THE INFRA-RED RADIATION OF HYDROGEN

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ABSTRACT

Measurement of higher members of Paschen series.—The atomic spectrum of H was investigated in the infra-red region by the photographic method. Neocyanin plates, hypersensitized by an ammonia bath, were used. A powerful discharge tube, maintained in the so-called black stage by careful adjustments, yielded under long exposures six higher members of the Paschen series, the third to the eighth inclusive. The measured wave-lengths agree with the values calculated from the Bohr theory to within the limits of experimental error.

Extension of infra-red secondary spectrum of hydrogen.—By changing the conditions of the discharge a strong molecular spectrum of H was produced. This was photographed in the region from 7500 to 10700A under a dispersion of 9A per mm. The wave-lengths of about 425 lines, mostly new, were measured and are given in tables. A number of these lines seem to be members of band groups analogous to the Paschen series of the elementary spectrum.

INTRODUCTION

IN VIEW of the fundamental and unique position held by hydrogen in the entire scheme of the elements, and of the important rôle it plays in every theory of atomic or molecular structure, there has always been a special interest in its spectrum. Despite this, the work done in the infra-red portion of this spectrum has been rather meagre. Paschen,[1] in 1908, discovered the first two lines of the third series of the elementary spectrum. Two members of a fourth series were discovered by Brackett[2] in 1922, and the initial member of a fifth series by Pfund[3] in 1924. Brackett also identified three further lines of the Paschen series,[1] but his apparatus—he worked with a thermocouple and prism—did not enable him to determine their wave-length to within less than 100A. At the same time a number of other maxima occurred in the same region of the hydrogen radiation curve, giving evidence of a fairly complicated spectrum. Of the secondary spectrum, some eighty lines between 6900 and 8029A have been published by Croze.[4] Since a good portion of the spectrum beyond this, including the region occupied by any members of the Paschen series that might be present, is accessible by the method of photography, it was thought worth while to investigate the region by this method. A similar investigation of the secondary spectrum was carried on by Allibone at the same time as the earlier work to be described, and a table of wavelengths far more comprehensive and accurate than Croze's, and including

[1] Paschen, Ann. d. Physik **27**, 537 (1908).
[2] Brackett, Astrophys. J. **56**, 158 (1923).
[3] Pfund, Jour. Opt. Soc. Amer. **9**, 106 (1924).
[4] Croze, Ann. d. Physique **1**, 48 (1914).

about twenty of the strongest lines beyond 8000A, has recently been published by him.[5]

I. The Elementary Spectrum of Hydrogen

Apparatus. The hydrogen tube was of the shape of an inverted and angular U, somewhat over two meters in length, of 14 mm bore, but widening out at the ends to about 4 cm in order to accommodate rather large cylindrical electrodes 15 cm long and 2 cm in diameter. Usually a smaller tube of about 10 mm bore was inserted in the central cross-piece of the tube to concentrate the discharge still more.

Hydrogen was fed into the tube by a fine capillary near one electrode, and the exhaustion was carried on continuously by a Hyvac pump. By careful adjustment of the capillary and the rate of exhaustion, the precise balance could be maintained to give a maximum of radiation of the type desired.

Excitation of the tube was effected by alternating current from a 6900 volt, 5 kilowatt transformer operating on a 110 volt, 60 cycle primary circuit, and the voltage regulation was by means of a rheostat in the primary.

The dispersion was produced by means of a 3.5 by 3 inch plane grating having 15,000 lines to the inch. It provided, together with the mirror to be described, a dispersion of approximately 18A to the mm. Since higher dispersion must be at the expense of intensity, it appeared best, with a source as weak as our discharge tube and the low sensitivity of the infra-red plates, to sacrifice higher dispersion and resolution that the intensity might be kept sufficient.

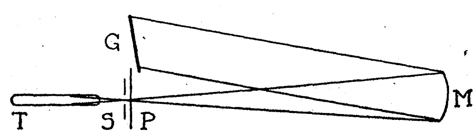


Fig. 1. Plan of apparatus.

The arrangement of the apparatus is clear from Fig. 1. Light was taken end-on from the central portion of the discharge tube. First filtered through a piece of Jena red glass to prevent the overlapping of a second order spectrum, it passed through the slit S to the concave mirror M, and was reflected as a parallel beam to the grating G. The diffracted beam was returned by the mirror to the plate P set directly beneath the slit. The mirror was of 90 cm focal length and 10 cm aperture. Slit, grating, mirror and plate were all solidly attached to a single I-beam and the whole was enclosed in a light-tight box. Since long exposures were necessary, a thermostat and heating coils were introduced to maintain the temperature constant to within about 0.1°C.

