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ROTATIONAL STRUCTURE OF THE RED BANDS OF SODIUM

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ABSTRACT

Three bands of the red band system of sodium photographed at high dispersion have been measured. Two strong series of lines run through the bands and from the combination relations it is quite certain that these series are bona fide P and R branches. From the combination relations we find $B_0''=0.15435, D_0''=-5.89\times10^{-7}$ and $B_0'=0.10846$. The final state values are in close agreement with those of the final state of the blue green system and the constant for the upper state yields $I_0'=255.3\times10^{-40}$ gm cm² and $r_0'=3.52\times10^{-8}$ cm. Search is made for other branches but none are found. From a discussion of the possible electronic transitions it is concluded that the electronic transition is the ${}^1S-{}^1S$ type.

THE absorption spectrum of molecular sodium consists of two band systems, one in the red and the other in the blue-green. Loomis[1] has analyzed the vibrational structure of the blue-green system from a study of Wood's[2] magnetic rotation spectrum of sodium and the writer and Watson[3] have analyzed the vibrational structure of both the red and the blue-green systems from the absorption spectrum. The agreement of the final state coefficients of the vibrational formulas for the two systems shows that the systems have a common final electronic state. By means of this vibrational data and a study of the heats of dissociation of Na_2 Loomis[1] has shown that the molecules in the common lower energy state dissociate into 3^2S atoms while the molecules in the excited state of both the red and the blue-green bands dissociate into a $3^2\,S$ atom and a $3^2\,P$ atom. Furthermore, Loomis and Wood[4] have worked out the rotational structure of the blue-green bands and have proved conclusively that the electronic transition for this system is ${}^1P-{}^1S$.

Since the excited molecules of both systems dissociate into a 3^2P and a 3^2S atom, the theoretically possible molecular states[5] for the upper state are ${}^3P$, ${}^3S$, ${}^1P$, and ${}^1S$. From the similarity of the sodium molecule and the CO molecule and by analogy with the Mg atom,[6] one would be inclined to assign the red system to a ${}^3P-{}^1S$ transition. Thus the red bands would be similar to the Cameron CO bands. These latter bands, however, show triple heads while the sodium bands show only single heads.[7] Mulliken[5] states that no

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[1] Loomis, Phys. Rev. **31,** 323 (1928).

[2] Wood, Astrophys. J. **30,** 339 (1909).

[3] Fredrickson and Watson, Phys. Rev. **30,** 429 (1927).

[4] Loomis and Wood, Phys. Rev. **32,** 223 (1928).

[5] Mulliken, Phys. Rev. **32,** 396 (1928).

[6] Mulliken, Phys. Rev. **28,** 493 (1926). Na_2 and CO are similar in that they have the same number of outer electrons.

[7] Ritschl and Villars, Naturwiss. **16,** 219 (1928).

reason is evident for such a contrast between the systems and suggests the possibility that the upper molecular state for the red bands is a ^1S state instead of a ^3P. It is with reference to the question of electronic transition that the following analysis is concerned.

The photographic plates of the spectrum were taken at the Ryerson Laboratory, The University of Chicago, using the twenty-one foot Rowland concave grating in the second order. The (6,0), (5,0) (4,0) bands were measured because they are among the most intense and show the least overlapping.

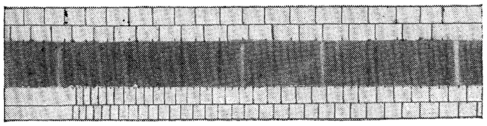

Fig. 1. The (5, 0) band of red Na_2 band system.

An enlargement of the (5,0) band is shown in Fig. 1. The ink lines at the bottom show two series which are of the same intensity and converge at the head of the band. At the top are shown two series which proceed through the band and converge at the head of the preceding band,—the (6,0). In each of the three bands measured two series are found,—the data being given in Table I.

The two series in each band were taken to be P and R branches and the determination of which was P and which was R was made with the aid of the combination relations. According to the band spectrum theory, the combination relations are

$$2\Delta F'(j) = R(j) - P(j) = 4B'(j+\tfrac{1}{2}) + 8D'(j+\tfrac{1}{2})^3$$

$$2\Delta F''(j) = R(j-1) - P(j+1) = 4B''(j+\tfrac{1}{2}) + 8D''(j+\tfrac{1}{2})^3$$

The method of assigning the various series in each band to R and P branches was to apply the last relation above to the series in the three bands measured and to shift the series until the best agreement between the final state combinations was obtained. When the assignment of the series to the P and R branches was once made, the B'' and D'' values were calculated. It is unfortunate that one could not apply the initial state combinations between bands but no two bands with the same initial state could be analyzed because of the overlapping of other bands. However, the initial state combinations for these bands were taken and from them the B' and D' values were calculated.

