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THE MANY-LINED SPECTRUM OF SODIUM HYDRIDE

By E. H. Johnson

Abstract

A direct current arc was maintained between a water-cooled iron cathode and a sodium anode in a hydrogen atmosphere up to pressures of 3 or 4 cms. With potential differences from 20 to 30 volts, a many-lined spectrum was obtained in which several bands and branches have been identified in the region between λ3900 and λ5100. Computations involving the usual quantum assumptions have led to the determination of the following molecular magnitudes:—

λ4333 band

Initial state	Final state
$I'=3.59\times10^{-40}$ gm cm^2	$I''=5.10\times10^{-40}$ gm cm^2
$r_0'=1.51\times10^{-8}$ cms	$r_0''=1.80\times10^{-8}$ cms

λ4655 band

Initial state	Final state
$I'=3.20\times10^{-40}$ gm cm^2	$I''=4.06\times10^{-40}$ gm cm^2
$r_0'=1.42\times10^{-8}$ cms	$r_0''=1.60\times10^{-8}$ cms

Some deviations from current quantum formulas are pointed out.

THE object of the present work was to obtain an emission spectrum that could be ascribed definitely to a diatomic molecule consisting of one atom of sodium and one of hydrogen. Previous work with such hydrides indicated that the spectra to be expected would be of the complicated, many-lined type.[1]

In the course of the present investigation many new points of technique had to be developed. The usual difficulties in handling metallic sodium were far exceeded by those which had to be overcome in securing the critical combination of conditions essential to the production of the desired spectrum. If this precise state were not maintained, quite a different spectrum was produced, either alone or so as to be dominant and altogether troublesome. Extensive work with widely different methods of excitation, showed the necessity of employing a relatively high gas pressure and a low-energy electric discharge so as to encourage molecular combinations and avoid all dissociative effects.

The essential parts of the apparatus that proved most satisfactory are shown in Fig. 1. The arc chamber was made from a heavy three-liter Pyrex flask in which the arc itself was maintained between a water cooled iron cathode 11 mm in diameter, and an anode consisting of several grams of metallic sodium in a porcelain cup 1.5 cms in diameter. The

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[1] W. W. Watson has reported a many-lined spectrum due to a lithium hydride combination. See Abstract in Phys. Rev. **25**, 887 (1925).

hydrogen with which the arc was surrounded during operation, was the commercial product drawn from steel cylinders. In so far as possible, all water and oxygen were removed by passing the gas through a hot tube containing copper and copper oxide, then over phosphorus pentoxide. It then passed through a charcoal trap which could be cooled in liquid air, although careful tests showed this step to have little if any advantage. A Geissler tube (not shown in the diagram) was permanently attached to the apparatus and always showed a pure hydrogen spectrum when the gas had been prepared as described.

Although the optimum pressure for the production of the desired spectra was found to be between 2 and 4 cms, the system was evacuated before each exposure by means of a Cenco Hyvac pump and a one-stage mercury diffusion pump. Then, with fresh hydrogen, the pressure was raised to the desired value. A second trap in liquid air was introduced before the diffusion pump to prevent the passage of mercury vapor back to the arc chamber, if this became necessary.

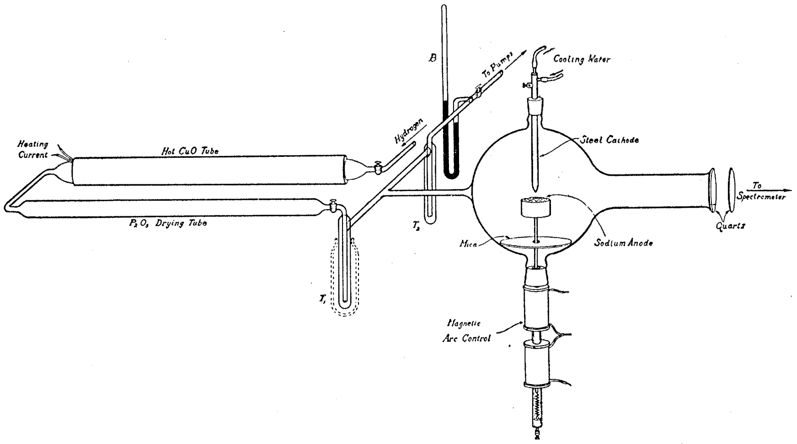

Fig. 1. General arrangement of apparatus.