Method. To excite the elementary spectrum, and therefore the Paschen series, the tube was brought by the adjustment of pressure and current density to the so-called "black" stage.[6] The dark space about the electrodes

[5] Allibone, Proc. Roy. Soc. **A112**, 196 (1926).
[6] Wood, Phil. Mag. **42**, 729 (1921).

was about 5 mm, and striations disappeared entirely except for two or three in the wide part of the tube immediately above the electrodes. The secondary spectrum was in evidence only in the same region near the electrodes. The spectrum of the rest of the tube, as seen through a direct vision spectroscope, consisted almost entirely of the pure Balmer lines. For this condition the current through the tube was usually maintained at close to half an ampere. The presence of water vapor seems to be absolutely essential for the elimination of secondary spectrum; other impurities seem rather to enhance it.

The plates used for the photographs were the recently developed neocyanin sensitized plates prepared by the Eastman Company. These were hypersensitized immediately before use by bathing them for about a minute in an ammonia solution at about 10°C and drying rapidly in a blast of warm air. A solution of about 8 to 10 cc ammonia (28 percent) to 100 cc of water seemed to give greatest sensitivity without causing noticeable fog. Rapid drying, however, is the most essential requisite for the sensitizing action. These plates have recorded the 11288 mercury line,[7] and dicyanin, too, has repeatedly brought out lines up to 11,000A under long exposure,[8] but in all these cases far more powerful sources of light like the mercury lamp and various metallic arcs were used.

While the performance of the plates, in general, was good, and quite regularly reliable up to the region of about 9000A, it was found that some of the plates were certainly more sensitive than others of the same batch. Such plates under proper treatment could be made to register lines over 10,000A if moderately strong—with a small prism spectrograph we have brought out the nitrogen bands at 1.04μ in 8-minute exposures—whereas repeated attempts with other plates treated by the same process and used under even more favorable conditions failed to reproduce similar results. It is probable that differences in the rate of drying after the original staining process may account for such differences.

For the comparison spectrum an iron arc was used whose light was focussed on the slit from the side by means of a lens and a right angled prism. In addition to this the second order lines of the secondary spectrum were sometimes introduced by the removal of the filter and the introduction of the proper diaphragm before the slit. As a check on the constancy of temperature during the exposure, a comparison spectrum was made before and after the hydrogen exposure.

The plates were measured on the large and excellent dividing engine of the University. The pitch of the screw is 1 mm and the head has a diameter of about 25 cm and its circumference is divided into 1000 parts, so that one division of the head moves the carriage one micron along the axis of the screw. This corresponds in the present case to about 0.018A. Second order standard iron lines were chosen at intervals of about 5 to 10 mm, the plate scale was determined for these intervals, and the wave-lengths were calculated on the basis of this scale from the engine readings.

[7] Dundon, Schoen and Briggs, Jour. Opt. Soc. Amer. **12**, 397 (1926).
[8] See, for example, Bull. Bur. Stds. **17**, 637 (1922).

Results. The effort to record some of the higher members of the Paschen series resulted in finding the third to the eighth inclusive. The lines are exceedingly faint, even despite the unusual length of exposure and the widening of the slit to about 0.2 mm. This precludes the satisfactory representation of them in a half-tone, but they are unmistakable. The first three of these, the third to the fifth of the series, are quite removed from the stronger portion of the molecular spectrum. Beyond the eighth member the secondary spectrum is already so complex that it would be hard to recognize lines as weak as these higher members of the series would naturally be.

A number of photographs were taken with a small Hilger constant deviation spectroscope receiving its light from the other end of the central section of the discharge tube. Since the instrument was not intended for photographic work only a small portion of the spectrum could conveniently be brought into focus. Fig. 2 (magnification, 3×) shows $P\gamma$ unmistakably. The heavy lines are oxygen 7774, 8446, and 9265. This exposure lasted 60 hours, though $P\gamma$ registered in as low as 15 hours with sharper focus.

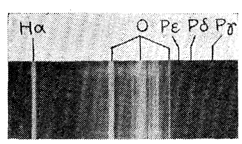


Fig. 2.

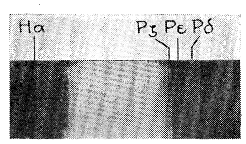


Fig. 3.

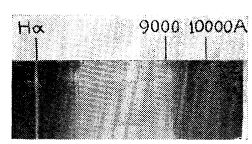
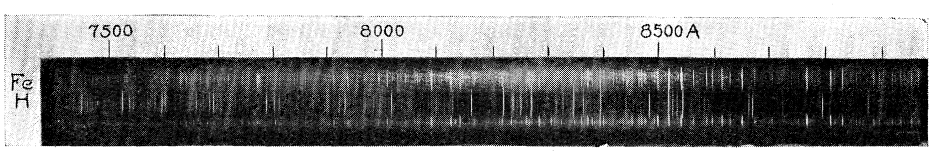


Fig. 4.



Figs. 2 and 3. Hydrogen, Paschen lines (magnification, 3x).
Fig. 4. Hydrogen secondary spectrum.
Fig. 5. Infra-red secondary spectrum of hydrogen.

