lines are designated by "x" and the fluorescent lines are marked by the symbol of the source.

#### Summary of the Magnetic Rotation and Fluorescent Data.

(1, 0) Band. There are no cadmium, lead, or silver lines. There are four magnetic rotation lines:<sup>8</sup> 20424.57 (-) is in the head of the band,<sup>9</sup> 20422.23 (+) falls on  $P(7\frac{1}{2})$  or  $Q_R$  (9 $\frac{1}{2}$ ), 20403.32 (+) on  $R(13\frac{1}{2})$ , and 20399.15 (+) on  $P(11\frac{1}{2})$ . The magnetic rotation line 20388.75 is undoubtedly in the head of the weak (2, 1) band. Barium has two lines in the band: 20415.82 on  $R(9\frac{1}{2})$  or  $Q_R(7\frac{1}{2})$ , and 20400.40 on  $R(14\frac{1}{2})$  or  $Q_P(12\frac{1}{2})$ . Lithium has a line 20417.07 on  $Q_P(6\frac{1}{2})$  or  $P(5\frac{1}{2})$ . Copper has a line 20417.48 on  $Q_P(7\frac{1}{2})$ , and magnesium has a line 20387.92 on  $Q_P(15\frac{1}{2})$ .

<sup>8</sup> The  $\nu$  values given in this summary are obtained directly from Wood's data. The (+) sign signifies positive rotation, the (-) sign signifies negative rotation.

<sup>9</sup> From Loomis' abstract (Phys. Rev. **29**, 607, 1927), we find that there is a magnetic rotation line in the head of each band.

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(1, 1) Band. Cadmium ( $\lambda$ 4800) and silver each have a line far out in the band. These lines may be a part of the (2, 2) band which is apparently unnoticeable, but if we consider them as belonging to the (1, 1) band, the cadmium line 20216.41 falls on  $Q_R(19\frac{1}{2})$  or  $P(17\frac{1}{2})$ , and the silver line 20206.60 on  $Q_R(21\frac{1}{2})$ . There are four magnetic rotation lines: 20267.64 (-) and 20262.71 are in the head of the band, 20245.89 falls on  $R(13\frac{1}{2})$  and 20230.73 on  $P(14\frac{1}{2})$  or  $Q_R(16\frac{1}{2})$ . Barium has three lines: 20261.07 on  $R(7\frac{1}{2})$ , 20247.94 on  $P(9\frac{1}{2})$ , and 20254.91 on a Q line. Copper has two lines: 20266.82 in the head and 20202.93 on  $Q_R(21\frac{1}{2})$ . Lithium has a line 20259.84 on a  $Q_P$  line and magnesium has a line 20208.65 on  $Q_R(20\frac{1}{2})$ .

(0, 1) Band. There are two doublets in this band. Lead ( $\lambda$ 5006.1) doublet has one component 20137.82 on  $R(6\frac{1}{2})$  and the other 20125.25 on  $P(8\frac{1}{2})$ . The cadmium ( $\lambda$ 5086) doublet has one component 20119.76 on  $R(14\frac{1}{2})$  and the other 20094.91 on  $P(16\frac{1}{2})$ . There are four magnetic rotation lines: 20145.53 and 20139.44 are in the head, 20108.25 falls on  $P(13\frac{1}{2})$  and 20131.33  $P(6\frac{1}{2})$ . The magnetic rotation line 20108.25 undoubtedly belongs to the (1, 2) band. Barium has a line 20103.80 which falls on  $R(18\frac{1}{2})$  or  $P(14\frac{1}{2})$ , or it may possibly belong to the (1, 2) band. Lithium has two lines: 20106.63 on  $Q_P(15\frac{1}{2})$ , and 20081.19. This last line was not included in the measurements. Copper and magnesium have the same line 20129.71 which falls on  $Q_R(8\frac{1}{2})$  and copper alone has a line 20143.50 which is in the head.