The method developed for controlling the arc is shown in some detail in Fig. 2. Bartels[2] made similar adjustments by means of a hammer-shaped lever which passed out through a flexible joint in the wall of the evacuated chamber. Others have used ground joints or rods or screws passing through stuffed joints to manipulate one of the electrodes. In the present work, where the entire arc chamber was to be at fairly high temperatures during prolonged periods of time, it was found best to use a magnetic control wholly contained within the evacuated system. In-

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[2] Bartels, Zeits. f. Physik **25**, 378 (1924).

asmuch as this arrangement is adaptable to many kinds of vacuum arc work, a brief description will be given.

The glass tube G (Fig. 2) was sealed to the arc chamber so as to form a part of the same vacuum system. An inclosed brass rod D and a flexible wire W connected the porcelain anode cup A to the external binding post P. Two iron collars or lugs, F_1 and F_2, were firmly secured to this rod, and between them was placed a loose hollow iron cylinder E, to act as an armature in the fields of the magnet coils, M_1 and M_2. These were arranged in the circuit indicated at the left, so that by means of the reversing switch K, the armature could be jerked either upwards or downwards through a distance of a few millimeters. These two motions were equalized by the spring S_3, which was of sufficient strength to just support the armature freely at the mid-point of its range of action. The springs S_1 and S_2 were fitted into the glass tube with considerable friction and served to hold the moving system at any desired height. The striking force of the armature could be regulated by means of the rheostat R, so that the anode could be moved up or down by steps of several milli-

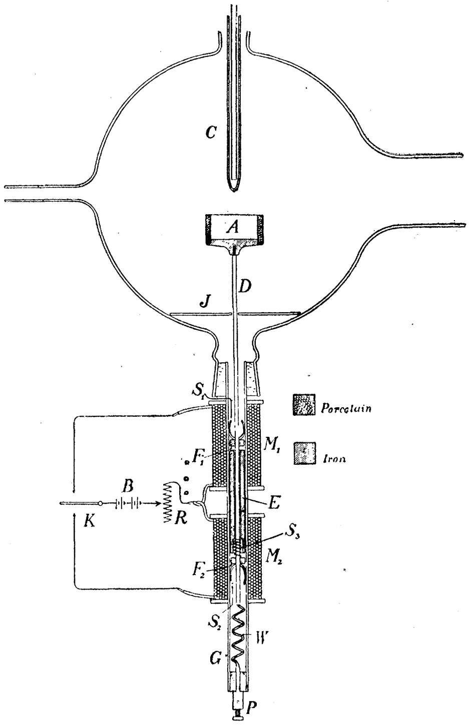


Fig. 2. Details of arc control.

meters each, or by amounts so small as to be scarcely perceptible. Its operation in this respect left nothing to be desired. The winding of the coils was merely determined by trial so as to give the best operation with the particular system built.

The construction of the iron cathode is clearly shown in Figs. 1 and 2. A central brass tube permitted the continual flow of cold water right at the tip of the electrode. With this construction not the slightest trace of the iron spectrum was ever found on any of the plates. In fact, *in all cases*, a layer of metallic sodium a millimeter or so in thickness formed over the end of this electrode soon after the arc was struck, so that *all of the exposures were made with an arc source between electrodes of metallic sodium only*. Hence, the spectrum was not altered when the arc polarity was reversed.

The alkali metals differ greatly in their behavior under arc conditions, each requiring a somewhat specialized technique. In operating the sodium arc of the type described, considerable care is necessary because of the sudden expansion of the sodium on approaching the boiling point, and the explosive violence of its initial boiling. However, it is possible to maintain a satisfactory performance throughout exposures of eight hours or more.

The operating potential difference was usually from 20 to 30 volts. All photographs were made through a quartz window. Satisfactory spectrum plates were obtained with a Hilger quartz spectrograph and a 5-foot concave grating giving a dispersion of 16.8A per mm in the first order. All computations were based on measurements of first order plates obtained with a 21-foot concave grating, the dispersion being about 2.6A per mm.

