

Bakerian Lecture: On the Spectrum of Hydrogen

T. R. Merton and S. Barratt

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X. Bakerian Lecture.—On the Spectrum of Hydrogen.

By T. R. Merton, D.Sc., F.R.S., Professor of Spectroscopy in the University of Oxford, and S. Barratt, B.A., Balliol College, Oxford.

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(1) Introductory.

Modern theoretical investigations have met with signal success in providing an explanation for the production of the primary spectrum of Hydrogen, generally known as the Balmer series, but the many-lined or secondary spectrum has hitherto proved to be a much more formidable problem. There can be little doubt that a completely satisfactory explanation of its genesis will mark an important step in our knowledge of the origin of spectra. The detection of regularities amongst such a vast number of lines is in itself an exceedingly difficult task, and one for which it is essential that the data relating to wave-lengths should be accurate and complete.

Although some of the early investigators were of the opinion that the secondary spectrum was to be referred to impurities in the discharge tube, it is now generally 3 F [Published April 27, 1922. VOL. CCXXII.—A 603.

agreed that both the Balmer series and the secondary spectrum are to be attributed to Hydrogen. The relative intensities of the two spectra vary in a surprising manner. Such traces of Hydrogen as are necessary to exhibit the earlier members of the Balmer series are indeed difficult to eliminate from luminous sources, but the secondary spectrum only appears in sources in which considerable quantities of Hydrogen are present, and its intensity relative to that of the Balmer series is greatly enhanced by the complete removal of all impurities.

It has long been known that in the spectrum of water vapour the lines of the secondary spectrum are very weak, and many investigations have shown that the intensity of the secondary spectrum is greatly reduced by the presence of small traces of mercury vapour and other impurities. The relative intensities of the two spectra are affected by variations in the electrical excitation, but for a high relative intensity of the secondary spectrum purity of the gas is essential. The appearance of the discharge in vacuum tubes containing Hydrogen of the highest degree of purity is indeed strikingly different from that observed in hydrogen tubes prepared without special precautions, the former being of an almost white colour whilst the latter show the familiar red glow, which is due to the predominance of the red line, Ha, of the Balmer series.* In a recent investigation, Wood ('Roy. Soc. Proc.,' A, 97, p. 455, 1920; 'Phil. Mag.,' 6, 251, p. 729, 1921) has described a number of interesting phenomena which he has observed in long vacuum tubes containing Hydrogen which were excited by a high potential transformer. Many of these observations cannot at present be explained fully, but the influence of traces of impurities is shown to be an important factor.

It is well known that the secondary spectrum appears under less energetic conditions of excitation than the Balmer series, the latter alone being found in vacuum tubes excited by powerful condensed discharges, and important investigations by Fulcher ('Astrophys. Journ.,' 34, p. 388, 1911; 37, p. 60, 1913) have shown that when Hydrogen is excited by the impact of cathode rays the relative intensity of the secondary spectrum increases as the velocity of the cathode rays is reduced. Fulcher also found similar variations in intensity amongst the lines of the secondary spectrum itself, and identified a number of lines as characteristic of low potential discharges. It was found that these low potential lines exhibited regularities somewhat resembling those associated with band spectra. These regularities and their relation to other phenomena will be discussed in a later section. Any method by which the lines of so complex a spectrum can be separated into different physically related groups, cannot fail to yield results which will prove of assistance in theoretical investigations.

It has been pointed out in a previous communication (Merton, 'Roy. Soc. Proc.,' A, 96, p. 382, 1920) that the relative intensities of the secondary lines are affected by the pressure in the discharge tube, the Fulcher bands being enhanced at low pressures, but

^{*} These remarks do not apply without amplification to the case of tubes excited by discharges of exceedingly low current density. In the presence of water vapour the intensity of the Balmer lines, relative to the secondary spectrum, increases very rapidly with the current density.

that a much more striking change can be brought about by the admixture of Helium. It was found that in the presence of Helium some of the lines were greatly enhanced and that a number of new lines appeared; another class of lines were apparently unaffected, whilst a third class showed a marked reduction in intensity.*

There are two other methods by which the lines have been classified. Dufour ('Ann. Chim. et Phys.' (9), 361, 1906; 'Journ. de Phys.' (4), 8, p. 258, 1909) has investigated the Zeeman effect for the secondary spectrum, and has found that a large number of the lines are not affected in the magnetic field. This classification of the lines has been shown by Fulcher (loc. cit.) to be related to the results which he obtained by varying the velocities of the exciting cathode rays, and to the regularities which he found in the spectrum. The Stark effect, the resolution of the lines into components in an electric field, has been studied by Takamine and Yoshida ('Mem. Coll. of Sci. Kyoto,' 2, p. 321, 1917), by Nitta (ibid., 2, p. 349, 1917) and by Takamine and Kokubu (ibid., 3, p. 271, 1919), who have found that the effect is exhibited by 54 lines in the spectrum. Such investigations and those of Dufour (loc. cit.), relating to the Zeeman effect, are necessarily restricted to the stronger lines of the spectrum, and their value as a means of classification is greatly increased when they can be correlated to changes in the spectrum of a kind which permit of observation for all the lines.

The wave-lengths of the lines in the secondary spectrum have been measured by Hasselberg ('Mem. Acad.,' St. Petersburg (7), 30, No. 7, 1882; *ibid.* (7), 31, No. 14, 1883; 'Phil. Mag.' (5), 17, p. 329, 1882), Ames ('Phil. Mag.,' 30, p. 33, 1890), Frost ('Astrophys. Journ.,' 16, p. 100, 1902), Watson ('Roy. Soc. Proc.,' A, 82, p. 189, 1909), Porlezza ('Atti Accad. Lincei,' 20 (2), p. 178, 1911), Porlezza and Norzi (*ibid.*, 20 (1), p. 822, 1911), and Croze ('Ann. de Phys.' (9), 1, 48, 1914), but the results obtained by these investigators differ widely in their estimates of the relative intensities of the lines, which is greatly dependent on the particular conditions under which the spectrum is produced, and it would appear also that the tables are by no means complete, more especially in the yellow green regions of the spectrum, for which it has only recently been possible to obtain photographic plates of a sufficiently high degree of sensibility for recording lines of low intensity with a moderately high dispersion.

There has been much difference of opinion as to whether the secondary spectrum is to be attributed to the Hydrogen atom or to the molecule. To the theoretical physicist this is a question of vital importance, for there appears to be little prospect of explaining the origin of the spectrum as due to the Hydrogen atom on the views which are at present accepted with regard to its structure. Evidence on this question has been sought in investigations of the Doppler effect in positive rays by Stark ('Astrophys. Journ.,' 25, pp. 23 and 170, 1907), Wilsar ('Ann. der Phys.,' 37, p. 1251, 1912) and Fulcher ('Astrophys. Journ.,' 35, p. 101, 1912), and more recently by Thomson ('Phil. Mag.'

^{*} Experiments on the effect of Argon on the secondary spectrum are now in progress. It would appear that if the presence of Argon gives rise to any changes similar to those produced by the presence of Helium, they are at any rate very much less conspicuous.

(6), 40, p. 240, 1920; *ibid*. (6), 41, p. 566, 1921), and Vegard (*ibid*. (6), 41, p. 558, 1921), but it would appear doubtful whether any conclusive evidence as to the origin of the spectrum can be obtained by these methods.