(0, 2) Band. Here we also have the doublets of cadmium and lead. The lead doublet has one component 19980.85 on  $R(6\frac{1}{2})$  and the other 19968.48 on  $P(8\frac{1}{2})$ . The cadmium doublet has one component 19962.90 on  $(R14\frac{1}{2})$  and the other 19940.20 on  $P(16\frac{1}{2})$ . Silver has a line 19905.66 which falls on  $Q_R(25\frac{1}{2})$ , or it may possibly belong to the (2, 4) band, although this band appears to be missing. Cadmium ( $\lambda$ 4800) has a line 19915.97 which falls on  $Q_P(22\frac{1}{2})$ . There are five magnetic rotation lines: 19988.04 (-) is in the head, 19982.45 on  $R(5\frac{1}{2})$ , 19969.28 on  $P(8\frac{1}{2})$ , 19965.69 on  $P(9\frac{1}{2})$ , and 19961.70 on  $R(14\frac{1}{2})$ . Barium has three lines: 19966.09 on  $Q_R(11\frac{1}{2})$ , 19954.93 on  $Q_P(14\frac{1}{2})$ , and 19947.3 on  $P(14\frac{1}{2})$ , although this last line may belong to the weak (1, 3) band. Lithium has three lines: 19967.28 on  $Q_P(10\frac{1}{2})$ , 19950.95 on  $R(17\frac{1}{2})$ , and 19949.35 on  $Q_R(16\frac{1}{2})$ . The last two lines may belong to the (1, 3) band. Copper has three lines: 19978.05 on either  $P(4\frac{1}{2})$  or on a Q line, 19953.73 on either  $Q_R(14\frac{1}{2})$  or  $Q_P(15\frac{1}{2})$ , and 19929.87 either on  $P(18\frac{1}{2})$  or in the (1, 3) band. The magnesium lines are too far out in the band to be accounted for.

As mentioned before, no confidence can be placed in the fluorescent lines due to the barium, magnesium, lithium and copper excitations as far as their being an aid in the location of the branches is concerned. Apparently, in the assignments made, these lines predominate on Q branches. Of the four bands measured, the singlets due to silver and cadmium  $\lambda$ 4800 appear only in two bands (1, 1) and (0, 2) and far out in each band. Therefore it is to be concluded that these singlets form in two series with initial vibrational levels 0 and 1.

The P-R initial and final state combinations between bands together with the typical P, Q, R combinations for one of the bands, are shown in Table V. The expected combination defect such as Eriksson and Hulthén<sup>10</sup> found in the AlH bands (also a  ${}^{1}S-{}^{1}P$  transition) is seen to be present. Since one of the Q branches lies close to the R branch, while the other lies close to the P branch we have designated them  $Q_R$  and  $Q_p$  respectively. Fig. 1 is a plot of the branches in one of the bands, showing the way in which the resonance lines and the magnetic rotation lines fit into this assignment.

Mulliken<sup>11</sup> has explained the combination defect in AlH on the basis of a  $\sigma$ -type doubling, and has suggested that the cause of the doubling may be

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<sup>&</sup>lt;sup>10</sup> Eriksson and Hulthèn, Zeits. f. Physik 34, 775 (1925).

<sup>&</sup>lt;sup>11</sup> Mulliken, Phys. Rev. 28, 1202 (1926).

j	$(0, 1) Band  \Delta_2 F'$	(0, 2) Band $\Delta_2 F'$	$(1, 1) Band \Delta_2 F'$	(1, 0) Band $\Delta_2 F'$	(0, 1) Band $\Delta_2 F^{\prime\prime}$	(1, 1) Band $\Delta_2 F^{\prime\prime}$				
$\begin{array}{c} 6\frac{1}{2}\\ 7\frac{1}{2}\frac{1}{$	$\begin{array}{c} 6.60\\ 7.65\\ 8.80\\ 9.80\\ 10.70\\ 11.60\\ 12.55\\ 13.60\\ 14.60\\ 15.22\\ 16.08\\ 16.72\\ 17.74 \end{array}$	$\begin{array}{c} 6.47 \\ 7.60 \\ 8.61 \\ 9.70 \\ 10.70 \\ 11.50 \\ 12.53 \\ 13.81 \\ 14.50 \\ 15.00 \\ 15.80 \\ 16.24 \\ 17.23 \end{array}$	$\begin{array}{r} 8.27\\ 8.99\\ 9.93\\ 11.15\\ 12.33\\ 12.87\\ 13.45\\ 14.88\\ 15.41\\ 16.48\\ 17.57\end{array}$	$\begin{array}{c} 7.79\\ 9.00\\ 10.10\\ 10.58\\ 11.34\\ 12.64\\ 13.67\\ 14.66\\ 15.52\\ 16.50\\ 17.65\end{array}$	$ \begin{array}{c} 11.90\\ 13.40\\ 14.90\\ 16.40\\ 17.85\\ 19.20\\ 20.60\\ 21.90\\ 23.60\\ 24.60\\ 25.90\\ \end{array} $	$\begin{array}{c} 11.70\\ 12.98\\ 14.40\\ 15.93\\ 17.33\\ 18.50\\ 20.03\\ 21.47\\ 22.17\\ 23.85\\ 25.46 \end{array}$				
Typical P, Q, R combination. (0, 2) Band										
j	$R(j) - Q_R(j)$	$\begin{array}{c} Q_R(j+1) \\ -P(j+1) \end{array}$	Diff	$R(j) - Q_P(j)$	$\begin{array}{c} Q_P(j+1) \\ -P(j+1) \end{array}$	Diff.				
9½ 10Å				5.00	4.90	. 10				