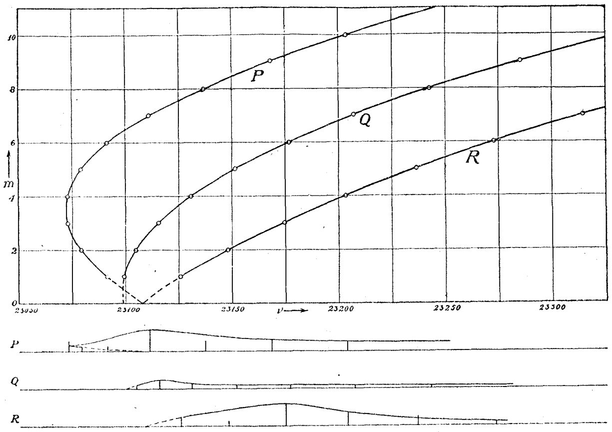
EXPERIMENTAL RESULTS

A first examination of the photographic plates shows little more than a multitude of fine lines, with no very apparent order. On the whole they are suggestive of the secondary spectrum of hydrogen. However, direct comparison with hydrogen plates of the same dispersion, shows the spectra to be entirely different.

In attempting to order these lines into series one meets with all of the difficulties usually ascribed to the analysis of many-lined spectra. Diffuseness from various causes renders the precise measurement of many of the lines well-nigh impossible. The large number of lines present on the plates makes it not improbable that some of the anomalous intensities recorded are due to the superposition of lines properly belonging to other systems on weak members of the branches being investigated.

A parallel case is mentioned by Sandeman[3] in discussing the difficulties in the analysis of the hydrogen secondary spectrum. Numerous attempts to improve the quality of the lines by altering the source conditions, such as current and pressure, were fruitless. Neither was there any appreciable increase in the sharpness of the lines when the grating slit was set at the smallest width practicable and the time of exposure greatly increased.[4]

In the tables of data and in the computations, vacuum frequencies have been employed, the necessary corrections having been made by means of the tables published by the Bureau of Standards.[5] The wave-lengths are given in air values.



λ 4333 Band

Fig. 3.

In ordering the lines into P, Q and R branches, the combination principle has been employed, as indicated in the following symbolic form:

$$R(m)-Q(m+1)=Q(m)-P(m+1).$$

The intensities of the lines were estimated visually when the plates were being measured. In the accompanying graphs (Figs. 3 and 4) it will be seen that the intensity curves follow the individual line intensities with few exceptions. In general they are of the form obtained by Richardson and Tanaka[6] for the hydrogen secondary bands. With the exception of one rather doubtful portion of a branch, *all of these bands degrade*

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[3] Sandeman, Proc. Roy. Soc. Lond. **A110,** 326 (1926).

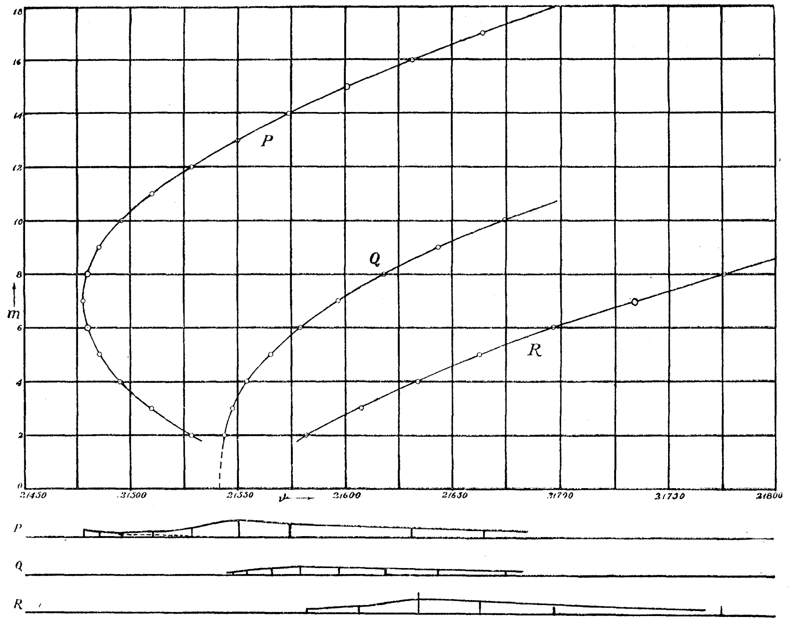
[4] Eriksson and Hulthèn mention a similar diffuseness of the lines in the AlO bands. See Zeits. f. Physik **34,** 785 (1925).

[5] Sci. Papers, 327 (1918). Also Bur. of Stan. Bull. **14,** p. 731.

