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Magnetic Rotation Spectrum of the Red Bands of Sodium

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The magnetic rotation spectrum of the red bands of sodium shows a large number of doublets. A doublet is interpreted as made up of an *R*-branch and a *P*-branch line having a common upper K' rotational level. The K' values for the doublets are calculated and it is found that the rotational levels in the various initial vibrational states from 0–12 which give rise to magnetic rotation doublets are 53, 45, 33, 14, 60, 52, 43, 31, 16, 58, 51, 40, 28 respectively. That just these levels give rise to magnetic rotation lines suggests that these levels are perturbed. Since a $^3\Pi$ state is predicted to lie below the upper $^1\Sigma$ state we have perhaps here evidence of a perturbation between a $^1\Sigma$ and a $^3\Pi$ state. To account for the magnetic rotation doublets it has been necessary to revise the vibrational numbering, increasing the initial state numbering by three.

SOME twenty-five years ago R. W. Wood[1] and his collaborators reported the magnetic rotation spectrum of the blue-green and red bands of sodium. The experimental procedure was to pass light through two nicols between which was placed a tube of absorbing vapor, the latter being arranged between the poles of an electromagnet in such a way that light passed through the tube in a direction parallel to the magnetic field. When the nicols were set for extinction, the magnetic rotation spectrum was produced upon the excitation of the magnetic field.

F. W. Loomis[2] has shown that in the blue-green system most of the magnetic rotation lines correspond to the first lines in the *R*-branch and from this fact he has been able to make a very accurate vibrational analysis of this system. The blue-green bands are due to a $^1\Pi-{}^1\Sigma$ electronic transition and Loomis and Nusbaum[3] have shown that the same electronic transition in other molecules shows the same magnetic rotation effect. Serber,[4] in a theoretical discussion of the problem, concludes that the magnetic rotation effect is associated with the Zeeman effect in such a way that lines showing large Zeeman splitting should also show large magnetic rotation. The magnetic rotation lines in the $^1\Pi-{}^1\Sigma$ bands agree with this conclusion.

The red sodium bands, however, are due to a $^1\Sigma-{}^1\Sigma$ transition and should therefore show no Zeeman or magnetic rotation effects. Yet one finds that the red bands show more magnetic rotation lines than the blue-green and that the rotation in the red system must be greater since the lines can be obtained with weaker magnetic fields. The red rotation lines also differ from the blue-green in that they show no relation to the band origins.

EXPERIMENTAL RESULTS AND INTERPRETATION

The magnetic rotation spectrum was obtained by the same method as used by Wood with the exception that a long solenoid was substituted for the electromagnet. The entire spectral region from the *D* lines to λ8000A was photographed with a one meter grating in a Rowland mounting and the region from the *D* lines to λ7400A was photographed in the first order of a twenty-one foot grating in a similar mounting. Some two hundred lines were measured on the low dispersion plates while over eight hundred were measured on the high dispersion plates. The great increase in the number of lines on the latter is mainly due to fact that what appears as a single broad line at low dispersion shows up as a group of lines at high dispersion.

Fig. 1A shows the spectrum at high dispersion. The spectrum falls into two distinct sections.

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[1] R. W. Wood, Phil. Mag. **10**, 408 (1905); **12**, 499 (1906); Wood and Hackett, Astrophys. J. **30**, 339 (1909).

[2] F. W. Loomis, Phys. Rev. **31**, 323 (1928).

[3] Loomis and Nusbaum, Phys. Rev. **38**, 1447 (1931); **39**, 89 (1932).

[4] Serber, Phys. Rev. **41**, 489 (1932).