12

16

18<sup>1</sup>/<sub>2</sub>

19<sup>1</sup>/<sub>2</sub>

 $20\frac{1}{2}$ 

21 <del>§</del>

5.18

5.85

5.88

6.10

5.80

6.01

6.30

6.58

6.50

8.62

8.65 9.12

9.70

10.45

11.23

11.29

11.90

 $6.51 \\ 7.12$ 

7.60

7.82

8.20

9.29

9.40

9.62

10.45

10.80

 $\begin{array}{c} 5.41 \\ 6.20 \end{array}$ 

6.70

6.81

6.54 6.85

7.63

8.17

7.70

8.05

1.10

1.01

1.66

2.44

1.77

1.45

75

2 2 75

.92

. 90

TABLE V Combinations in sodium bands. P and R-branch combinations.

the presence of "secondary  $\rho$ 's." Should this be the case, it seems plausible that if the  $F_B$  and  $F_A$  states have different  $\rho$ 's, the  $\rho_A$  appears with both + and - signs, and thus the cross-over transitions from  $F_A \pm$  to  $F_B$  should give rise to two *Q* branches.

 $3.44 \\ 2.80 \\ 3.24$ 

3.60

4.65 5.23

5.01

5.32

It is impossible to verify with any certainty this analysis by consideration of the intensity distribution in the various branches, since estimates of the intensities of absorption lines such as these are much more unreliable than those of emission lines. Roughly, however, the relative intensities are as expected for a  ${}^{1}S - {}^{1}P$  transition; the Q branches are the strongest, while the R branch is stronger than the P branch.

Potassium bands. As mentioned above, the analysis of the fine-structure of the K<sub>2</sub> bands verifies the prediction based on the general similarity of the two systems that the blue-green Na<sub>2</sub> and the K<sub>2</sub> bands are identical in every respect. No fluorescence data being available, the assignment of the lines of the K<sub>2</sub> bands into branches is a more difficult problem than that presented by the Na<sub>2</sub> bands. When the (0, 1), (0, 2), (1, 0), and (2, 0) bands (the only bands free from the overlapping of neighboring bands of the same groups) are measured and plotted to a large scale, however, it becomes apparent that



Fig. 1. Na<sub>2</sub>,  $\lambda$ 5001 band, (0, 2) = (n', n''). Curves of the *j*,  $\nu$  variation. The magnetic rotation lines are designated by  $\times$  and the fluorescent lines are marked by the symbol of the source.