In their investigations of the widths of spectrum lines Buisson and Fabry ('Journ. de Phys.' (2), p. 442, 1912) were led to conclude that the secondary spectrum was to be referred to the Hydrogen atom. This conclusion was based on a measurement of the limiting order at which interference fringes could be observed for a line in the secondary spectrum, the relation between the limiting order of interference N and the mass M of the radiating particle (in terms of the Hydrogen atom as unity) being given by the expression $N = k\sqrt{(M/\theta)}$, where k is a constant and θ the absolute temperature (cf. Rayleigh, 'Phil. Mag.' (6), vol. 29, p. 274, 1915; Schönrock, 'Ann. der Phys.,' 20, p. 995, 1906).

For the constant k Buisson and Fabry, following Schönrock, adopted the value $1 \cdot 22 \times 10^6$, and the value of N which they found experimentally was in approximate agreement with the view that the spectrum was to be referred to the atom. This result has recently been criticised by Saha ('Phil. Mag.' (6), 40, p. 159, 1920) on the ground that Buisson and Fabry obtained a much smaller value for N in the case of the line Ha, the first member of the Balmer series, and that if the value of k in the formula given above were calculated from the observed limit of interference for the line Ha, the secondary line would yield a value of M more nearly appropriate to the molecule H₂. The ground of this criticism does not appear to us to be justified, for it is well known that the line Ha is complex and could not therefore be expected to yield results in accordance with the theory for a single line, and moreover Saha appears to have overlooked the fact that the value of k adopted by Buisson and Fabry was tested experimentally with lines of the rare gases, and was found to give results in close agreement with the known atomic weights of these gases.

It must, however, be pointed out that any cause of broadening of the lines other than that due to motion in the line of sight will yield too low a value for the mass of the radiating particles; and it follows that measurements of this kind can only set an inferior limit to the mass, unless the possibility of broadening of the lines by any other cause can be excluded.

In the present investigation we have remeasured the wave-lengths of the lines of the secondary spectrum in International Ångström units, and have been able to add a considerable number of lines to those hitherto recorded. We have also investigated the effect of variations in the conditions of electrical excitation, and of the pressure in the discharge-tube, on the relative intensities of the lines, and have compared the results obtained with other methods of classification; previous investigations (Merton, loc. cit.) of the changes in the spectrum which are produced by the admixture of Helium have been extended to the more refrangible regions. The widths of several lines in the secondary spectrum have been measured by a new method with which it is believed that a high degree of precision has been attained, and under conditions of excitation

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which have made it possible to establish the conclusion that the secondary spectrum is to be referred to the Hydrogen molecule.

(2) Experimental.

As the source of the spectrum vacuum tubes of the H type have been used, and have been designed on lines indicated by the investigations of Wood (loc. cit.) so as to give the secondary spectrum as strongly as possible. The usual capillary tube of a few inches in length was replaced by tubes of from 20 to 50 cm. in length and of about 5 to 8 mm. internal diameter. The electrodes consisted of spirals of aluminium ribbon, and the tubes were provided with palladium tubes, which were sealed through the intermediary of short platinum tubes into side tubes in the usual manner. Pure Hydrogen could be admitted by heating these palladium tubes in a flame or in a current of Hydrogen, or alternatively the Hydrogen in the tubes could be removed by heating the palladium in an atmosphere from which Hydrogen was absent. In some cases the tubes were cleaned before exhaustion by washing them out with a very dilute solution of hydrofluoric acid, followed by distilled water; this procedure was found to be very effective. The tubes were exhausted by means of an oil pump, and the evacuation was completed by means of a bulb containing charcoal, which was cooled with liquid air. For some of the tubes a Gaede mercury pump was used and in all cases the tubes were washed out during the process of exhaustion by the frequent admission of Hydrogen through the palladium tubes. In the case of tubes containing Helium, this gas was prepared by heating powdered Thorianite in a fused silica tube, and was purified before entering the vacuum tubes by passage through a U-tube containing charcoal cooled with liquid air.

The tubes were excited by the current from a large induction coil provided with a mercury jet interrupter, and in some experiments a 15,000 volt $\frac{1}{4}$ kilowatt step-up transformer was used. It should be mentioned that although the utmost care was taken to remove the carbon compounds and other impurities with which vacuum tubes are liable to be contaminated, before the tubes were sealed off, the highest degree of purity, as shown by the intensity of the secondary spectrum relative to that of the Balmer series, was never attained until a discharge had been passed for several hours and the aluminium mirrors, which were deposited on the tubes around the electrodes, had removed the last traces of impurities which had been present in such small quantities when the tubes were sealed off that they could not be detected by any characteristic bands or lines in the spectrum.

(3) Wave-length Measurements.

The earliest tables of wave-length of the secondary spectrum are due to Hasselberg (loc. cit.), and although his measurements were made visually, and are not accurate enough for modern requirements, they are more complete than later photographic

records in the green regions of the spectrum, in which the sensibility of the eye is a maximum and that of most panchromatic plates a minimum. Frost (loc. cit.) and Ames (loc. cit.) have published short lists of some of the stronger lines, but the most comprehensive and accurate table is due to Watson (loc. cit.), who has recorded most of the lines in the red and yellow, and in the ultra-violet, but has not included a considerable number of lines in the green regions of the spectrum. Watson found no lines of wave-length greater than the Balmer line Ha. Porlezza (loc. cit.) and Porlezza and Norzi (loc. cit.) have published tables which supplement those of Watson, and Croze (loc. cit.) has measured lines in the infra-red down to $\lambda 8000$ A.

The measurements included in the present investigation extend from Ha to the limits imposed in the ultra-violet by the thin glass wall of the discharge-tube, the shortest wave-length recorded being $\lambda 3375$ A, but the continuous spectrum of Hydrogen could be traced on the plates to wave-lengths shorter than \$\lambda 3000 A, and as there were no indications of lines superposed on the background in this region, we did not resort to the use of vacuum-tubes provided with quartz windows. It is intended ultimately to extend the measurements into the infra-red. We have used an Anderson concave grating ruled with 20,000 lines to the inch, and having a radius of curvature of 120 cm., which gave a dispersion of very nearly 10 A per millimetre. The mounting was of the type described by Eagle ('Astrophys. Journ.,' 31, p. 120, 1910), which involves three adjustments in focussing, of which two determine the angles made respectively by the grating and by the photographic plate with the incident light, whilst the third is used to vary the distance between the grating and the plate. The necessary adjustments for different regions of the spectrum were found from experimentally prepared tables. Plates of especially thin glass were used and were bent to the appropriate curvature in the plate-holder.

The regions from \$\lambda 6560\$ to \$\lambda 5400\$ were photographed on Wratten and Wainwright Panchromatic plates, from \$\lambda 5400\$ to \$\lambda 4860\$ on Marion's Iso-Record plates which are specially sensitive to this region, and from \$\pmu4860\$ to the ultra-violet on Ilford Ordinary The vacuum tubes were used end-on, the light from the capillary being focussed upon the slit of the spectrograph by means of a quartz lens of about 30 cm. focal length. The exposures required to bring up the faintest lines which were measured were five hours with the Panchromatic plates and three and a half hours with the Iso-Record and Ilford plates. The International Secondary standards were used as a comparison spectrum, the source of light being a Pfund ('Astrophys. Journ.,' 27, p. 296, 1908) arc burning with a current of about 3 amps. at 100 volts. The comparison spectrum was limited by a movable stop in the spectrograph to a narrow strip running across the middle of the Hydrogen spectrum. It was found impossible to ensure the absence of very small shifts between the Hydrogen and the comparison spectra, which were photographed consecutively on the same plate, and to eliminate errors, due to these shifts, from the measurements the following procedure was adopted. A tube containing Helium and Hydrogen was substituted for the tube containing pure Hydrogen and a

series of plates taken throughout the spectrum, the series lines of both elements and also most of the secondary Hydrogen spectrum being recorded. The wave-lengths of the first six members of the Balmer series, and of the Parhelium lines included in the range required, were measured on these plates, together with those of about 100 secondary Hydrogen lines.