Fig. 3 is the result of a 21 hour exposure. The more pronounced secondary and less strong oxygen lines are simply due to the fact that the plate was taken under a completely different set of conditions. The detail in the negative of the central portion of the spectrum was sacrificed in printing to bring out the fainter lines. The region of the visible was absorbed by a deep red filter. Removal of this filter for a few seconds showed the Hα line, quite out of focus but much stronger than the Paschen lines. Now the neocyanin plates are particularly *insensitive* in the region of Hα; still the time of exposure for Hα on this plate was of the order of 1/10,000 of that used to obtain the Paschen lines. One questions the propriety of speaking of such plates as being *sensitive* out to the region of 10,000A.

The Paschen lines, of course, are produced according to the Bohr theory by the falling of an electron into the third stable orbit from higher orbits. Hence their wave-lengths are predicted by the theory from the formula:

$1/\lambda = 109{,}677.7(1/3^2 - 1/n^2)$. For the lines recorded on the plates, $n=6$, 7, 8, 9, 10, 11. Errors of measurement in this region might easily be as large as 1A due to the faintness of the lines and the width of the slit used. As may be seen from Table I, the observed values agree to within this limit with the

TABLE I

Observed and calculated values of the Paschen lines of hydrogen.

Line	λ Observed in Air (I. A.)	Calculated Value
$P\alpha$	18751.3 (Paschen)	18751.4
$P\beta$	12817.6 (")	12818.3
$P\gamma$	not measured (Brackett 1.09μ)	10938.2
$P\delta$	10049.8	10049.5
$P\epsilon$	9546.2	9546.0
$P\zeta$	9229.7	9229.1
$P\eta$	9015.3	9014.9
$P\theta$	8863.4	8862.9

calculated. The lines are averaged from a half-dozen plates. The lines originally discovered by Paschen are included in the table for the sake of the completeness of the series.

II. THE SECONDARY SPECTRUM OF HYDROGEN

It was evident from the work described in Part I that there was a strong secondary hydrogen spectrum in the region from 7000 to 9000A on which practically nothing had been published. Accordingly this spectrum was also photographed with the apparatus already described. It was found that with exposures of from 12 to 15 hours with a slit as narrow as 0.1 mm or less, about 350 lines could be measured between 7250 and 9300A.[9] This suggested that the investigation be made under higher dispersion so that higher accuracy might be obtained, since errors in this preliminary work might have amounted to 0.5A.

Apparatus and Method. An entirely new spectrograph was built up, very similar to that already described in Part I. For greater convenience the slit was mounted to the side and the entering beam was reflected by a silvered interferometer plate to the concave mirror at the other end of the *I*-beam. This was of 6 ft focal length and of 5 inch aperture. The 7 inch plane grating used was ruled with 15,000 lines to the inch and had a strong second order for the visible. The combination supplied a dispersion of about 9A per mm. The whole spectrograph was made perfectly light-tight and well insulated, and a thermostat and heating coils maintained the temperature constant to within 0.1°C.

The discharge tube was made of Pyrex; this eliminated the minute punctures which had caused frequent trouble in the previous work. For part of the work, in order to enhance the secondary spectrum, a second Pyrex tube, 40 cm long and 13 mm bore, lined with small aluminum cylinders was inserted in the central section of the tube and the radiation taken end-on through its

[9] Poetker, Nature **119,** 123 (1927).

center. The most important factor for producing a strong secondary is the thorough elimination of water vapor. Hence the hydrogen was passed through tubes of phosphorous pentoxide as it was fed continuously from a H_2SO_4 electrolytic generator. The pressure was kept considerably higher than for the atomic spectrum. Applied potentials were somewhat over 2000 volts and the currents through the tube ranged from 1/3 to 2/3 amperes. Striated discharge would occupy the entire tube and the elementary spectrum would shade into insignificance.

A comparison spectrum was provided by the second order lines of a Pfund[10] iron arc. It was registered above and below the hydrogen by means of the usual occulting shutter. The arc with the lens used to focus it on the slit was, after alignment, kept permanently in its position. By means of a screw arrangement the tube with its mounting and appurtenances could be lowered and returned to position without any change of orientation, the leads to pump, hydrogen supply, etc., being made flexible. This enabled the initial alignment of the system to be maintained indefinitely. The iron comparison spectrum was taken before and after, but no shifts due to change of temperature or alignment could be detected between them.

Exposures averaged 20 hours for the range below 8900A and 40 hours for the range beyond. The slit widths used were about 0.04 and 0.1 mm respectively. One exposure of 3.5 days was tried with a slit of 0.25 mm but the whole plate became rather fogged. Success depends far more on optimum sensitizing than on mere length of exposure. Deep red filters which had been tested previously were used for the elimination of the second order spectrum.