The following is a summary of the constants:

$B_0''=0.15435$ $\quad B_6'=0.10555$ $\quad D_6'=-3.59\times10^{-7}$

$D_0''=-5.89\times10^{-7}$ $\quad B_5'=0.10611$ $\quad D_5'=-3.36\times10^{-7}$

$B_4'=0.10664$ $\quad D_4'=-2.61\times10^{-7}$.

Assuming the formula $B'_n=B'_0-\alpha_1 n'-\alpha_2 n'^2$ we find that $B'_0=0.10846$, $\alpha_1=0.000395$, and $\alpha_2=0.000015$.

TABLE I. *Lines in the red* Na$_2$ *bands.*

	6−0		5−0		4−0	
j	*R*	*P*	*R*	*P*	*R*	*P*
10½					15458.02	15453.60
11½					57.20	52.10
12½					56.00	50.60
13½	15677.69	15671.83	15566.62	15560.78	55.10	49.50
14½	76.52	70.39	65.50	59.24	53.78	47.71
15½	75.31	68.75	64.26	57.67	52.63	46.00
16½	73.90	66.98	62.80	56.00	51.24	44.18
17½	72.46	65.11	61.75	54.22	49.89	42.42
18½	70.98	63.10	60.16	52.18	48.30	40.35
19½	69.24	61.12	58.52	50.33	46.71	38.49
20½	67.56	58.92	56.86	48.29	44.65	36.49
21½	65.74	56.64	55.03	45.98	43.08	34.10
22½	63.89	54.30	53.21	43.63	41.25	31.40
23½	61.79	51.86	51.12	41.24	39.10	29.10
24½	59.58	49.38	49.16	38.82	37.09	26.75
25½	57.49	46.77	46.99	36.17	34.90	24.13
26½	55.30	44.12	44.61	33.47	32.60	21.57
27½	52.73	41.16	42.27	30.61	30.22	18.60
28½	50.32	38.27	39.77	27.77	27.82	15.73
29½	47.68	35.25	37.19	24.81	25.45	12.74
30½	44.82	32.14	34.60	21.72	22.69	9.60
31½	42.18	28.92	31.78	18.54	20.38	6.85
32½	39.34	25.61	29.06	15.25	17.84	3.35
33½	36.30	22.27	26.00	11.96	15.00	15400.62
34½	33.31	18.84	23.03	8.44	12.14	15397.32
35½	30.04	15.19	19.93	4.87	9.02	94.00
36½	26.80	11.52	16.66	1.34	5.88	90.49
37½	23.44	7.81	13.43	15497.69	2.66	86.70
38½	19.96	3.89	9.96	93.77	15399.30	82.89
39½	16.48	0.00	6.43	89.77	95.80	79.00
40½	12.84	15595.94	2.88	85.80	92.40	75.25
41½	9.07	91.74	15499.20	81.71	88.68	71.22
42½	5.31	87.57	95.47	77.55	85.00	67.05
43½	1.35	83.15	91.63	73.34	81.03	62.71
44½	15597.47	78.82	87.54	68.94	77.22	58.51
45½	93.19	74.29	83.54	64.47		
46½	89.05	69.69	79.30	59.82		
47½	84.75	65.04	75.07	55.36		
48½	80.25	60.15	70.77	50.51		
49½	75.90	55.32	66.40	45.84		
50½	71.27	50.33	61.95	40.77		
51½	66.62	45.27	57.24	35.80		
52½	61.92	40.17	52.63	30.76		
53½	57.00	34.90	47.80	25.45		
54½	52.18	29.59	43.10	20.38		
55½	46.99	24.03	37.98	15.00		
56½	41.80	18.64	33.00	9.54		
57½	36.84	13.03	27.82	3.94		
58½	31.34	7.35	22.59	15398.34		
59½	26.09	1.34	17.19	92.72		
60½	20.62	15495.47	11.59	86.87		

It is interesting to compare the final state values of the red system with those of the blue-green.[4]

(blue green)	$B_0''=0.15431$	$D_0''=-5.86\times10^{-7}$
(red)	$B_0''=0.15435$	$D_0''=-5.89\times10^{-7}$.