The deviations of the series line determinations from the values given by Curtis ('Roy. Soc. Proc.,' A, 46, p. 147, 1920) for Hydrogen and by Merrill ('Astrophys. Journ.,' 46, p. 357, 1917) for Helium enabled the shifts in the comparison spectrum to be eliminated, and the corrected values obtained for the selected secondary Hydrogen lines were then used as standards in measuring the remaining lines of the spectrum from plates taken with pure Hydrogen tubes. The plates were measured on a Hilger travelling micrometer, with a screw-pitch of 1 mm. and reading by a vernier on the drum to 0·001 mm. Three plates were measured for each region, each plate, following the usual procedure, being measured in both directions to eliminate personal errors in setting. Each series of readings so obtained was repeated before altering the position of the plate on the stage of the micrometer. The two values rarely differed by more than 0·003 mm., and their mean was adopted in subsequent reduction. In all, twelve settings were made on each line, except in the case of some of the faintest lines which were not visible on all the plates; these exceptions have been noted in the tables given.

The reduction of micrometer readings to wave-lengths was simplified by the fact that the dispersion was almost exactly 10 A per millimetre. In the region $\lambda6560-\lambda4860$ the readings were reduced to approximate wave-lengths by the addition of a constant, and the final adjustment was made from an error curve drawn either by means of the iron standards or the Hydrogen standards prepared from them. In the blue and ultraviolet regions a preliminary linear correction was applied so as to reduce the slope of the error curve. The arithmetic mean of the six values calculated in this way was adopted as the final value. The wave-lengths and wave-numbers in vacuo have also been tabulated, the corrections for this purpose being taken from the tables of Meggers and Peters ('Bureau of Standards Publications,' p. 698, 1918).

For all but a few of the weakest lines and a few diffuse lines the probable error of the mean wave-length adopted was less than 0.02 A, and for most lines it was considerably smaller than this. It is believed that the values given can be relied on to two hundredths of an Ångström unit. The weakest lines were much more sharply defined in the visible regions than in the ultra-violet, where they were superposed on the continuous background, and it is possible that this may slightly affect the accuracy of some of these wave-lengths. Our measurements agree in general very closely with those of Watson (loc. cit.), when the latter are transposed into International Units, but Porlezza's (loc. cit.) measurements differ from ours, in extreme cases by almost an Ångström unit.

Several hundred new lines have been recorded, these lines occurring for the most

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part in the red and yellow, and particularly in the green regions, in which it would have been impossible to record so many faint lines without the use of the Iso-Record plates. It is believed that lines due to impurities have been excluded, all the photographs used for measurement having been taken with tubes which had been run for some hours, and in which the discharge appeared to be white throughout the capillary.

(4) The Continuous Spectrum.

In addition to the Balmer series and the secondary spectrum, vacuum tubes containing Hydrogen always emit a continuous spectrum. The intensity and extent of this continuous background depends greatly on the pressure of the Hydrogen in the discharge tube. If the pressure is reduced to the stage at which the glass begins to show a green fluorescence, the continuous spectrum almost disappears and the secondary lines are sharp against a clear background, even in the ultra-violet. At about 50 mm. pressure the continuous spectrum extends into the green, and at still higher pressures it covers the whole spectrum. The introduction of capacity into the discharge circuit has no very marked effect on the continuous spectrum, but appears to weaken it to some extent, an effect which can also be produced by an admixture of Helium. According to Lyman ('Spectroscopy of the Extreme Ultra-violet'), the continuous spectrum fills the gap between the end of the secondary spectrum and the Hydrogen lines in the Schumann region, but the intensity distribution in this spectrum has not been studied.

(5) The Classification of the Lines.

In the tables of wave-lengths, under the heading "Intensity" will be found the estimated intensities of the lines, on the usual scale of 0 to 10, when the discharge tube containing Hydrogen at a pressure of a few millimetres was excited by an uncondensed discharge. Under these conditions the discharge is at its brightest, being intrinsically weaker both at higher and at lower pressures. In the column succeeding those in which the intensities are given, the effects of changes of pressure and other conditions on the relative intensities of the lines are shown. In all such cases the intensity changes have been estimated by examining a standard plate in juxtaposition with a plate taken under the conditions in question and exposed for a time appropriate to the intrinsic brightness of the source. A + denotes that the line is enhanced and ++ that it is greatly enhanced, — and = denoting in the same way that the line is somewhat or greatly weakened as the case may be. The observations referred to under "High Pressure" were made with tubes containing Hydrogen at pressures greater than 50 mm. of mercury, and under these conditions the discharge was much less luminous and of a bluishwhite colour, the spectrum lines being superposed on a rather strong continuous background. The changes which were found in the relative intensities of the lines are shown in the tables under the column "High Pressure," and in the succeeding column are given the changes observed at low pressures. By "Low Pressure" we refer to a

pressure at which the walls of the vacuum tube show a vivid green fluorescence and the intrinsic intensity of the light is greatly reduced.

It has long been known that when powerful condensed discharges are passed through vacuum tubes containing Hydrogen, the secondary spectrum disappears and the lines of the Balmer series alone remain, but we have observed that with a condenser and a rather small spark-gap in the circuit a group of lines extending from $\lambda6000$ to $\lambda5600$ are very prominent; these lines are intrinsically weakened by the inclusion of the condenser and spark-gap in the circuit, but they are strong in comparison with the remaining lines of the secondary spectrum. If the length of the spark-gap is adjusted carefully, the effect is very striking if the spectrum is examined with a small direct vision instrument of low dispersion. These changes in intensity are given in the column headed "Condensed Discharge."

Under "Helium Effect" are shown the changes of relative intensity which take place when Helium, at pressures up to 40 mm. and more, is admitted to the discharge tube with the Hydrogen. The phenomena which occur have already been described by one of us (T.R.M.) (loc. cit.), but in the present investigation we have extended this classification of the lines into the more refrangible portions of the spectrum by adopting a suitable standard of intensity in the comparison-plates.

We have confirmed the previous observation, in the presence of Helium, of a number of lines which do not appear under ordinary conditions, and the wave-lengths of these lines in the tables are given in brackets.

In the next column are given the results obtained by Dufour (loc. cit.) in his investigations of the Zeeman effect; all the lines examined by Dufour have been marked O or Z in the tables, according to whether they show or do not show the Zeeman effect.

The lines which have been arranged by Fulcher into bands have been noted in the succeeding column, and in the last column the results obtained by Takamine and Yoshida (loc. cit.), Nitta (loc. cit.) and Takamine and Kokubu (loc. cit.) in their investigations of the Stark effect are given.

These different methods of classification are related to one another, but there are numerous exceptions to any broad generalization. In the red and yellow regions all the lines which were found by Dufour to show the Zeeman effect are "High Pressure" lines, and most of them are strengthened in the condensed discharge; many of these lines also are enhanced by the presence of Helium, but there are exceptions to this rule.

The Fulcher band lines are essentially "Low Pressure" lines, and are weakened in the condensed discharge.