Results. The plates revealed some 425 lines between 7500 and 10700A. Over 350 of these are below 8900A. These are reproduced from a typical plate in Fig. 5. It is roughly at 8900A that the sensitivity of the neocyanin plates drops off very rapidly. Still it is evident from comparison with work in other spectra that the secondary hydrogen radiation becomes noticeably weaker in the same vicinity. Under low dispersion with the small Hilger spectroscope traces of lines could be followed as far as 1.15μ (Fig. 4). Though no attempt was made to measure wave-lengths by these small spectrograms because of the low dispersion, they provided a convenient preliminary exploration of the remoter field. Besides, they afford about the only possibility of registering the higher lines with sufficient intensity to have them brought out in a reproduction. Using the Paschen lines for reference, the correspondence between these plates and those of higher dispersion was perfectly evident—additional proof that the absorbing filters were trustworthy.

For comparison standards the international secondary iron standards were supplemented by many of the interferometer measurements of Burns, Meggers and Merrill.[11] These standards were selected at intervals of 20 to 40A and were measured with the hydrogen lines on the comparator. From an initial and final standard the average dispersion or the plate constant was

[10] Pfund, Astrophys. J. **27**, 296 (1908).

[11] Burns, Meggers and Merrill, Bull. Bur. Stds. **13**, 245 (1916).

calculated for the whole plate. Since the spectrum is not entirely normal a large-scale correction curve was then drawn from the known values of the frequent standards on coordinate paper, from which the necessary correction for the hydrogen lines could easily be read off.

The values given in Table II up to 8900 are calculated from the measurements of three plates, each of which was measured twice. Above 8900A about six plates were used varying somewhat in range, slit-width, and success of registration. The general rule was followed not to include lines in the table which could not be measured at least on two plates. This meant the dropping of some fifty lines and quite a few more which were doubtful. Several of the strongest lines were examined for ghosts, but since none was detected we think the lines included in the table are real.

One of the somewhat inferior plates showed some additional lines the origin of which is unknown. Their wave-lengths were measured as: 8694.57, 8693.80, 8680.27, 8679.50, 8668.36, (wave-numbers, 11498.28, 11499.30, 11517.22, 11518.24, 11533.04). It is suspected that they are due to impurities, that the exposure was begun before the tube had been sufficiently washed out by the stream of hydrogen, since the oxygen 8446 and the sodium doublet 8194, 8183 were also visible. We know of no impurity lines on the other plates.

The wave-lengths up to 8900A are thought to be accurate, in general, to within 0.03 or 0.04A. While the agreement between different plates for many of the lines was closer than this, it also was not always attained, especially in the case of very faint or diffuse lines which were rather difficult to measure with the high power eye-piece in the comparator telescope. In such cases the error might amount to 0.1A. A number of lines where the disagreement was most noticeable have been marked with an asterisk. Even assuming no defects in the plates themselves due to unequal drying or the like, the several sources of error in the measurement itself hardly justify higher expectations.[12]

Beyond the limit of the lower range plates the possible error increases even more. Hence above 9000A the wave-lengths are given only to tenths of an angstrom, and the error may approach 1A. This error was unavoidable and due to a variety of causes, the widening of the slit (in some cases to 0.2mm) and consequent fusion of standards with neighboring lines, the extreme faintness of most of the lines, occasionally bad fogging or streaks. For the measurement of these plates a low power eye-piece was usually put on the comparator telescope, which of itself likewise lowered the accuracy of measurement though necessary to find the fainter lines with certainty. But even this reduced accuracy is certainly much higher than could be obtained by a prism instrument or by the ordinary radiometric methods.

The wave-lengths in air and the wave-numbers in vacuo are given in Table II for the region measured. The wave-numbers were calculated by means of Kayser's tables which at the same time reduce to vacuum values. For the wave-lengths beyond 10,000A the correction for the refraction of air was

[12] See Kayser, Hauptlinien der Linienspektra, Preface, p. IV.

Table II

Wave-lengths and wave-numbers of the infra-red lines of the hydrogen spectrum. In the second column the numbers are a visual estimate of the intensities, while the letters denote the character of the line; h, hazy, diffuse; d, perhaps double; b, broad; v, shades toward violet; r, shades toward red.