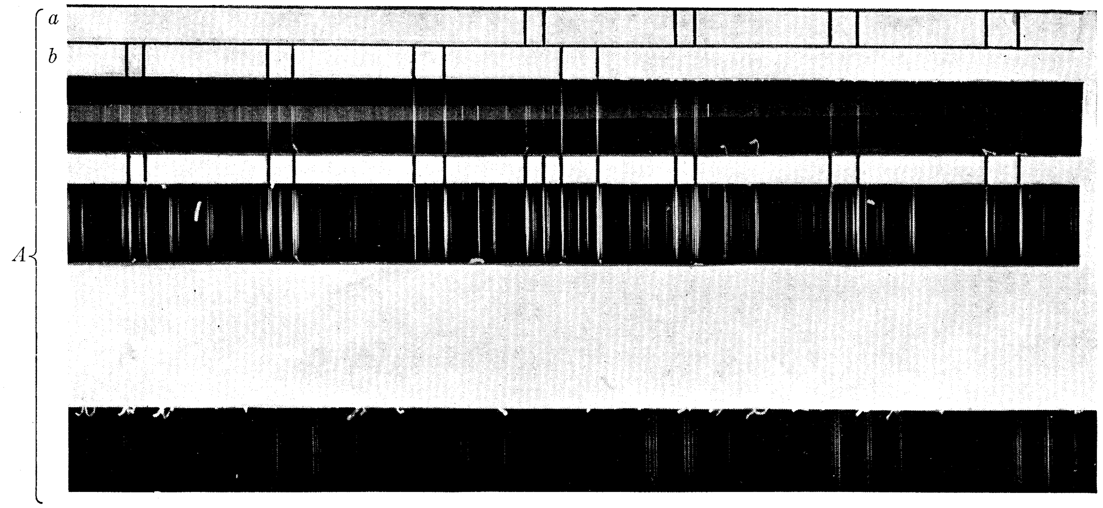

FIG. 1A. High dispersion magnetic rotation spectrum of sodium.

The first, typified by the middle strip, extends from the D lines to about 6800A and shows a large number of doublets. The second, designated by the bottom strip, shows groups of lines forming doublets. The top strip covers exactly the same region as the middle but the temperature of the absorbing vapor in this case is considerably less than for the middle strip. This top strip shows only two series of doublets, a and b, which increase in doublet separation as the series progresses to the red. Most of the high-wave number components of doublet show negative rotation (see Table I) while the other component shows positive rotation which, according to Serber,[4] should correspond to an R and P branch line, respectively.

The immediate interpretation of a doublet was that it consisted of an R and P line having a common upper K' level. Two interpretations of a series seemed possible. The first being that a series arises from transitions (in absorption) to a common upper vibrational state from lower vibrational states (i.e., doublets similar to those observed in fluorescence series). If such were the case the doublet spacing should decrease slowly as the series progressed to the red while it was observed that the spacing rapidly increased. The second interpretation was that since these doublets, shown on the top strip, appeared when the vapor was relatively cold they must all be due to transitions from low final vibrational states to various upper levels.

This latter interpretation could be tested in the following way: The doublet separation is $R(K''-1)-P(K''+1)$ and therefore can be equated to the expression for the final state combination. Thus,

$$\text{doublet separation}=\Delta_2F''=(4K''+2)B''+(8K''^3+12K''^2+12K''+4)D''.$$

Using the B's and D's obtained from the rotational analysis of the blue-green[5] and red[6] bands, we could calculate the value of K'' which is numerically the value of K' of the upper level

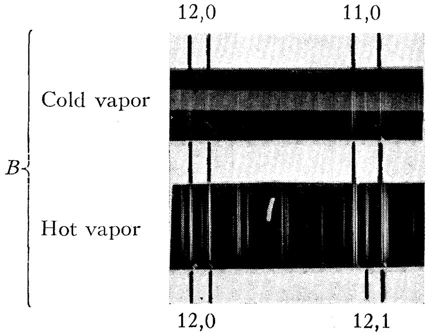

FIG. 1B. Part of Fig. 1A showing that the 12,1 band appears only on the hot vapor plate.