[6] Richardson and Tanaka, Proc. Roy. Soc. Lond. **A106,** 663 (1924).

towards the violet. This is of special interest since Stücklen[7] practically implied that the bands of all of the metals and metal hydrides in the first group of the periodic table degrade towards the red.

Frequently it has been stated that in emission bands consisting of P, Q and R branches, the P branch is stronger than the R branch. Dieke[8] and others have brought forth a certain amount of theoretical argument for such a rule. However, as Eriksson and Hulthèn[9] have pointed out, experimental evidence does not justify such a generalization. It seems that the P branch may be much less intense than the Q or R branch, or again, all three may be of about the same intensity. This departure from the "rule" is quite in keeping with the results obtained in the present investigation. The intensity distribution curves show approximately the same average intensity in the P and R branches, a fact which increases the difficulties in the analysis. In these bands, degrading as they all do, towards the shorter wave-lengths, the intensity maximum in a P branch is nearer the head than is that of the associated R branch. In the cases analyzed, the Q branches are by far the weakest of the three.



λ 4655 Band

Fig. 4.

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[7] Stücklen, Zeits. f. Physik **34,** 562 (1925).

[8] Dieke, Zeits. f. Physik **33,** 161 (1925).

[9] Eriksson and Hulthèn, Zeits. f. Physik **34,** 775 (1925). "Uber die Bandenspektra von Aluminium," see footnote, p. 777.

There was no evidence of a continuous spectrum on any of the plates, and no reversed lines.

In Tables IV, V, IX and X, giving the initial and final terms, parentheses have been placed around values in the columns of "means" in all cases where the numbers could be obtained from one quantity only. The gap responsible for this is evident in one of the two preceding columns. In some instances these are due to the absence of a line in the body of the branch, as will be seen by reference to the corresponding tables giving the wave-lengths and frequencies.

TABLE I

λ4333 Band. P Branch.

		λ		Differences	
m	Intensity	(cms $\times 10^8$)	$\nu = 1/\lambda$	1st	2nd
2	000	4332.909	23079.18		
				− 6.26	
3	1	4332.870	23072.92		−6.26
				0	
4	1	4332.870	23072.92		6.26
				6.26	
5	000	4332.909	23079.18		6.03
				12.29	
6	000	4329.389	23091.47		7.29
				19.58	
7	2	4325.721	23111.05		6.34
				25.92	
8	1	4320.876	23136.97		5.28
				31.20	
9	1	4315.056	23168.17		4.34
				35.57	
10	1	4308.442	23203.74		

TABLE II

λ4333 Band. Q Branch.

		λ		Differences	
m	Intensity	(cms $\times 10^8$)	$\nu = 1/\lambda$	1st	2nd
1	000	4329.107	23099.45		
				5.51	
2	000	4328.075	23104.96		5.08
				10.59	
3	00*	4324.880	23115.55		4.78
				15.37	
4	000	4323.217	23130.92		5.33
				20.70	
5	000*	4318.142	23151.62		4.45
				25.15	
6	000	4314.665	23176.77		5.37
				30.52	
7	000	4308.990	23207.29		5.10
				35.62	
8	000	4302.387	23242.91		6.81
				42.43	
9	1	4294.547	23285.34		5.70
				48.13	
10	00	4284.487	23333.47		

*Double

TABLE III

λ4333 Band. R Branch.

m	Intensity	λ (cms×10^8)	$\nu=1/\lambda$	Differences 1st	Differences 2nd
1	1	4322.957	23125.83		
				22.14	
2	000	4320.033	23147.97		4.56
				26.70	
3	2*	4313.846	23174.67		2.37
				29.07	
4	1	4308.442	23203.74		3.97
				33.04	
5	1	4302.316	23236.78		3.20
				36.24	
6	000	4296.820	23273.02		5.62
				41.86	
7	1	4287.904	23314.88		

*Double

TABLE IV

λ4333 Band. Initial terms.

$\Delta F'=R(m)-Q(m)=Q(m+1)-P(m+1)$

m	$R(m)-Q(m)$	$Q(m+1)-P(m+1)$	$\Delta F'(m)$ (mean)
1	26.38	25.78	26.08
2	43.01	42.63	42.82
3	59.12	58.00	58.56
4	72.82	72.44	72.63
5	85.16	85.30	85.23
6	96.25	96.24	96.24
7	107.59	105.94	106.76
8	———	117.17	(117.17)
9	———	129.73	(129.73)

TABLE V

λ4333 Band. Final terms.