The exceptions to this rule are as follows:—

 $\lambda 6197 \cdot 05$ high pressure line.

 $\lambda 6093 \cdot 83$ somewhat enhanced in condensed discharge.

λ5989·22 high pressure line, enhanced by condensed discharge.

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 $\lambda 5552 \cdot 52$ enhanced by condensed discharge.

 $\lambda 5543 \cdot 41$ $\lambda 5317.90$ high pressure line.

"Low Pressure" lines are weakened by the condensed discharge, which enhances the "High Pressure" lines, and the lines which are enhanced by the condensed discharge are also enhanced to a smaller extent by admixture of Helium; but there are exceptions, and the changes in intensity amongst the lines which do conform to these rules vary greatly in magnitude. We are inclined to the view that many of the exceptions may be explained by the assumption that the exceptional lines are in reality close unresolved doublets.

With regard to the lines showing the Stark effect, this attribute appears to bear no relation to any of the other methods of classification, but attention may be drawn to lines at $\lambda\lambda 4185 \cdot 4$, $4123 \cdot 9$, $4021 \cdot 7$, $3927 \cdot 3$ and $3846 \cdot 0$, which are described as showing the Stark effect, but which do not appear on any of our plates. If these lines are indeed Hydrogen lines, it is possible that they make their appearance only in the powerful electric fields which are necessary for the investigation of the Stark effect.

(6) Comparison of the Secondary Hydrogen Spectrum with the Solar Spectrum.

The presence of lines of the secondary Hydrogen spectrum in celestial spectra has not been established, but in view of the fact that we have separated the secondary spectrum into groups, which vary in intensity under different physical conditions, we have made a careful comparison of a number of secondary lines with Rowland's solar wave-lengths, and with the sun-spot lines recorded by Hale and Adams ('Astrophys. Journ.,' vol. 23, p. 11, 1906). The most prominent lines of each class amongst the secondary lines were selected and were reduced from International Units to Rowland's scale of wave-lengths. A table showing the comparison would be redundant, but it may be stated that there are very few coincidences within the limits of experimental error, and these coincidences appear to be accidental, for the relative intensities of the lines which might seem to be represented are not in harmony with their intensities on any scheme of classification which has been found. It is therefore probable that the secondary spectrum is not represented in the solar spectrum, though the range of wave-lengths relating to the sun-spot spectrum is not as great as might be desired.

(7) The Widths of Spectrum Lines.

In a previous section we have referred to the widths of spectrum lines and to their importance in setting an inferior limit to the molecular weight of the radiating particles. The distribution of intensity in a spectrum line, in the case in which the sole cause of broadening is that due to the motion of the radiating particles in the line of sight, is

given by the expression $I = I_0 e^{-kx^2}$, where I is the intensity at a difference of wavelength x from the maximum, where the intensity is I_0 , and k is a constant depending on the mass and the temperature of the radiating particles. Rayleigh (loc. cit.) has shown that if the "half-width" of the line $\delta\lambda$ be defined as the value of x when $I/I_0 = 0.5$, then $\delta\lambda/\lambda = 3.57 \times 10^{-7} \sqrt{(\theta/m)}$, where θ is the absolute temperature of the gas and m the mass of the radiating particles in terms of the Hydrogen atom as unity. Measurements of the width of a line are usually carried out by determining the limiting order of interference at which fringes can still be seen with such instruments as the Michelson or Fabry and Perot interferometer, in which the difference of path between successive interfering beams can be progressively increased.

The theory of this method has been fully discussed by Rayleigh (loc. cit.) and by Schönrock (loc. cit.). If N is the limiting order of interference at which the fringes can still be seen it is shown that $N = K\sqrt{(m/\theta)}$, where K is a constant for which Rayleigh gives the value 1.427×10^6 , whilst Schönrock adopts the appreciably smaller value 1.22×10^6 . The exact value of this constant depends on an estimate of the limiting visibility of fringes which can just be seen, and its value can be checked by observations on lines of the rare gases, following Buisson and Fabry (loc. cit.), where the mass of the radiating particles can be assumed. It is doubtful, however, whether a high degree of accuracy can be attained by this method, since the point at which the fringes cease to be visible is necessarily difficult to determine, and might well be affected by the intrinsic intensity of the light, by the wave-length in visual observations, and by other circumstances.

We have therefore endeavoured to avoid the personal errors which are inherent in these methods by adopting a different procedure, in which the determination of the half-widths does not depend on any estimate of visibility in the ordinary sense of the word, but is calculated from the positions of certain definite points on a photographic plate, which can be measured with a micrometer to an accuracy which is limited only by the ordinary instrumental and personal errors which arise in the measurement of spectrum lines.

It is of course a first essential that the resolving power of the spectroscope should be sufficiently great, but if this condition be satisfied the method is applicable, with slight modification, to any form of spectroscope. In the present investigation we have used an echelon diffraction grating, consisting of 35 plates of glass each 15 mm. thick, which had a resolving power adequate for the lines in question.

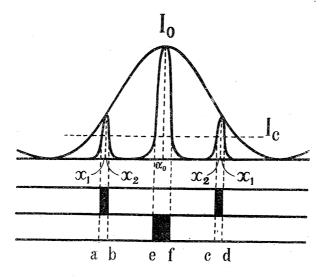
The procedure simply consists in taking photographs of a line under investigation, firstly with the grating in the double-order position and then in the single-order position, with exactly the same times of exposure and without altering the conditions of excitation of the discharge tube. In practice we bracket photographs in the single-order position between photographs in the double-order position, this precaution being taken to provide for the possibility of a gradual change in the luminosity of the discharge tube, and the photographs are taken on adjacent portions of the same plate. The photographs

were taken on Ilford Rapid Process Panchromatic plates, which were developed with a Hydroquinone and Potash developer which gave very great contrast, and by a slight "cutting" of the plates after development with a solution of Potassium Ferricyanide the contrast became so great that the positions of the edges of the black lines could be measured on a photo-measuring micrometer to a few thousandths of a millimetre. The half-widths of the lines were deduced from the measured "apparent widths" in the single- and double-order positions. The theory of the method, as involving the use

of the echelon grating, is given in the succeeding section. With other instruments of high resolving power it would be necessary to vary the intensity of the incident light in successive exposures, e.g., by the interposition of a filter of known absorbing power for the radiation in question.

(8) Theoretical.

The theory of the method can be seen from the figure in which the upper curve represents the distribution of intensity by the echelon which is given by the equation



 $I_n = \sin^2 \alpha/\alpha^2$, where $\alpha = \pi \theta \sigma/\lambda$, σ denoting the step of the grating, λ the wave-length and θ the angle of diffraction.

In the same figure are shown the intensity distribution curve of a spectrum line, as seen in the single-order position, with the two curves showing the line in the doubleorder position on either side. Although the actual distribution of intensity in the line is given by the equation $I = e^{-kx^2}$, the observed distribution of intensity differs somewhat from this as the distribution of intensity given by the echelon is superposed.

In the two strips below these curves are shown the appearance of the line as seen on the plate, with exposures of equal duration, in the double- and single-order positions respectively. (The absence of disturbance due to irradiation can be seen by an

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inspection of the ends of the lines (cf. Nicholson and Merton, 'Phil. Trans.,' A, vol. 216, p. 459, 1916).) The edges of the lines at a, b, e, f, c and d denote a certain critical intensity, I_c, which is represented by a dotted line in the upper part of the figure. It will be seen that we assume only that a constant degree of blackening of the plate is produced by a light of constant but entirely unspecified intensity.