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

[6] Fredrickson, Phys. Rev. **34**, 207 (1929).

which is common to both members of a doublet. Then taking the P-branch component of a doublet together with the value of the B's and D's and increasing the K value by one since for the P-branch $K''=(K'+1)$, the origin of the band to which the doublet belonged could be calculated from the expression[7]

$$\nu_P=\nu_0-(B'+B'')K''+(B'-B''+D'-D'')K''^2 \\ -2(D'+D'')K''^3+(D'-D'')K''^4.$$

Since it is known that the R-branch turns at very low K values, the head of the band should be very close to the origin and thus the calculated origins should agree with the heads of the bands as measured in absorption.

In Table I are listed the nine doublets observed in the top strip of Fig. 1. The first column gives the wave numbers of the lines, the second the rotation observed by Wood, the third the doublet separation, the fourth the calculated upper K' level, the fifth the calculated origin of the band, and the sixth the observed absorption band. The agreement between the fifth and sixth columns is good,—only one doublet (No. 7) showing any disagreement. As seen from the last two columns, what appeared on the photographic plate as two separate series is really only one progression arising from a common vibrational state $v''=0$.

TABLE I. *Magnetic rotation doublets appearing on top strip of Fig. 1.* The sign of the rotation is taken from Wood and Hackett's paper, Astrophys. J. **30**, 339 (1909).

	Doublets	Rot.	Separation	K'	ν_0 (calc.)	ν_H (absorption)	Vibrational assignments old	Vibrational assignments new
1	14973.5		36.2	60	15121.3	15121.5	1,0	4,0
	14937.3	+						
2	15125.1	−	31.9	52	15236.7	15236.8	2,0	5,0
	15093.2	+						
3	15273.3	−	26.5	43	15348.8	15349.3	3,0	6,0
	15246.8	+						
4	15423.9	−	19.5	31	15461.1	15461.7	4,0	7,0
	15404.4	+						
5	15566.1	−	10.3	16	15574.1	15574.4	5,0	8,0
	15555.8	+						
6	15537.2	−	35.0	58	15684.9	15684.0	6,0	9,0
	15502.2	+						
7	15685.4	−	31.3	51	15798.6	15794.8	7,0	10,0
	15654.1	+						
8	15823.8	−	24.7	40	15902.8	15904.0	8,0	11,0
	15809.1	+						
9	15981.1	−	17.5	28	16013.0	16012.3	9,0	12,0
	15963.6	−						

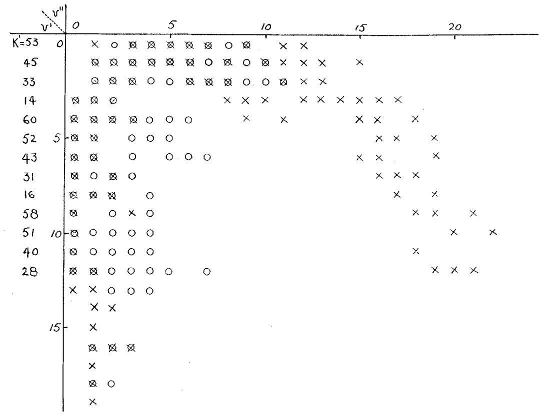

FIG. 2. Square array of vibrational analysis. Circles represent the magnetic rotation data, crosses the absorption data.

If this interpretation is correct, bands with final vibrational states other than zero should likewise show similar doublets. For example, if the rotational level $K=28$ in the upper vibrational state $v'=12$ gives rise to a doublet in the 12,0 band, it should also give rise to almost identical doublets in the (12,1) (12,2), etc., bands. There is evidence that these doublets do appear as indicated in Fig 1B. Here the 12,1 band appears quite clearly on the hot vapor plate while it can scarcely be detected on the cold vapor plate. The bands with v'' other than zero which have been identified are shown schematically in Fig. 2. Not many doublets are assigned to these bands but this failure of the bands to make their appearance is really what might be expected since the vibrational distribution follows a wide Condon parabola and, as seen from Fig. 2, one likewise finds only a few absorption bands.