λ(air) I. A.	Int.	ν (vacuo)	λ(air) I. A.	Int.	ν (vacuo)	λ(air) I. A.	Int.	ν (vacuo)	λ(air) I. A.	Int.	ν (vacuo)
10654.5		9383.2	8884.12	2	11252.95	8440.72	1	11844.05	8187.47	1	12210.43
10650.0		9387.1	81.82	1	55.86	21.86	1v	70.60	84.84	1	14.36
10510.0		9512.1	77.40	1	61.47	17.46	1	76.81	81.74	1	18.99
10460.5		9557.1	75.78	4	63.53	16.06	1	78.78	79.92	1*	21.71
10429.8		9585.2	46.11	0	11301.30	14.18	2v	81.44	70.02	0*	36.51
10426.3		9588.5	8840.87	2	11308.00	09.35	2	88.26	65.88	0	42.72
10330.3	h	9677.6	07.39	3	50.99	8406.43	1	11892.39	64.41	5	44.92
10284.6		9720.6	8796.17	1	65.47	8399.54	0	11902.15	55.88	1	53.22
10265.9		9738.3	94.64	5	67.45	98.04	7	04.27	41.46	1	79.44
10115.2		9883.4	89.80	3	73.71	89.60	0	16.25	38.98	2	83.18
10085.3		9912.7	76.93	0*	90.38	8386.93	2	11920.04	38.24	0	84.30
10074.3		9923.5	67.18	1	11403.05	80.88	1	28.65	30.38	3	96.20
10057.4		9940.2	64.77	1	06.18	78.85	2	31.54	28.82	2	12298.53
10045.0		9952.5	50.31	1	25.03	75.33	0	36.55	25.85	1	12303.03
10010.5	b	9986.8	48.21	0*	27.77	73.97	0	38.49	24.42	1	05.19
9910.4		10087.6	46.71	2	29.73	71.60	2h	41.87	8123.27	1	12306.93
9881.9		10116.7	39.00	1	39.82	69.85	1	44.36	19.11	0	13.24
9868.4	h	10130.6	32.57	1*h	48.24	68.03	0	46.96	17.81	1*	15.21
9830.6		10169.5	23.88	3	59.65	66.63	4	48.96	17.08	0*	16.32
9743.1	1	10260.9	14.82	0*	71.56	63.75	0	53.08	16.19	1	17.67
9715.2	0	10290.3	08.57	1	79.79	60.87	0*	57.20	14.77	3	19.82
9642.3	1	10368.1	01.81	1*h	88.71	59.59	1	59.03	08.24	1	29.75
9581.0	0	10434.5	8693.69	0	99.43	57.00	1	62.73	07.47	1	30.92
9578.3	0	10437.4	88.68	0	11506.07	50.84	2	71.56	8103.96	2	36.26
9573.2	0	10443.0	70.52	6	30.17	49.35	10	73.69	8099.88	3	42.48
9567.4	1h	10449.3	63.57	5	39.42	45.49	0	79.23	94.41	2	50.81
9561.2	1h	10456.1	56.95	1	48.25	43.82	1	81.63	92.57	0	53.62
9553.1	1h	10464.9	40.90	0	69.69	37.78	1	90.31	91.02	2b, d	56.00
9524.5	0h	10496.4	33.09	0	80.16	35.91	0*	93.00	86.13	2	63.46
9444.1	0	10585.7	28.89	1	85.80	34.38	1	11995.20	75.94	0h	79.00
9429.6	0h	10602.0	8623.62	0	11592.87	30.10	4	12001.36	70.98	2	86.66
9410.6	1	10623.4	8599.92	1	11624.83	23.91	0*	10.29	65.73	0	12394.73
9403.3	0	10631.7	94.44	1	32.24	19.30	1	16.94	59.60	1	12404.16
9389.5	1h	10647.3	90.77	2	37.20	17.21	4	19.96	58.59	2h	05.71
9338.5	1b, d	10705.5	85.03	1	44.99	8303.39	1	39.97	55.97	1*	09.75
9318.6	0	10728.3	83.66	3	46.84	8298.47	0	12047.11	54.25	3	12.55
9314.1	0	10733.5	74.59	3	59.17	96.40	1b, d	50.11	50.16	2	18.70
9299.7	0h	10750.1	67.11	0	69.35	91.74	0*	56.89	48.33	0*	21.53
9292.1	0	10758.9	61.50	1	76.99	86.69	0b, d	64.23	47.08	1	23.46
9288.4	1	10763.2	60.20	1b, d	78.77	84.59	1	67.29	41.82	2	31.58
9276.0	0	10777.6	58.20	1b, h	81.49	83.74	1	68.53	8039.66	0	12434.92
9266.1	0	10789.1	55.68	0*	84.93	80.75	1h	72.89	36.29	2	40.14
9252.0	0	10805.5	53.88	0*h	87.39	74.06	1	82.65	31.80	1	47.09
9242.7	0	10816.4	51.90	0	90.10	73.07	8	84.09	27.60	1	53.60
9237.2	0	10822.8	47.75	0	95.77	69.28	1	89.63	24.08	0	59.07
9218.8	1b, d	10844.4	46.00	8	11698.17	64.94	2	12095.98	22.74	2	61.15
9212.4	0h	10852.0	41.42	1h	11704.44	55.62	2	12109.63	19.31	0	66.48
9184.7	0	10884.7	35.42	5	12.67	53.79	4	12.32	18.47	5	67.78
9178.8	1h, d	10891.7	33.47	0	15.35	51.51	1	15.67	13.04	3	76.23
9172.4	0	10899.3	27.78	5	23.17	46.64	3	22.82	07.91	1	84.22
9162.9	0	10910.6	22.62	3	30.26	42.66	1	28.68	06.72	2	86.08
9160.0	0	10914.0	20.11	8	33.72	40.49	4	31.87	8000.24	1b, d	96.19
9158.1	2h	10916.3	16.62	1	38.52	38.42	3	34.92	7998.15	0	12499.46
9129.7	0	10950.3	11.98	1	44.93	37.46	2	36.33	97.03	4	12501.21
9084.6	1h	11004.6	08.90	0	49.18	35.50	2	39.22	94.88	0*	04.57
9075.8	0	11015.3	8504.02	0	11755.92	33.51	1	42.15	93.34	1	06.98
9068.1	1	11024.6	8495.81	1	67.28	22.68	7	58.15	91.38	2	10.05
9022.0	2h	11081.0	85.78	6	81.19	19.94	1	62.20	87.21	0	16.58
9017.5	1h	11086.5	78.34	1	91.53	17.92	0*	65.19	85.61	2	19.08
9016.0	1h	11088.4	74.59	0*	11796.74	14.51	1h	70.24	83.97	1	21.66
8978.86	0	11134.22	71.72	0*	11800.74	8209.53	1	12177.62	81.91	0*h	24.89
8972.07	0	42.65	69.79	1	03.43	08.23	1	79.55	81.06	1	26.22
66.84	3	49.15	66.78	0	07.62	06.57	1	82.02	69.91	3	43.75
47.82	1	72.84	63.26	1	12.54	03.13	1	87.12	68.57	1	45.86
30.70	1	94.27	56.77	2h	21.60	8201.48	1	89.57	67.21	3	48.00
08.19	0	11222.55	51.46	0h, d	29.03	8199.89	0	91.94	7963.26	1	12554.22
01.64	2	30.81	48.64	0	32.98	98.80	0*	93.56	62.35	1	55.66
8898.44	3	34.85	47.69	0*	34.31	95.82	0	12197.99	60.35	0	58.81
96.54	2h	37.25	44.35	2	38.99	93.74	0	12201.09	58.38	0	61.92
85.81	0*	50.81	43.38	2	40.35	90.75	1	05.54	56.93	1	64.21