This agreement is as close as can be expected. When the $2\Delta F''$ values are calculated from the above constants and then compared with the experimental values, one cannot say which set better fits the data.

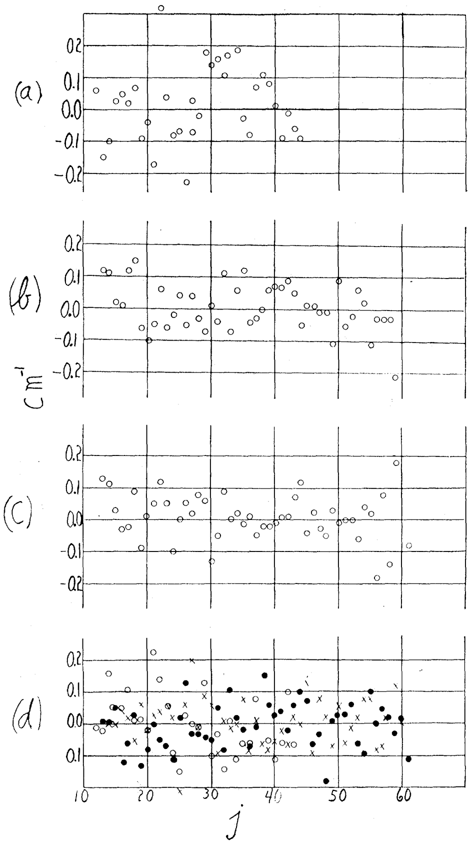

Fig. 2. Differences between the calculated and observed $2\Delta F$ values. (a), (b), (c) give the $2\Delta F'$ values for the (4, 0), (5, 0), (6, 0) bands and (d) gives the $2\Delta F''$ values for the three bands, crosses are the (6, 0), dots are the (5, 0) and circles are the (4, 0).

As to the initial state constants, they agree fairly well with those predicted by Loomis[8]. If we take our values and apply them to the empirical relations of Mecke and Birge which Loomis used in making his predictions we find that B_0/ω_0 which should remain constant in any transition has the values $B_0''/\omega_0''=0.00097$ and $B_0'/\omega_0'=0.00091$, and the value $R=2\times B_0/\alpha$

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[8] Loomis, Phys. Rev. **32**, 875 (1928).

which also should remain constant in a transition has the values $R''=1.73$ and $R'=1.83$. With the value of $B'_0=0.10846$ we find the moment of inertia $I'_0=255.3\times10^{-40}$gm cm^2, and the radius of the molecule $r'_0=3.52\times10^{-8}$ cm.

The deviations of the $2\Delta F$ values from the calculated values are shown in Fig. 2. It can be seen from the figure that practically all the deviations are within 0.1 wave-number which is as good as can be expected. The (4,0) band shows the greatest deviations. This band, however, also has the most overlapping.