$\Delta F''(m)=R(m)-Q(m+1)=Q(m)-P(m+1)$

m	$R(m)-Q(m+1)$	$Q(m)-P(m+1)$	$\Delta F''(m)$ (mean)
1	20.87	20.27	20.57
2	32.42	32.04	32.23
3	43.75	42.63	43.19
4	52.12	51.74	51.93
5	60.01	60.15	60.08
6	65.73	65.72	65.73
7	71.97	70.32	71.14
8	———	74.74	(74.74)
9	———	81.60	(81.60)

TABLE VI

λ4655 Band. P Branch.

m	Intensity	λ (cms×10^8)	$\nu=1/\lambda$	Differences 1st	Differences 2nd
2	1	4643.804	21528.06		
				18.28	
3	00	4647.750	21509.78		3.45
				14.83	
4	000	4652.255	21494.95		5.32
				9.51	
5	000	4653.016	21485.44		——
				——	
6	——	———	———		——
				——	
7	1	4656.031	21477.52		——
				——	
8	——	———	———		——

TABLE VI—Continued

λ4655 Band. P Branch.

m	Intensity	λ (cms × 10^8)	$\nu = 1/\lambda$	Differences 1st	Differences 2nd
9	000	4654.399	21485.05		——
				10.91	
10	00	4652.036	21495.96		2.91
				13.82	
11	00	4647.750	21509.78		4.46
				18.28	
12	1	4643.804	21528.06		3.50
				21.78	
13	3	4639.110	21549.84		2.03
				23.81	
14	2	4633.989	21573.65		(3.05)
				(26.86)	
15	—	———	(21600.51)#		(3.05)
				(29.91)	
16	2	4621.692	21631.05		(3.05)
				32.96	
17	1	4614.661	21664.01		

#Interpolated values.

TABLE VII

λ4655 Band. Q Branch.

m	Intensity	λ (cms × 10^8)	$\nu = 1/\lambda$	Differences 1st	Differences 2nd
2	000	4641.702	21543.82		
				3.53	
3	000	4639.646	21547.35		3.12
				6.65	
4	00	4638.214	21554.00		4.59
				11.24	
5	000	4637.091	21565.24		2.58
				13.82	
6	0	4632.828	21579.06		3.78
				17.60	
7	00	4629.052	21596.66		3.66
				21.26	
8	00	4624.500	21617.92		3.94
				25.20	
9	00	4619.115	21643.12		5.77
				30.97	
10	00	4612.514	21674.09		

TABLE VIII

λ4655 Band. R Branch.

m	Intensity	λ (cms × 10^8)	$\nu = 1/\lambda$	Differences 1st	Differences 2nd
2	000	4632.251	21581.75		
				25.72	
3	000	4626.737	21607.47		0.69
				26.41	
4	2	4621.088	21633.88		2.24
				28.65	
5	1	4614.977	21662.53		5.79
				34.44	
6	000	4607.651	21696.97		
7	———	———	———		
8	0	4590.921	21776.04		

TABLE IX

λ4655 Band. Initial terms.

$\Delta F' = R(m) - Q(m) = Q(m+1) - P(m+1)$

m	$R(m)$ $-Q(m)$	$Q(m+1)-$ $P(m+1)$	$\Delta F'(m)$ (mean)
1	———	15.76	(15.76)
2	37.93	37.57	37.75
3	60.12	59.05	59.59
4	77.00	79.80	78.40
5	97.29	———	(97.29)
6	117.91	119.14	118.53
7	———	———	———
8	158.12	158.07	158.10
9	———	178.13	(178.13)
10	———	194.67	(194.67)

TABLE X

λ4655 Band. Final terms.

$\Delta F''(m) = R(m) - Q(m+1) = Q(m) - P(m+1)$

m	$R(m)-$ $Q(m+1)$	$Q(m)-$ $P(m+1)$	$\Delta F''(m)$ (mean)
2	34.40	34.04	34.22
3	53.47	52.40	52.94
4	68.64	68.56	68.60
5	83.47	———	(83.47)
6	100.31	101.54	100.93
7	———	———	———
8	———	132.87	(132.87)
9	———	147.16	(147.16)
10	———	164.31	(164.31)
11	———	177.36	(177.36)

The work of Kratzer,[10] and Kramers and Pauli[11] has resulted in the following general expression:

$$\Delta_1 F(j) = 2B(j+\tfrac{1}{2}\mp\epsilon) \mp \frac{B\epsilon\sigma^2}{j(j+1)} + \cdots,$$

where j is the total angular momentum; σ is the component of the angular momentum of the electron normal to the vector angular momentum of the nuclei; ϵ is the component of the same vector parallel to the vector angular momentum of the nuclei.