TABLE II (continued)

λ(air) I. A.	Int.	ν (vacuo)	λ(air) I. A.	Int.	ν (vacuo)	λ(air) I. A.	Int.	ν (vacuo)	λ(air) I. A.	Int.	ν (vacuo)
7954.67	0	12567.78	7824.86	0	12776.27	7716.47	0	12955.73	7609.75	1	13137.42
53.26	2	69.98	22.36	0	80.36				06.06	3	43.80
50.22	1	74.81	15.95	0d, h	90.83	14.04	0b, d	59.81	03.17	4	48.79
47.22	0	79.56				09.08	1*	68.15	7602.39	1	50.14
42.46	2	87.10	13.24	2	95.27	07.41	0	70.31	7597.76	3	58.16
			12.23	3	12797.03	06.02	3	73.30			
40.74	2	89.82	09.12	1h, r	12802.02	04.75	2	75.44	96.83	4	59.77
37.07	3	95.65	07.07	1	05.38				95.58	1	61.94
35.74	0	12597.76	05.56	1	07.86	7702.98	2	78.42	93.43	1	65.66
32.96	5	12602.17				7698.05	2h	86.73	84.20	4r	81.68
26.54	1*	12.38	7804.15	3	12810.18	94.48	0*	92.76	79.16	2	90.45
			02.60	1	12.72	92.53	2	96.05			
23.22	2	17.67	7800.39	0*	16.35	91.84	3	12997.22	7576.06	2	13195.85
22.54	1	18.75	7798.76	1	19.03				71.37	3	13204.02
12.91	1	34.10	96.41	1	22.89	90.17	1	13000.04	68.63	0	08.80
08.58	0h	41.02				85.26	3	08.35	66.83	1	11.94
06.31	0v, d	44.65	89.54	5	34.20	83.41	0	11.48	64.97	1	15.19
			87.26	0	37.96	79.52	1	18.07			
03.45	2	49.23	83.98	0	43.37	73.39	1	28.47	61.01	2	22.11
02.52	2	50.72	79.55	1h	50.68				58.52	2	26.47
7900.09	3	54.61	77.21	1	54.55	72.19	2	30.51	55.85	0	31.14
7897.95	0*	58.04				69.63	1	34.86	48.32	1	44.34
95.76		61.55	73.95	2	59.94	68.83	1	36.22	44.74	2	50.62
			68.78	0*	68.50	67.25	0	38.90			
7886.70	1	12676.09	61.87	0	79.95	65.03	1	42.68	41.71	2	55.95
85.29	0*	78.36	59.97	0	83.11				38.07	2	62.35
75.14	2	12694.70	56.69	1	88.56	7663.23	0	13045.74	36.85	2	64.50
63.80	0*	12713.00				62.37	0	47.21	34.57	1	68.51
62.56	1	15.01	54.84	2	91.63	61.25	2	49.11	31.42	1	74.06
			51.81	0	12896.67	60.36	3b	50.63			
60.27	0	18.72	45.30	1	12907.51	54.17	3	61.18	28.18	0	79.77
59.15	0*	20.53	39.71	2	16.83				27.11	0	81.66
56.39	3	25.00	37.23	1	20.97	51.77	0	65.28	25.77	1	84.02
53.37	0	29.89				50.50	3	67.45	24.39	4	86.46
47.70	1	39.09	34.23	0	25.98	47.45	3	72.66	22.02	1	90.65
			32.58	3	28.74	44.76	1	77.26			
45.67	1	42.39	30.42	0	32.36	43.14	1	80.03	21.15	1	92.18
43.03	0*	46.67	28.80	1	35.07				20.20	1	13293.86
40.49	0	50.80	24.16	1	42.83	41.47	1	13082.89	12.03	2	13308.32
37.91	1	55.00				31.21	2	13100.48	07.63	2	16.12
36.77	1	56.85	7723.05	1	12944.69	22.35	2	15.71	06.71	2	17.70
			21.51	2	47.27	20.48	2	18.93	7504.51	2	13321.66
33.94	1	61.46	18.83	2	51.77	13.61	1	30.76			
29.57	1h	68.59	17.73	0*	53.62						