j	Ŗ	QR	QP	P ·	R	QR	QP	Р		
101		(0, 1)	Band		15177.26	(0, 2) 15173.91	Band 15173.14	15169.16		
12 <sup>1</sup> / <sub>2</sub> 13 <sup>1</sup> / <sub>2</sub>	$15263.55 \\ 60.39$	$15259.10 \\ 56.05$	$15258.60 \\ 55.22$	$15253.48 \\ 49.92$	74.96 72.46 69.92	71.28 68.53 65.46	$70.50 \\ 67.74 \\ 64.74$	63.10 59.69		
14½ 15½	57.59 $54.40$	$52.68 \\ 49.19$	$\begin{array}{c} 51.74\\ 48.10\end{array}$	$46.38 \\ 42.48$	66.97 63.90	62.26 58.90	$61.35 \\ 57.93$	$56.15 \\ 52.16$		
$16\frac{1}{2}$ $17\frac{1}{2}$	50.92 47.32	$45.41 \\ 41.39 \\ 37.05$	44.43 40.53	$38.13 \\ 33.54 \\ 20.11$	60.63 57.03	55.13 51.39	54.15 50.18	47.99 43.69		
$10\frac{1}{2}$ $19\frac{1}{2}$ $20\frac{1}{2}$	39.24 34.90	37.03 32.47 27.77	31.33 26.55	29.11 24.02 18.84	49.15 44.81	47.02 42.74 37.96	43.82 41.47 36.82	39.21 34.32 29.19		
$21\frac{1}{2}$ $22\frac{1}{2}$	30.28 25.32	$22.70 \\ 17.36$	21.36 16.20	$\begin{array}{c}13.33\\07.56\end{array}$	40.27 35.59	33.05 27.96	$31.86 \\ 26.60$	$\begin{array}{c} 23.94 \\ 18.43 \end{array}$		
$23\frac{1}{2}$ $24\frac{1}{2}$ $25\frac{1}{2}$	20.17 14.92 09.14	$     \begin{array}{r}       11.88 \\       06.28 \\       00.28     \end{array} $	$10.57 \\ 04.61 \\ 98.60$	01.77	$30.54 \\ 25.34 \\ 19.84$	22.64 16.87 11.12	$21.17 \\ 15.60 \\ 09.78$	$12.76 \\ 06.56 \\ 00.39$		
26 <sup>1</sup> / <sub>2</sub> 27 <sup>1</sup> / <sub>2</sub> 28 <sup>1</sup> / <sub>2</sub>	03.23 197.13				$14.16 \\ 08.15 \\ 02.21$	$\begin{array}{c} 05.21\\ 98.84\end{array}$	03.55 97.21			
101	15422 20	(1,0)	Band	15404 69		(2,0)	(2,0) Band			
$   \begin{array}{c}     102 \\     112 \\     122 \\     132 \\     141   \end{array} $	29.58 (27.00) 23.87	26.05 23.13 19.81	13428.38 25.56 22.39 18.98	$ \begin{array}{r} 15424.08\\ 21.48\\ 18.06\\ 14.29\\ 10.38 \end{array} $	$15501.26 \\ 498.35 \\ 05.13$	15500.68 497.56 94.29 00.80	15499.99 96.74 93.48	15495.85 92.52 88.75 84.70		
$14\frac{1}{2}$ $15\frac{1}{2}$	17.19	12.44	11.40	06.25	91.70	86.83	85.92	80.62		
$16\frac{1}{2}$ $17\frac{1}{2}$ $18\frac{1}{2}$ $20\frac{1}{2}$ $21\frac{1}{2}$ $23\frac{1}{2}$	13.33 09.29 (05.15) 00.55	08.26 03.96 399.50 94.46	07.25 02.80 398.14 93.20	01.67 397.00	87.88 83.81 79.52 74.89 70.00 64.84 59.45 53.84	82.68 78.46 73.60 68.62 63.52 58.07 52.36 46.41	$\begin{array}{c} 81.65\\ 77.29\\ 72.57\\ 67.47\\ 62.30\\ 56.71\\ 50.95\\ 45.01\\ 20.02\\ 45.01\end{array}$	$\begin{array}{c} 76.04 \\ 71.20 \\ 66.25 \\ 60.77 \\ 55.13 \\ 49.52 \\ 43.50 \\ 37.30 \\ 37.00 \end{array}$		
24 <u>3</u> 25 <u>1</u>		-			48.27 42.10	40.52 34.50	38.88			

TABLE VI Potassium bands. every fourth line is a member of the same series. The usual combination relations are sought among the lines of these four series, and their designation as R,  $Q_R$ ,  $Q_P$ , and P branches thus made. Table VI gives the assignments for the four bands, the *j* values having been obtained by extrapolation of the  $\Delta F$ 's to zero value. Since the lines become so fused together near the head of a band, it is impossible to follow any of the branches accurately to the zero-point. However, it is evident that the zero-points are very close (within  $1 \text{ cm}^{-1}$ ) to the head in every case.