The marked weakness of the Q branches in the bands analyzed in the present work suggests the application of this equation, using the lower (+) signs. By the assignment of probable j values (putting $j=m+s(\frac{1}{2})$, where s may have the values 0, ± 1, ± 2, etc.) and solving simultaneously the several similar expressions thus obtained so as to get the values of ϵ and σ, it is possible to draw some conclusion as to the general validity of the equation.

The restrictions prescribed by the theory in its present state are that while ϵ and σ may both have irrational values, ϵ should be of the order of $k/2$ (where k has the values 0, 1, 2, 3, etc.), and that σ should be unity or very small. Having made the substitutions thus required, we obtain initial and final values for $2B$.

Now,

$$2B = h/4\pi^2 Ic,$$

whence the moment of inertia is given by

$$I = h/8\pi^2 cB$$

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[10] Kratzer, Naturwiss. **27**, 577 (1923).

[11] Kramers and Pauli, Zeits. f. Physik **13**, 351 (1923).

If we now assume that the body having this moment of inertia is a simple dipolar molecule, consisting of one atom of hydrogen and one atom of sodium, rotating about their common center of gravity, we can obtain the nuclear separation r_0 in the existing state. The values found in the above manner for the bands λ4333 and λ4655 are presented in Table XI.

TABLE XI

Molecular constants of sodium hydride

Initial state	Final state
λ 4333 Band	
$j=m$	$j=m$
$B'=7.70$	$B''=5.42$
$\epsilon'=0.325$	$\epsilon''=0.496$
$\sigma'^2=(-)0.156$	$\sigma''^2=(-)0.82$
$I'=3.59\times10^{-40}$ gm cm^2	$I''=5.10\times10^{-40}$ gm cm^2
$r_0'=1.51\times10^{-8}$ cms	$r_0''=1.80\times10^{-8}$ cms
λ 4655 Band	
$j=m-\frac{1}{2}$	$j=m$
$B'=8.64$	$B''=6.81$
$\epsilon'=0.645$	$\epsilon''=0.76$
$\sigma'^2=(-)5.37$	$\sigma''^2=(-)11.8$
$I'=3.20\times10^{-40}$ gm cm^2	$I''=4.06\times10^{-40}$ gm cm^2
$r_0'=1.42\times10^{-8}$ cms	$r_0''=1.60\times10^{-8}$ cms

CONCLUSION

From these values of I and r_0 we are justified in concluding that the carrier of these bands is actually the NaH dipole. They are entirely in accord with the trend of values found for other metal hydride molecules in the first part of the periodic table, which has been pointed out by Watson.[12]

These results have several other significant features. The j-values employed were retained as the most suitable ones after numerous computations with other values differing by half-integral steps. The values of ϵ are of the required order of $k/2$, where $k=1$, in the present cases. However, the values obtained for σ, which is the component of the angular momentum of the electron normal to the vector angular momentum of the nuclei, raise new questions. The general equation was developed with the signs $\mp$ before the σ term, but the nature of this quantity (σ) requires the use of the positive sign if ϵ is to be positive, and this procedure, in the present work, leads to imaginary values of σ. It would seem that some modification of the general theory is necessary if it is to lead to an expression that can be applied closely to bands of the type investigated here. The same difficulty has been pointed out by Mecke.[13]

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[12] Washington Meeting, Amer. Phys. Soc., Apr. 24, 1925. See Abstract No. 24, Phys. Rev. **25,** 887 (1925).

[13] Mecke, Zeits. f. Physik **36,** 795 (1926).

In addition to the bands here described, a number of other branches have been traced out for appreciable distances. All agree in general character. There is considerable evidence that several of these bands are members of the same system. A further paper will deal with these extended series relations.

The writer wishes to express his appreciation to Dr. W. W. Watson at whose suggestion and under whose guidance the investigation covered in part in the present paper was carried out. Very excellent plates of the secondary spectrum of hydrogen for comparisons were continually available through the kindness of Dr. K. O. Lee. The author also wants to record his thanks to Professors Gale and Lemon for various suggestions.

Ryerson Physical Laboratory,
University of Chicago.
June 2, 1926.