In extending the interpretation to the region to the red of λ6800A one has difficulty because the lines appear in groups. By plotting the groups to a large scale it was observed that the lines in the various groups were somewhat similarly spaced. Taking a line representing a so-called center of gravity of a group, one obtains doublets whose doublet separation is practically constant and whose spacing between the successive doublets indicates that they belong to low v'' values. Following the procedure for the doublets mentioned above, the origins were cal-

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[7] Mulliken, Rev. Mod. Phys. **2**, 69 (1930).

TABLE II. *Magnetic rotation doublets and absorption band heads in the region beyond 6800A.*

v'	v''	Doublets	Separation	K'	ν_0 (calc.)	ν_H (absorption)	ν_H (calc.)	v'	v''	Doublets	Separation	K'	ν_0 (calc.)	ν_H (absorption)	ν_H (calc.)
0	1					14499.1	14501.2								
0	2	14241.5 14210.3	31.2	53	14342.8	———	14344.9	1	7	13638.6 13610.3	28.3	45	13701.5		13703.2
0	3	14088.6 14057.1	31.5	53	14187.0	14190.6	14190.1	1	8	13489.2 13461.3	27.9	45	13550.4	13556.2	13556.0
0	4	13938.8 13906.7	32.1	53	14034.2	14038.0	14036.8	2	1	14696.1 14675.7	20.4	33	14735.0	14734.7	14734.2
0	5	13789.7 13757.9	31.8	53	13882.9	13886.8	13885.1	2	2	14539.8 14519.6	20.2	33	14577.6	14575.9	14577.9
0	6	13642.2 13610.6	31.6	53	13732.6	13731.8	13734.8	2	3	14387.0 14366.3	20.7	33	14423.3	14421.2	14423.1
0	7	13496.2 13464.8	31.7	53	13584.3	13581.6	13586.2	2	4	14235.0 14214.8	20.2	33	14270.8	———	14269.8
0	8	13351.6 13320.0	31.6	53	13433.0	———	13439.0	2	5	14085.3 14065.3	20.0	33	14120.6	———	14118.1
0	9	13182.9 13211.0	31.9	53	13296.0	13292.4	13293.6	2	6	13933.6 13913.8	19.8	33	13968.0	13967.4	13967.8
1	1	14545.6 14517.6	28.0	45	14619.6	14618.0	14618.2	2	7	13786.2 13766.4	19.8	33	13819.6	13818.2	13819.2
1	2	14387.0 14359.1	27.9	45	14459.3	14461.6	14461.9	2	8	13636.6 13617.1	19.5	33	13669.2	13665.0	13672.2
1	3	14235.0 14207.0	28.0	45	14306.0	14308.7	14307.1	2	9	13492.5 13472.2	20.3	33	13523.3	———	13526.6
1	4	14085.2 14057.1	28.1	45	14153.5	14154.5	14153.8	3	0	15003.3 14994.4	8.9	14	15008.6	15006.7	15008.0
1	5	13933.6 13905.7	27.9	45	14000.4	14003.0	14002.1	3	1	14845.4 14836.2	9.2	14	14850.1	14850.4	14850.2
1	6	13781.6 13754.3	27.3	45	13847.0	13848.3	13851.8	3	2	14688.6 14679.1	9.4	14	14692.8	14691.9	14693.9