Let x_1 and x_2 denote the distances of a and b, or c and d, respectively from the true maximum of intensity of the line in the double-order position ($x=0, \alpha=\pi/2$), and α_0 the distance of e and f from the maximum in the single-order position ($x = 0, \alpha = 0$). Then expressing α_0 and x in circular measure we have for the single-order position

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and for the double-order position

$$I_c/I_0 = e^{-kx_1^2} \sin^2 \alpha_1/\alpha_1^2, \qquad I_c/I_0 = e^{-kx_2^2} \sin^2 \alpha_2/\alpha_2^2, \qquad . \qquad . \qquad . \qquad (ii.), (iii.)$$

where α_1 and α_2 are the angles corresponding to the points a and b, or d and c, respectively.

Putting

$$\sin^2 \alpha_0/\alpha_0{}^2 = R$$
, $\sin^2 \alpha_1/\alpha_1{}^2 = P$, and $\sin^2 \alpha_2/\alpha_2{}^2 = Q$,

we have

$$\log (R/P) = k\alpha_0^2 - kx_1^2$$
, $\log (R/Q) = k\alpha_0^2 - kx_2^2$. . . (iv.), (v.

Now the plates are measured with a photo-measuring micrometer with which readings of the positions of the points a, b, c, d, e and f are obtained on an arbitrary scale, and since x_1 is not exactly equal to x_2 , the number of micrometer divisions between a and c, or b and d, does not correspond to an angle n.

Since it is not possible to measure directly the number of micrometer divisions which are equal to the separation of successive orders, both equations (iv.) and (v.) are required to solve for k.

The measurements give $2\alpha_0$ and $(x_1 + x_2)$ in micrometer divisions, and it is necessary to find a value of (x_1-x_2) such that equations (iv.) and (v.) give the same value for k, from which the value of $\delta\lambda$, the half-width, at once follows, since the difference in wave-length corresponding to the separation of successive orders is known from the optical constants of the grating. (x_1-x_2) is very small, and can readily be found by trial of a series of values, which can be plotted against the resulting values of $[k_{\text{(from (iv.))}}-k_{\text{(from (v.))}}]$ on squared paper.

(9) Experimental Results.

We have measured, in the manner described in the preceding section, the half-widths of three lines in the secondary spectrum, $\lambda\lambda$ 6018, 6028 and 6225 A, and also the half-

width of the Helium line $\lambda 5015$ A as a check on the accuracy of the method. choice of lines in the secondary spectrum is limited in the first place by their brightness, and in the second by the possibility of their being isolated completely from neighbouring lines in the spectrum by means of the constant deviation spectroscope which was used for preliminary analysis of the spectrum. It was necessary that the exposures should be comparatively short to avoid disturbances due to the effect of changes of temperature on the echelon grating. An inferior limit to the temperature of the gas in the discharge tube was found in the following manner. The discharge was passed through the vacuum tube for a considerable time, in order to reach a state of equilibrium between the heating of the gas by the discharge and the cooling of the walls of the tube by radiation and convection. The temperature of the walls of the tube was then measured by putting specks of organic substances of known melting point on to the wall of the tube, and observing which of them melted.

The temperature of the outer walls of the tube being thus measured we deduce the temperature of the gas as follows:—It is clear that when thermal equilibrium has been established the temperature of the outer wall of the capillary must lie between that of the radiating gas within the tube and the temperature of the room. An inferior limit to the temperature of the radiating gas is obtained by assuming that the interchange of energy takes place by radiation only, since an undue allowance for the effects of convection currents might lead to too high a value for the temperature of the gas. further assumed that the conduction of heat by the glass tube is infinite compared with that of the gas and of the surrounding air. The temperature of the radiating gas in the discharge tube is thus given by $T_{gas}^4 - T_{glass}^4 = T_{glass}^4 - T_{room}^4$, and it will be noted that the assumptions are such as to lead to an inferior limit for the temperature of the This is an important consideration, for an inferior limit to the theoretical limit to the widths of the lines under the conditions of experiment is required. It is also important to note that any ill-adjustment of the apparatus, resulting in a loss of definition, will give rise to too great a value for the determined half-widths of the lines, and therefore to too small a value for the mass of the radiating particles. It follows that when values for the half-width and the temperature have been determined in the manner described, the masses of the radiating particles must exceed a certain specified amount.

With a discharge of suitable intensity it was found that small specks of cinnamic acid were just melted. The melting point of this substance is 133° C., and applying the correction in the manner described above, the temperature of the radiating gas is found to be 456° Absolute. In the following Table are given the results obtained for the three secondary Hydrogen lines and also for the green Parhelium line. In the latter case the temperature of the radiating gas was probably somewhat higher, as the gas was contained in a vacuum tube with a narrow capillary, the walls of which were much thicker than in the case of the Hydrogen tube, but the theoretical half-width has been calculated on the assumption that the temperature was the same in both cases.

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δλ (found).	δλ (found) (mean value).	δλ calcı 456° Al	llated at
	(mean varue).	Atom.	Molecule.
6018 0.037, 0.036, 0.034, 0.030	0.034	0.046	0.032
6028 0.032, 0.033, 0.032	0.033	0.046	0.032
6225 0.034, 0.033, 0.038, 0.039, 0.032 .	0.035	0.048	0.034
5015He 0.024, 0.022	0.023	0.019	

It will be seen that the results are uniformly in agreement with a molecular origin for the secondary lines, the half-widths found being very close to the values calculated for the molecule. In the case of the Helium line the fact that the half-width found is slightly greater than the calculated value is perhaps to be explained in part by the conservative estimate of the temperature in the case of the Helium tube, but it is believed that the limiting theoretical widths of the lines are more nearly attained in the tubes with wide capillaries and in which the current density is consequently lower, than in the tubes with narrow capillaries of the conventional Plucker form. λλ6018 and 6225 are both "Fulcher" lines, are enhanced at low pressures, and are weakened by the condensed discharge. Neither of them shows the Zeeman effect. line \$\lambda 6028\$ belongs to an entirely different class, being a high-pressure line which shows the Zeeman effect. Since these are the two most important classes of lines it is probable that the whole of the secondary spectrum is due to the Hydrogen molecule.

(10) The Separation of Gases in Vacuum Tubes.

In a previous communication (Merton, 'Roy. Soc. Proc.,' A, vol. 98, p. 255, 1920) an account has been given of a curious effect, which, on further investigation, seems to throw some light on the phenomena observed in vacuum tubes containing Hydrogen. It was found that when a vacuum tube containing Helium at a comparatively high pressure, and also a little Hydrogen, was excited by an uncondensed discharge and was observed through a direct-vision prism, the lines of both Helium and Hydrogen appeared with uniform intensity throughout the capillary. On putting a condenser and a spark gap in the electrical circuit the Hydrogen lines became much weaker in the centre of the capillary, but showed brightly at the two ends. This is in agreement with an observation of Curtis ('Roy. Soc. Proc.,' A, vol. 89, p. 146, 1914); but it was found that on cutting out the condenser the Hydrogen lines did not immediately reappear with uniform brightness, but gradually extended from bright spots at the ends of the capillary until the intensity became uniform, which took a considerable time to occur, depending

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on the total amount of Hydrogen present and the pressure of Helium in the discharge tube.