The P-R combinations between the bands are given in Table VII, together with a typical set of data showing the extent to which the R(j) - Q(j)=Q(j+1)-P(j+1) relation holds for one of the bands. A slight combination

$\begin{array}{c c c c c c c c c c c c c c c c c c c $											
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		(0, 1) ba	nd ) 2) band	(0, 1) bai	nd (0	1) band	(0,1) ba	und (0	1) hand	(1,0) ban	d 0) band
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	j	$\Delta_2 F'$	$\Delta_2 F'$	$\begin{vmatrix} R(j) \\ -Q_P(j) \end{vmatrix}$	$Q_P(j+1) - P(j+1)$	) Diff.	$R(j) - Q_R(j)$	$Q_R(j+1) - P(j+1)$	) Diff. 1)	$\Delta_2 F''^2$	$\Delta_2 F^{\prime\prime}$
$20\frac{1}{2}$ 16.00 15.62 8.35 8.03 +.32 7.13 9.37 -2.24 21 $\frac{1}{2}$ 16.95 16.33 8.92 8.64 +.28 7.58 9.80 -2.22 224 17 76 17 16 9.12 8.81 +.31 7.06 10.11 -2.15	$\begin{array}{c} 12\frac{1}{2}\\ 13\frac{1}{2}1$	10.47 11.21 11.92 12.79 13.78 14.30 15.22 16.06 16.95 17.76	10.23 10.82 11.74 12.64 13.34 13.97 14.83 15.62 16.33 17.16	$\begin{array}{c} 4.95 \\ 5.17 \\ 5.85 \\ 6.30 \\ 6.49 \\ 6.79 \\ 7.42 \\ 7.91 \\ 8.35 \\ 8.92 \\ 9.12 \end{array}$	5.30 5.36 5.62 6.30 6.99 6.88 7.31 7.71 8.03 8.64 8.81	$\begin{array}{r}35 \\19 \\ +.23 \\ +.00 \\50 \\09 \\ +.11 \\ +.21 \\ +.32 \\ +.28 \\ +.31 \end{array}$	4.45 4.34 4.91 5.21 5.53 6.36 6.77 7.13 7.58 7.96	6.13 6.30 6.71 7.28 7.85 7.94 8.45 8.93 9.37 9.80	-1.68 -1.96 -1.80 -2.07 -2.34 -2.01 -2.09 -2.16 -2.24 -2.22	16.62 17.62 19.01 20.19	16.47 17.73 19.04 20.50

TABLE VII Combinations in potassium bands.

defect of the order of magnitude to be expected is apparent when the  $Q_P$ branch is used. The defect for the  $Q_R$  branch is larger and seems to have an approximately constant value of about  $2 cm^{-1}$ . Except for the extra *Q* branch, we are dealing here apparently with a typical  ${}^{1}S - {}^{1}P$  transition. A possible explanation of this doubling of the Q branch is that given above for the sodium bands.

## TABLE VIII

			Sum	nary of the	constant	s of the N c	12 and K2	molecules	•			
				α'	$I_0' \times$					$I_0 \times$		
	$B_0'$	$B_1'$	$B_{2}'$	$B_0 - B_1$	1038	B .''	$B_1^{\prime\prime}$	$B_{2}^{\prime\prime}$	$\alpha^{\prime\prime}$	1039	ω0'	ωο''
Na <sub>2</sub>	0.264	0.245		0.019	1.05	0.384	0.375	0.367	0.0087	7,20	123.84	157.57
K <sub>2</sub>	0.1985	0.1807	0.165	0.018	1.39	0.317	0.308	0,299	0.009	8.72	74.58	92.01

Table VIII summarizes the constants for the Na<sub>2</sub> and K<sub>2</sub> molecules in the two states represented by these bands. One notes that a change of over 60 percent occurs in the moment of inertia. The ratio B'(B''-B') is 1.65, showing that the R branch turns at a very low number and the zero-point is just about at the head. It is thus clear why a magnetic rotation line is found exactly at the head of every band.

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