TABLE III. *Additional band heads from absorption plates.*

v'	v''	ν (obs.)	ν (calc.)	v'	v''	ν (obs.)	ν (calc.)	v'	v''	ν (obs.)	ν (calc.)
0	11	13008.3	13007.4	3	16	12670.3	12669.9	6	19	12619.4	12619.8
0	12	12864.7	12866.8	3	17	12534.3	12537.7	7	16	13123.2	13123.5
1	13	12846.2	12844.8	4	9	13760.0	13757.1	7	17	12993.1	12991.3
1	14	12706.4	12707.5	4	11	13473.2	13470.9	7	18	12861.6	12860.8
2	11	13239.1	13240.4	4	15	12918.5	12918.3	8	17	13101.5	13102.8
2	12	13098.6	13099.8	4	16	12783.5	12784.4	8	19	12842.3	12843.6
2	13	12960.2	12960.8	4	18	12522.3	12521.8	9	18	13087.5	13083.1
3	8	13787.6	13788.2	5	11	13585.1	13584.7	9	19	12960.2	12954.4
3	9	13641.5	13641.6	5	12	13442.6	13444.1	9	21	12706.4	12702.3
3	10	13499.4	13498.8	5	16	12899.3	12898.2	10	20	12942.3	12937.5
3	12	13214.2	13285.8	5	17	12764.8	12766.0	10	22	12693.7	12689.0
3	13	13076.2	13076.8	5	19	12507.2	12506.7	12	20	13156.1	13155.2
3	14	12942.3	12939.5	6	15	13145.4	13145.2	13	21	13140.8	13137.8
3	15	12802.9	12803.8	6	16	13008.3	13011.3	13	22	13017.2	13014.5

culated. These origins, however, corresponded to nothing in the known absorption vibrational analysis but agreed quite well with what the absorption heads would be if we increased the numbering of the initial state vibrational levels by three. These doublets are listed in a manner similar to the preceding table in Table II,—the vibrational assignments in the first two columns being the new assignments required to account for the magnetic rotation doublets.

VIBRATIONAL ANALYSIS

The suggested change in the vibrational assignments demanded a reinspection of the absorption bands. A change in the vibrational numbering was not altogether unexpected for it had been shown by Loomis[8] that the formula for the final state vibrational levels, which he was able to determine very accurately from the magnetic rotation data, of the blue-green bands, failed to represent the red bands in their reported position.[9]

The region beyond λ6800A was therefore rephotographed. The new measurements are listed in the next to the last column in Table II and in Table III. The band heads agree quite well with Loomis' formula for the final state and the entire system can be represented by the formula

$$\nu=14{,}680.4+117.6(v'+\tfrac{1}{2})-0.38(v'+\tfrac{1}{2})^2 -159.23(v''+\tfrac{1}{2})+0.726(v''+\tfrac{1}{2})^2 +0.0027(v''+\tfrac{1}{2})^3;$$

the last three terms are the recent values given by Loomis and Nusbaum[10] for the final state of the green bands. The last column in Table II represents the wave numbers of the bands as calculated from the above formula. The last three columns should agree in value and it is observed that the agreement is fairly good.

CONCLUSION

In Fig. 2 we have the usual square array for representing vibrational data. The circles represent the bands in which the origins could be calculated from the magnetic rotation doublets and the crosses represent the measured absorption heads. The magnetic rotation doublets have not been recorded beyond λ7400A because beyond that region we have only low dispersion plates and the magnetic rotation lines on these plates are very broad,—each line undoubtedly made up of many lines belonging to a number of bands.

At the left in Fig. 2 are listed the K' values of the various rotational levels of the various upper vibrational states which give rise to magnetic rotation doublets. It is interesting to see how the numbering seems to repeat itself at every fifth vibrational state.

That just these levels should be the ones which give rise to magnetic rotation doublets is strong evidence that these levels are perturbed. We have previously mentioned that the red bands, being a $^1\Sigma-{}^1\Sigma$ system, should show no magnetic rotation because there exists in neither state a magnetic moment along the internuclear axis. It has been considered possible, however, that the molecule may develop a magnetic moment at high rotational quantum numbers[11] because of the uncoupling of the orbital angular momentum, but if such were the case we would expect all high levels to cause rotation. The presence of only an isolated doublet in a band practically limits the interpretation to that of perturbation between the upper $^1\Sigma$ state and some state which has a magnetic moment.