We have extended these results, and with a vacuum tube containing Helium at a pressure of 56 mm. and a little Hydrogen, in addition to the phenomena described above, it has been observed that on putting in the condenser there is a bright instantaneous flash of the Hydrogen lines throughout the capillary before they appear at the ends of the capillary only.* In addition to the Hydrogen, the proportion of which could be controlled by means of a palladium regulator, the tube showed traces of Mercury, Sulphur, Oxygen, the Angström Carbon bands and a few other lines due to impurities which have not been completely identified. When the uncondensed discharge was first passed through the tube the Mercury lines were scarcely visible, but they gradually developed, though still very faint and somewhat stronger in the centre of the capillary than at the ends. On putting in the condenser the Mercury lines gradually became brighter, but appeared only in the centre of the capillary. On cutting out the condenser they appeared at once with great brilliance in the centre of the capillary, gradually spreading out towards the ends and at the same time becoming fainter. The Mercury lines behaved in exactly the opposite way to the Hydrogen lines, and it looked as if the effect of the condensed discharge was to collect all the Mercury in the tube to the centre of the capillary. The lines due to Sulphur, Oxygen, &c., behaved in the same manner as the Mercury lines. In Plate 3 (a) shows the appearance of the capillary, as photographed in the red and yellow regions of the spectrum while the tube was excited by the condensed discharge; (b) shows the appearance immediately after the condenser was cut out, this photograph being obtained by repeatedly putting the condenser in and out, and only exposing the plate immediately after the condenser had been cut out, and in (c) the lines are seen uniformly distributed throughout the capillary when the tube was excited by the uncondensed discharge. In (d), (e) and (f) respectively the same phenomena are shown in a more refrangible region, in which the behaviour of the Hydrogen line $H\beta$ and the green Mercury line can be seen. (The Mercury line was too weak for reproduction in (d) and (f).)

The same phenomena can be observed at lower pressures of Helium in the discharge tube, but the condition of uniform intensity in the capillary after the condenser is cut out is very much less rapidly attained at high pressures.

The possibility of the removal of Hydrogen by absorption by the glass walls of the capillary during the passage of the condensed discharge has been considered; but it is believed that this explanation cannot be upheld, for in this case either it should be possible to reach a steady state in which the phenomena are no longer observed when the tube has been run for some time, or else the whole of the Hydrogen in the tube should rapidly disappear; but there is no evidence of an approach to a steady state, or

^{*} It has also been observed that when the quantity of Hydrogen in the discharge tube is sufficiently great to show the secondary lines, the latter also appear only at the ends of the capillary when the condenser is cut out.

of a rapid disappearance of the gas. In the case of mercury an explanation based on some action of the walls of the capillary is even less satisfactory, as it would be necessary to assume that the glass walls were an almost inexhaustible source of mercury which was rapidly absorbed by the electrodes; for in this case also there is no evidence of any approach to a steady state.

It has not been possible to make any quantitative comparison of the rates at which the Hydrogen lines spread into, and the mercury lines out of, the capillary; but the speed of the Hydrogen lines relative to those of mercury suggests forcibly that the gases actually move in opposite directions, and that the Hydrogen and mercury do not appear at the centre and the ends of the capillary respectively immediately after the condenser is cut out, for the simple reason that they are not there. In the case of lines due to sulphur, &c., there is no doubt that the glass capillary of the vacuum tube may be a source of these impurities, and that their appearance immediately after the condenser is cut out may be due in part to their being liberated from the walls of the capillary by the powerful condensed discharge.* The evidence for a separation of the gases is therefore not clear in such cases. The Angström bands behaved like the Hydrogen lines, but in this case the spectrum is due to a compound which is certainly broken up by the condensed discharge, and which would therefore require some time to reform or accumulate in the capillary when the condenser is cut out.

With this exception all lines due to the heavier elements appear in the centre of the capillary when the condenser is cut out. If a partial separation of the gases takes place it is clear that, whatever the mechanism by which this occurs may be, the degree of separation is not proportional to the total energy flowing through the tube in a given time but must increase rapidly with the current density; for the total energy of the condensed discharge was no greater than that of the uncondensed discharge, and was in fact somewhat smaller. It is, however, to be expected that some separation should be effected by the uncondensed discharge, and in addition to the effect recorded above in the case of the mercury line, we have often noticed that when heavy, uncondensed discharges are passed through Hydrogen tubes containing a little water vapour, the series lines of oxygen appear exclusively in the central portions of the capillary.†

These observations seem to provide an explanation of the greater part of the phenomena described by Wood (*loc. cit.*), who found that in long Hydrogen tubes which were not absolutely free from impurities, the Balmer series appeared strongly in the central portions of the capillary whilst the secondary spectrum was more strongly developed at

- * It has been noticed that when very powerful condensed discharges are employed, "are" lines of the constituents of the glass walls of the tube appear with great brilliance for a short space of time after the condenser is cut out, and experiments which are now being made seem to show that this may be developed into a convenient method of producing the spectra of many substances.
- † The phenomena are evidently of an entirely different character to those recorded by Sir J. J. Thomson ('Roy. Soc. Proc.,' 58, p. 247, 1895). In the latter experiments the discharge was, in the main, unidirectional, and differences were observed in the spectra at the two poles. In our experiments the tubes were excited by high potential alternating discharges, and the spectra at the two electrodes were identical.

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the ends. Since the lines of the Balmer series are strongly enhanced relatively to the secondary spectrum by very small traces of impurities, it is evident that the phenomena can be explained by an accumulation of the oxygen or other impurities in the central portions of the discharge tube. When however the total amount of impurity is excessively small, the accumulation of the greater part of it in the centre of the capillary may not be sufficient to weaken the secondary spectrum appreciably, and the capillary thus appears of a uniform white colour throughout its entire length. There are a number of other observations which appear to be related to these effects, but in the absence of any theory we do not venture to discuss them in the present communication.

(11) On Impurities in Vacuum Tubes.

It may perhaps be considered remarkable that any profound influence on the spectrum of a gas can be exerted by impurities which are present in such small quantities that their presence cannot be detected by any characteristic lines or bands in the spectrum. The difficulty of eliminating such impurities as those which give rise to the Angström carbon bands is of course familiar to all who have worked with vacuum tubes, but with the aid of charcoal cooled with liquid air there should be no difficulty in preparing tubes containing Hydrogen or Helium which would show no lines or bands other than those peculiar to these gases. This is indeed the case under the conditions usually obtaining, when the gases are contained in the tubes at pressures of a few millimetres; but it has been found that the difficulties are very much greater when it is desired to obtain vacuum tubes containing Helium at higher pressures up to 60 mm., which show no trace of impurities. The relative intensities of lines and bands due to impurities are enormously enhanced as the pressure increases, and the form in which the impurities appear is also often unusual. The influence of Helium on the secondary spectrum of Hydrogen is by no means unique, and a remarkable instance has been observed in the case of tubes containing Helium at high pressures and a very small trace of some carbon compound. If any considerable quantity of carbon is present the Ångström and Swan bands can be seen, but with a very small trace of carbon the "Comet" bands first observed by Fowler ('Monthly Notices R.A.S.,' vol. 70, p. 484, 1910) appear quite brightly in the bulbs of the tubes just outside the capillary. This effect was first observed by one of us in an investigation in collaboration with Dr. T. TAKAMINE, to whom we are indebted for a photograph which shows the "Comet" bands almost free from other bands associated with carbon compounds. Fowler (loc. cit.) has found that these bands appear with the greatest relative intensity in tubes in which the pressure is so low (0.01 to 0.005 mm.) that the luminosity of the discharge is very small, and yet we find them here in tubes containing Helium at pressures from 15 to 50 mm. This is only one example of the changes which may occur, and a number of other lines and bands have been observed in the case of other impurities. investigation of the phenomena is required, and we do not venture to discuss them in the present communication.