obtained by simple extrapolation of the Meggers and Peters values below 10,000. The intensities adjoined are only visual estimates and hence make no pretence at accurate quantitative value, but are intended rather for purposes of identification. The value 0 indicates a line that is barely measurable. The change of sensitivity of the plates at about 8700 to 8900A should be allowed for in judging actual relative energy intensities between the sections above and below this. Above 9800A no intensities are given since obviously only the strongest lines can be detected.

A comparison of the wave-lengths in Table II with the corresponding measurements of Allibone shows that within the region of greatest sensibility of dicyanin he has listed all the moderately strong lines. It will be noticed that for most of the overlapping region of the two investigations there is a difference of about 0.3A which must be due to some general shift between the Fe and H spectra in one of the researches. In view of the good agreement between our different plates, the care we took to establish and maintain perfect alignment, and the perfect functioning of our temperature control, we are loath to believe the existence of such shifts in our work. The residual differences in the values obtained and the failure of Allibone to resolve some of the doublets can be easily accounted for by the lower dispersion (25A per mm) used in his work.

A rather cursory examination was made to find new band relations among these lines. Richardson[13] has recently arranged the various known bands in the visible into groups which he calls the $H\alpha$, $H\beta$, etc., bands because of the electron levels involved. Applying simple combination principles, band groups analogous to the Paschen series, $P\alpha$, $P\beta$, etc., can be calculated from

TABLE III

Band groups analogous to the Paschen series.

Group	$n' \to n''$	m	λ(IA) air	Wave-number (vac) Obs.	Calc.	Defect	Combination Method
$P\beta$	3→1	1	8184.84	12214.36	12213.19	−1.17	$({}_1\gamma_1 - {}_1\alpha_1)$
		2	8193.74	12201.09	12200.27	− .82	+(5, 3−5, 1)
$P\beta$	4→2	1	8378.85	11931.54	11931.13	− .41	$({}_2\gamma_2 - {}_2\alpha_2)$
		2	8389.60	11916.25	11917.54	−1.19	+(5, 4−5, 2)
$P\gamma$	1→0	1			11787.72		$({}_0\delta_0 - {}_0\alpha_0)$
		2	8485.78	11781.19	11781.04	− .15	+(6, 1−6, 0)
		3	8495.81	11767.28	11768.86	+1.58	
		4	8508.90	11749.18	11750.21	+1.03	
		5	8522.62	11730.26	11731.39	+1.13	
$P\gamma$	2→1	3	8623.62	11592.87	11593.27	+ .40	$({}_1\delta_1 - {}_1\alpha_1)$ +(6, 2−6, 1)
*$P\gamma$	2→0	1	7218.35	13849.76	13850.45	+ .69	$({}_0\delta_0 - {}_0\alpha_0)$
		2	7225.33	13836.39	13837.88	+1.49	+(6, 2−6, 0)
*$P\gamma$	3→1	1	7460.29	13582.67	13583.08	+ .41	$({}_1\delta_1 - {}_1\alpha_1)$
		2	7467.01	13570.29	13570.84	+ .55	+(6, 3−6, 1)
*$P\gamma$	4→2	1	7514.77	13303.46	13303.00	− .46	$({}_2\delta_2 - {}_2\alpha_2)$
		2	7524.39	13286.46	13285.60	− .86	+(6, 4−6, 2)
$P\delta$	0→0	1	9573.2	10443.0	10443.02	.0	$({}_0\epsilon_0 - {}_0\alpha_0)$
		2	9578.3	10437.4	10438.22	+ .8	
**$P\delta$	1→0	1	7947.22	12579.56	12582.30	+2.74	$({}_1\epsilon_1 - {}_0\alpha_0)$
		2	7950.22	12574.81	12575.94	+1.13	+(2, 1−2, 0)
		3	7956.93	12564.21	12565.31	+1.10	
		4	7963.26	12554.22	12554.34	+ .12	
$P\delta$	2→1	1	8054.25	12412.55	12411.67	− .88	$({}_2\epsilon_2 - {}_1\alpha_1)$
		2	8055.97	12409.75	12409.71	− .04	+(2, 2−2, 1)
		3			12400.01		
		4	8075.94	12379.00	12378.26	− .74	
		5	8094.41	12350.81	12350.75	− .06	
$P\delta$	3→2	1	8130.38	12296.20	12295.38	− .82	$({}_3\epsilon_3 - {}_2\alpha_2)$
		2			12290.17		+(2, 3−2, 2)
		3	8138.24	12284.30	12285.24	+ .94	
$P\delta$	4→3	1	8235.50	12139.22	12139.89	+ .67	$({}_4\epsilon_4 - {}_3\alpha_3)$
		2	8237.46	12136.33	12135.65	− .68	+(2, 4−2, 3)
		3			12125.81		
		4	8255.62	12109.63	12108.13	−1.50	
		5	8273.07	12084.09	12084.43	+ .34	