We may speculate as to what that perturbing state might be. A $^3\Pi$ state is predicted to lie below the upper $^1\Sigma$ state[12] and recently Van Vleck[13] has shown that perturbations between such states are possible. If the $^3\Pi_1$ or $^3\Pi_2$ are the perturbing levels we could account for the magnetic rotation by the presence of the magnetic moment in these states. If the perturbing level is $^3\Pi_0$ we would expect no magnetic rotation unless the state had developed a magnetic moment at high rotation due to the uncoupling

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[8] Loomis, Phys. Rev. **31**, 328 (1928).

[9] Fredrickson and Watson, Phys. Rev. **30**, 431 (1927).

[10] Loomis and Nusbaum, Phys. Rev. **40**, 383 (1932).

[11] Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 260.

[12] Mulliken, Rev. Mod. Phys. **4**, 16 (1932).

[13] Van Vleck, presented at the Washington Meeting of the Am. Phys. Soc., April, 1933. Phys. Rev. **43**, 1047A (1933).

of the angular and spin momenta as in case *b* or in Paschen-Back effect. It is found that the observed doublets do have large K' values which is in agreement with the preceding requirement.

The fact that the K' value seems to repeat itself at every fifth state suggests that the perturbing state closely parallels the $^1\Sigma$ state and has very nearly the same r_e and ω_e values.

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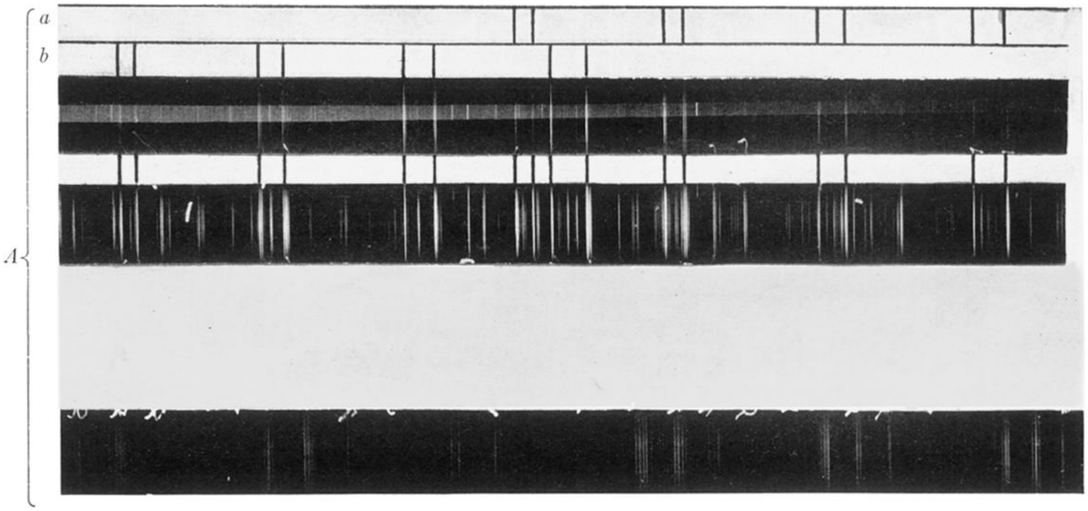

FIG. 1A. High dispersion magnetic rotation spectrum of sodium.

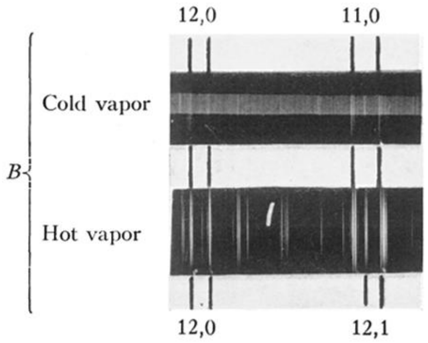

FIG. 1B. Part of Fig. 1A showing that the 12,1 band appears only on the hot vapor plate.