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(12) Summary.

- (1) A discussion is given of the conditions under which the Balmer series and the secondary spectrum of Hydrogen are produced.
- (2) The wave-lengths of about 1,200 lines in the secondary spectrum have been measured.
- (3) It has been found possible to classify the lines into different physically related groups under different conditions depending on the pressure of the gas in the discharge tube, the electrical conditions of excitation, and the presence of Helium.
- (4) These methods of classifying the lines have been compared with the results obtained by other investigators relating to the Stark and Zeeman effects, and with the regularities observed by Fulcher.
- (5) A comparison has been made of the wave-lengths of lines of different classes in the secondary spectrum with the Fraunhofer and Sunspot spectrum. the presence of the secondary Hydrogen in the Sun has been obtained.
 - (6) A new method of measuring the widths of spectrum lines has been developed.
 - (7) It has been shown that the secondary spectrum is due to the Hydrogen molecule.
- (8) Experiments have been made which appear to show that when electrical discharges are passed through vacuum tubes, a partial separation of the gases takes place, and this appears to afford a satisfactory explanation of a number of phenomena which have been observed.
- (9) A number of observations relating to the appearance of impurity lines in vacuum tubes are discussed.

We wish to express our thanks to the Department of Scientific and Industrial Research for a grant which has been made to one of us (S. B.) during the course of this investigation.

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(13) TABLE of Wave-lengths, &c., in Secondary Hydrogen Spectrum.

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.A.)	In Vacuo.	37.57	31.95	26.53	23.45	20.25	11.47	09.02	98.786	99.43	98.76	95.51	88.23	84.69	83.15	06.00	76.58	75.73	71.33	69.44	65.87	04.20	67.00	57.31	54.87	53.17	50.17	48.58	47.87	45.76	45.49	41.06	39.61	37.03
λ (Ι.Α.)	In Air.	35·85 32·99	30.23	24.81	21.73	18.53	09.75	07.31	01.15	97.72	97.05	93.80	86.52	82.98	8I.44	76.18	74.88	74.03	$69 \cdot 63$	67.74	64.17	02.20	59.58	55.61	53.17	51.47	48.47	46.88	$\frac{46.17}{63}$	44.06	41.13	39.36	37.91	35.34
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λ (Ι.Α.)	In Air.	6540·53	27.35	24.63	06.22	12.22	02.03	6499.87	97.88	87.76	75.32	73.63	96.56	65.22	11.92	50.02	45.31	41.50	40.65	37.81	34.80	33.47	98.10	18.33	11.77	05.71	04.01	6399.45	97.44	*96.53	92.99	87.87	88.88	80.11

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* Lines measured on one plate only.

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Table of Wave-lengths, &c., in Secondary Hydrogen Spectrum (continued).

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	In Vacuo.	53.29 52.51 50.93 48.91	45.07 44.18 43.03 41.45	40.77 39.38 37.59 34.50	32.61 30.39 27.17	26·14 24·41 23·69 20·92	19.22 18.00 16.61	13.09 09.87 09.20	06.27 06.27 05.53 03.47	800.55 98.19 96.25	93.34 91.45 89.85	86.81
λ (Ι.Α.)	In Air.	51.67 50.89 49.31 47.29	43.45 42.56 41.41 39.83	[39.15 37.77 35.98 32.89	31.00 [28.78 25.56	22.80 22.08 22.08	17.61 16.39 15.00	11.48	04.66 03.93 01.87	01.14 5798.95 96.59	91.74 89.85 88.25	85.91
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* Unresolved doublets.

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

TABLE of Wave-lengths, &c., in Secondary Hydrogen Spectrum (continued).

DR. T. R. MERTON AND MR. S. BARRATT

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	n. In Vacuo.	20.12	25.62	35.33	54.66	89.92	81.24	84.55	94.72	18408.17	07.79	14.48	24.83	27.17	33.96	37.63	40.80	45.52	52.57	58.69	80.26	83.30	91.16	94.96	03.40	16.80	19.79	31.56	39.73	43.52	53.88	58.93	02.09	63.24	76.26	82.30	04.13	05.30
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4 .)	In Vacuo.	58.48	56.84	53.95	48.21	41.68	40.33	39.35	36.34	32.37	32.48	30.07	27.46	26.77	24.77	23.69	22.76	21.40	19.30	17.50	11.18	10.29	08.53	98.98	02.20	401.40	66.63	96.20	93.82	92.72	89.71	$88 \cdot 24$	$87 \cdot 73$	86.99	83.21	81.29	78.04	74.81
λ (I.A.)	In Air.	56.97	55.33	52.44	46.70	40.17	38.82	37.84	34.83	30.86	[29.97	29.00	25.96	25.27	23.27	22.19	21.26	19.90	17.80	[16.00]	89.60	08.79	$\begin{bmatrix} 07.03 \\ 0.00 \end{bmatrix}$	05.38	90.TO	06.6666	98.13	194.70	92.32	91.22	88.21	86.74	86.24	85.50	[81.72	78.87	76.55	73.32
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	n. In Vacuo.	17572.31	88.10	91.33	93.02	17612.49	16.49	19.25	23.32	29.03	33.80	39.89	54.15	57.58	96.09	64.50	69.87	76.22	79.34	86.97	17702.47	06.39	16.87	42.02	43.49	50.03	65.11	75.19	79.04	85.81	17800.56	12.35	37.52	46.91	50.99	67.69	17909.41	06.23
Ł.)	In Vacuo.	12.06	85.66	84.62	84.07	77.79	76.50	75.61	74.30	72.46	70.93	16.89	64.39	63.29	65.40	61.07	59.35	57.32	56.35	53.88	48.93	47.68	44.34	36.34	35.87	39.30	99.01	25.82	24.60	22.46	17.80	14.08	06.16	03.21	01.93	81.66	85.82	84.65
λ (I.A.)	In Air.	5689.19	84.09	83.05	82.50	76.22	74.93	[74.04	72.73	10.89	69.36	67.40	62.82	$61 \cdot 72$	*60.83	*59.50	57.78	55.75	54.75	52.33	[47.37]	*46.12	42.78	34.78	*34.31	52.25 +30.74	97.45	24.26	23.04	20.90	16.24	12.53	†0 4 ·61	01.66	00.38	5597 - 63	06.18	83.10

† Unresolved doublets.

ON THE SPECTRUM OF HYDROGEN.

* Lines measured on one plate only.

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

TABLE of Wave-lengths, &c., in Secondary Hydrogen Spectrum (continued).