* Values taken from Allibone's table.
** Richardson called attention to this probable band. (Loc. cit.)

[13] Richardson, Proc. Roy. Soc. **A113,** 368 (1926).

the known vibration intervals of the upper levels of these so-called Balmer term groups. Since a number of these bands would fall in the region investigated, the values of the lines composing them were computed. The fact that the higher band groups given by Richardson are fragmentary and undeveloped makes the data for the application of the combination principle somewhat meagre and unsatisfactory. Still, using the data provided by his tables, a number of our lines were found to fit in well as members of bands of some of the Paschen term groups, so that they hardly seem mere coincidences. A number of such lines are listed in Table III. They would give considerable irregularities in first and second differences, but this was the case also with the band groups from which they were calculated. Their presentation will at least confirm the reality of the higher Balmer term groups. In the second-last column the difference between calculated and observed wave number is given; because of the uncertainty of the data defects as large as 1.5 were admitted. In the last column the method of applying the combination principle is indicated. For convenience Richardson's notation is retained, the α, β, $\cdots$, indicating that the electronic levels involved correspond to those for Hα, Hβ, etc., and the subscripts giving the initial and final vibration levels.

There are traces also of a sequence of the Hα bands farther in the infra-red than the sequence given by Richardson. A few of the lines correspond quite well; on the other hand, some of the calculated wave-lengths lie so close together that they would not be resolved by our plates.

Whether these fragmentary bands be authentic or not, the greater number of the new lines and the most intense are not involved in them. Since it now appears[14] that the secondary hydrogen spectrum is rather analogous to that of the helium atom, new sets of relations between its lines are suggested, and it is hoped this new material may reveal such relations and thus bring us closer to the solution of this complex spectrum.

This work was carried on at the suggestion of Dr. Pfund to whom I am indebted for numerous helpful suggestions. I wish to express my appreciation to him, to Professor Wood for his kindly interest, and to Professors Ames and Herzfeld for their encouragement and support.

JOHNS HOPKINS UNIVERSITY,
May 31, 1927.

[14] Richardson, ref. 13, see Additional Notes, p. 400.

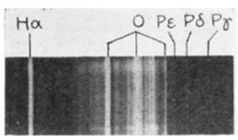


Fig. 2.

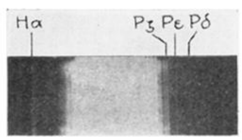


Fig. 3.

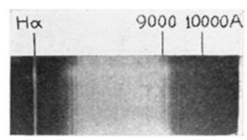
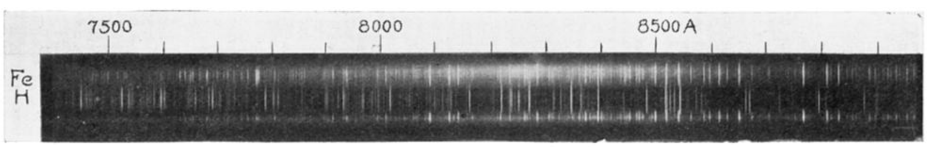


Fig. 4.



Figs. 2 and 3. Hydrogen, Paschen lines (magnification, 3x).
Fig. 4. Hydrogen secondary spectrum.
Fig. 5. Infra-red secondary spectrum of hydrogen.