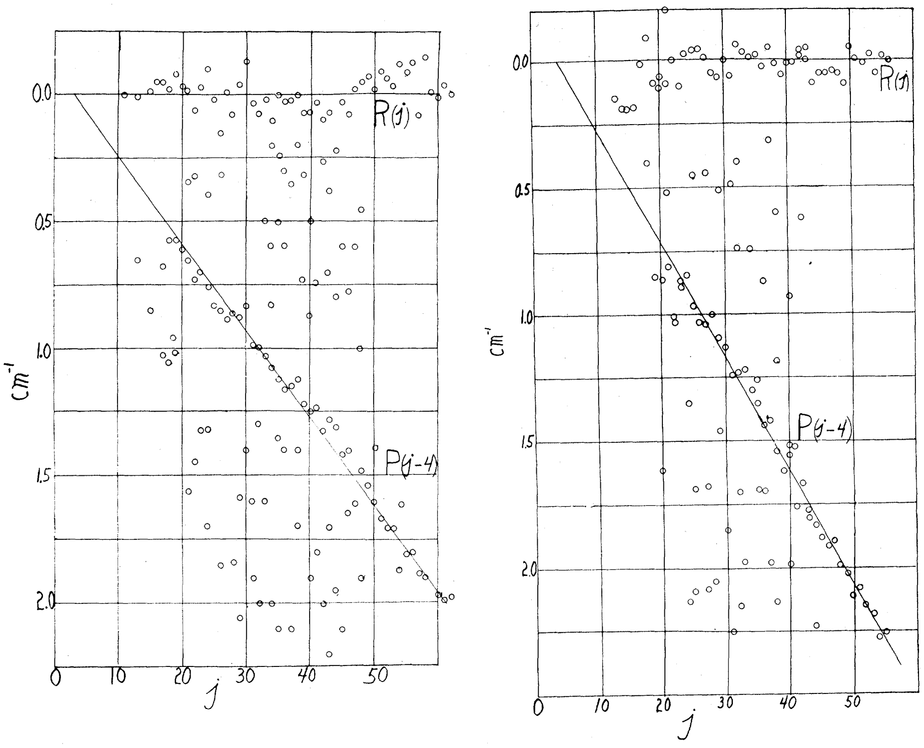


Fig. 3. The circles give the differences between lines in bands and their adjacent calculated R lines for the (5, 0) and (6, 0) bands.

From the agreement of the final state combinations and the agreement of the final state coefficients with those of the blue-green system, it seemed reasonable to suppose that the two branches are bona fide P and R branches. It was desired, however, to determine whether any other branches could possibly be present. Following a method used by Loomis and Wood[4] the R branches for the (5,0) and (6,0) bands were calculated from the formula

$$\nu=A+2B'(j+\tfrac{1}{2})+(B'-B'')(j+\tfrac{1}{2})^2+4D'(j+\tfrac{1}{2})^3+(D'-D'')(j+\tfrac{1}{2})^4$$

where the B and D values are those given above and the A was determined by equating the right hand of the above equation to the frequency of some one line in the band. The difference in frequencies of every line and its adjacent R line is plotted. Figure 3 shows the situation for the (5,0) and (6,0) bands.

It is seen that most of the points group themselves along two lines, the (0,0) line which represents the R branch and the inclined line which represents the P branch. Should any other branches be present, one would expect the other points to group themselves along other lines. Some of the points scattered throughout the graphs are due to branches from the preceding band. Figure 4 shows the (5,0) band after the lines belonging to the (6,0) band have been removed. From these graphs one would conclude that in the region of quantum numbers higher than 13 in each band only two branches appear. In the region below quantum number thirteen we are unable to say because the lines are too close together and too weak in intensity.

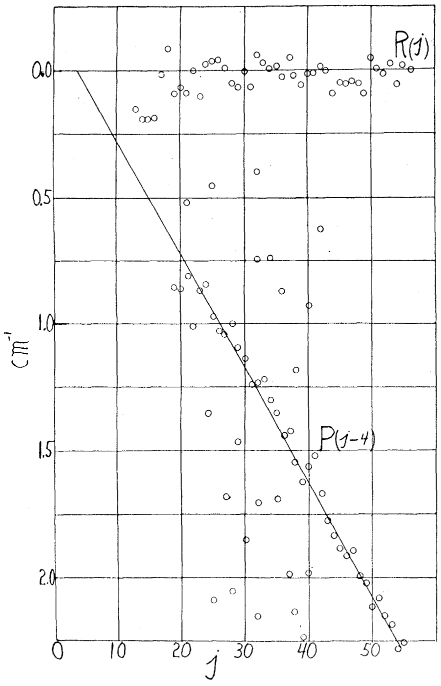
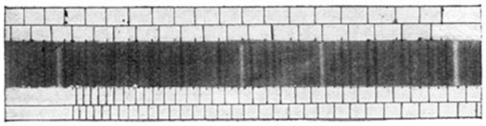


Fig. 4. Same as the (5, 0) band in the preceding figure except that known (6, 0) lines are omitted.

The presence of only two branches appears to confirm the assignment of electronic transition to the $^1S-{}^1S$ type. If the electronic transition was of the $^3P_1-{}^1S$ type, one would probably expect the same structure and intensity distribution as for the $^1P-{}^1S$ type—single P, Q, R branches with the Q branch the most intense.

In conclusion the writer wishes to thank Dr. W. W. Watson and Dr. R. S. Mulliken for their interest and advice in the work.



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