DR. T. R. MERTON AND MR. S. BARRATT

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s	In Vacuo.	19804.42	29.35	36.43	58.17	66.54	73.73	79.77	95.04	19904.34	11.75	26.03	28.93	34.14	36.56	42.41	49.80	56.13	02.00	19.79	00.00	93.68	20002.68	07.52	13.49	18.02	61.11	72.83	78.23	81.77	86.13	88.31	20101.92	08.02	79.11	27.89
4.)	In Vacuo.			41.23					29.14	24.03	22.16	18.56	17.83	16.52	15.91	14.44	12.58	10.99	76.60	08.30	00.60						<del>,</del>				78.56	78.02	74.65	73.14	02.27	68.23
λ (Ι.Α.)	In Air.	47.98	41.63	39.83	34.31	32.19	30.37	28.84	24.98	22.63	20.76	17.16	16.43	15.12	14.51	13.05	11.19	09.60	00.00	08.70	00.65	00.19	4997.94	96.73	95.24	94.11	83.38	80.47	79.13	78.25	77.17	76.64	73.27	71.76	70.97	98.99
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s	In Vacuo.	19001.87	11.4	18.39	$41 \cdot 7$	51.36	58.08	61.71	10.69 91.68	19108-77	16.9	26.97	35.3	38.72	61.65	46.93	0.89	71.45	9.97	90761	6.80 14.9	17.87	26.8	30.7	35.43	38.84	20.00	60.84	68 - 75	97.4	$19319 \cdot 37$	25.6	33.34	43.5	46.63	72.41
4.)	In Vacuo.	62.64	59.98	58.07	51.61	48.97	47.12	46.12	12.64	33.20	30.97	28.22	25.92	25.01	24.21	22.77	17.02	16.09	14.67	06.53	3.50	03.49	201.05	200.01	98.74	97.82	94.40	91.88	89.75	82.03	76.15	75.27	72.40	69.69	98.89	61.98
λ (Ι.Α.)	In Air.	5261.18	58.55	56.61	50.15	47.51	45.66	44.66	43.75 30.04	+31 · 75	129.52	26.77	24.47	23.56	22.76	21.32	15.57	14.64	13.22	05.09	6.40 6.50	02.05	5199.61	[98.57	97.30	86.38	95.02	90.44	88.31	80.59	74.71	73.83	96.07]	68.25	67.42	60·55

† Unresolved doublets.

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51.91	73.01	85.91	98.31	26.91	29.11	39.07	40.71	51.36	53.00	56.78	60.71	64.09	69.22	84.02	98.10	303.04	09.56	14.80	18.39	23.22	34.91	40.13	51.31	65.89	69.03	86.07	94.92	98.83	$20417 \cdot 25$	39.11	50.73	59.27	70.07	79.59	04.07	0.±0 0.503 0.503	07 000	10.15	10.01	30.59	40.59	85.07	00.312.00
62.31	57.12	53.95			43.37	40.94	40.54	37.94	37.54	36.62	35.66	34.84	33.59	29.99							17.65		13.69	10.17	09.40	04.99	03.18		$97.82 \mid 2$	92.58	89.80	87.78	\$1.68	89.93	70.48			#0.01	14.41	70.78	68.41		00 02
	55.74		.9.53 4.81	42.53	41.99	*39.57	39.17	36.57	36.17	35.25	34.29	33.47	32.22	28.62	25.20	24.00	22.42	21.15	20.28			-			08.03	03.55	01.81	88.00	4896.46	91.22	88.44	86.40	20.00	82.75 27.75	78.10	75.99	100	75.78	GA.67	69.42	67.05	56.54	70 07
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* Lines measured on one plate only.

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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Table of Wave-lengths, &c., in Secondary Hydrogen Spectrum (continued).

λ (I.A.)

In Air

Stark Effect.

Fulcher Lines.

Zeeman Effect.

Helium Effect.

Low Pressure.

High Pressure.

n. Vacuo.

In

λ (I.A.)

In Vacuo.

In Air.

Intensity.

Discharge. Condensed

#### DR. T. R. MERTON AND MR. S. BARRATT Stark Effect. Fulcher Lines. Zeeman Effect. 0 $\mathbf{Z}$ 0 88888 $\mathbf{Z}$ $\mathbf{Z}$ $\mathbf{Z}$ 10 Helium Effect. ++0 0 Discharge. Condensed ++ Low Pressure. High Pressure. ++ Intensity. 46.85 46.85 51.68 63.23 80.84 85.33 97.80 97.80 96.30 96.33 97.80 96.33 97.80 96.33 97.80 96.33 97.80 96.33 96.33 97.80 96.33 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97.80 97 $\frac{n}{V}$ acuo. In

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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

TRANSACTIONS SOCIETY A

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TRANSACTIONS SOCIETY A

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† Unresolved doublets.

* Lines measured on one plate only.

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TABLE of Wave-lengths, &c., in Secondary Hydrogen Spectrum (continued).

# DR. T. R. MERTON AND MR. S. BARRATT

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	n. In Vacuo.	15.48 $28.26$	30.91 $73.73$	80.45	$23501 \cdot 10$ $23500 \cdot 27$	04.58	60.12	91.80 $23613.92$	48.77	68.19	77.16 $23732.23$	45.75	51.06 56.18	68.56	73.97 89.81	97.68	$23804 \cdot 13$	27.51	63.04	16.24	19.95	29.91	99.03 44.64	E0 EE	82.42	87.88	24001.88
A.)	In Vacuo.	07.47	$04.61 \\ 96.69$	95.45	55.27	54.49	44.46	38·76 34·79	28.55	25.08	23.48	11.28	10.34	07.24	03.48	02.09	200.95	96.83	90.58	81.26	80.61	78.87	17.07	72.46	69.72	68.77	66.34
λ (I.A.)	In Air.	$\begin{array}{c} 06.26 \\ 03.89 \end{array}$	03.40	94.25	19.42 $54.07$	53·30 46·72	43.27	†31.57 †33.60	27.36	23.89	$\frac{122.30}{12.50}$	$\frac{10.10}{16}$	03.16 *08.25	90.90	02.30	00.91	4199.77	95.65	89.40	\$0.08	79.54	01.77	75.13	71.29	68.55	09.19	65·17 63·52
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ssure. d d trge. ffect. ffect.	In Vaccio.  Intensity.  High Pres Condensee Discha Helium E	10.39 22171.03 0 06.89 88.25 3	$06 \cdot 16 \begin{vmatrix} 91.84 \\ 03.94 \end{vmatrix} \begin{vmatrix} -22202.78 \\ 0 \end{vmatrix}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	500.83 18.12 0	23·31 2 + 0 25·39 6 + Z	94.93	2 ++ + +	87:30 85:12 3 Z S5:49 94:11 0	84.70 98.04 0	83.28   22305.10   1 + + 82.53   08.83   0	80.95 16.70 0	78.30 29.90 1	75.49 $43.92$ $2$ $+$ $++$ $Z$ $73.10$ $55.41$ $1$ $1$	$72.84$ $57.16$ $1$ $\pm$	68.37 79.53 3 +++ 0	$65 \cdot 37 \qquad 94 \cdot 56 \qquad 1 \qquad ++ \qquad Z \qquad 62 \cdot 21 \qquad 294 \cdot 10 \cdot 49 \qquad 5 \qquad ++ \qquad Z$	60.11  20.97  1  +  Z	58.02 31.48 2 0	54.27 50.37 1 ++	53.97 51.88 1	59.08 61.41 0	51.17 66.01 1 +	48.80 77.97 4 ++ Z	46.48 89.69 3	.20 45.44 94.96 1	0 69.10622 11.

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# ON THE SPECTRUM OF HYDROGEN.

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† Unresolved doublets.

* Lines measured on one plate only.

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DR. T. R. MERTON AND MR. S. BARRATT ON THE SPECTRUM OF HYDROGEN.

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Wave-lengths, &c., in Secondary Hydrogen Spectrum MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES LABLE of TRANSACTIONS COLLECT SOCIETY

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Stark Effect.

Fulcher Lines.

Zeeman Effect.

Helium Effect.

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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Unresolved doublets.

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* Lines measured on one plate only.