THE CONTINUOUS SPECTRUM OF HYDROGEN

By W. H. Crew and E. O. Hulburt

Abstract

Effect of the source on the continuous spectrum of hydrogen.—The continuous spectrum of hydrogen is observed to be of similar character, although of differing intensity, in a number of sources, a Wood tube, an ordinary discharge tube, the separate striations of the positive column, the condensed spark in hydrogen at pressures above atmospheric, and in the water spark. It is of appreciable intensity near $H\alpha$, rises slowly to a maximum in the near ultra-violet and descends slowly in intensity from λ300 to 220$\mu\mu$.

Theory of the continuous spectrum of hydrogen.—Bohr's idea, which attributes a continuous spectrum near the Balmer lines to an electron plunging from an unquantized energy region to the second orbit, together with Wright's theory that such unquantization may exist from any given orbit outwards, is given statistical formulation on the assumption that the plunging electrons obey a Maxwellian law of distribution. A formula for the distribution of energy across the continuous spectrum is obtained which involves an unknown probability, a_n, that the atom exist through the nth orbit, the region beyond being unquantized. When a_n is evaluated roughly from general physical considerations the formula agrees qualitatively with the continuous spectra observed in the hydrogen stars and the laboratory sources. It is recognized that the theory is a simple type of the more general theory of retardation spectra.

THE continuous spectrum of hydrogen has been the subject of many investigations, for example those of Stark,[1] Gehrcke and Lau,[2] Carst,[3] Richardson and Tanaka,[4] Steubing,[5] Blackett and Franck,[6] Schüler and Wolfe,[7] and others. Nevertheless, its origin and exact character remain uncertain. Bohr has suggested that a continuous spectrum extending into the ultra-violet due to hydrogen atoms should begin sharply at the Balmer series limit, λ3646A. In simple terms Bohr's theory is that an electron may fall into the second quantum orbit of the atom nucleus with an unquantized energy $mv^2/2$ greater than that necessary to emit the limiting line of the Balmer series. Thus, since $mv^2/2$ may increase continuously from zero, frequencies extending continuously from the series limit into the ultra-violet would be radiated. A continuous spectrum of about this sort occurs at the limit of the principal series of sodium

[1] Stark, Ann. d. Physik **52**, 221 (1917).
[2] Gehrke and Lau, Preuss. Akad. Wiss Berlin. Ber. **24**, 242 (1923).
[3] Carst, Ann. d. Physik **75**, 665 (1924).
[4] Richardson and Tanaka, Proc. Roy. Soc. **106**, 640 (1924).
[5] Steubing, Zeits. f. Physik **32**, 159 (1925).
[6] Blackett and Franck, Zeits. f. Physik **34**, 389 (1925).
[7] Schüler and Wolfe, Zeits. f. Physik **33**, 42 (1925).

and of potassium[8,9,10]; in these instances the continuous spectrum and the series lines were observed in absorption. In hydrogen a continuous spectrum exists in the region of the Balmer lines, but instead of originating at the Balmer limit it begins always on the red side of the Balmer limit. Therefore the simple theory of Bohr, which attributes a continuous spectrum to the hydrogen atom, if it is to be retained at all, requires modification. Such a modification is developed in the following pages. It follows in the main certain ideas sketched out very briefly by Wright,[11] but departs from those ideas at certain points. Spectrograms of the continuous spectrum of hydrogen have been obtained under a variety of experimental conditions and are discussed in the light of the theoretical formulas.

Theoretical

The frequency ν_n of a Balmer line is given by the relation

$$h\nu_n = W_n - W_2 \tag{1}$$

where W_n and W_2 are the negative energies of the electron in the nth and the second quantum orbits, respectively. We assume with Wright[11] that an atom may possess quantum orbits out through the nth only. The orbits beyond the nth are broken off, so to speak, and the region is unquantized. It follows that an electron can fall into the second orbit from the nth with an energy greater than its orbital energy in the nth orbit by an amount $mv^2/2$, which may vary continuously from zero to infinity. Radiation of frequency ν will be emitted, where $h\nu = W_n + mv^2/2 - W_2$. This together with (1) yields

$$h\nu = h\nu_n + mv^2/2 \quad . \tag{2}$$

As $mv^2/2$ takes values from zero to infinity, ν maps out a continuous spectrum, either of emission or absorption, associated with each Balmer line, which begins at the line and extends to the shorter waves.

The distribution of energy across the continuous spectrum is calculated by statistical methods. In an assemblage of atoms of luminous hydrogen we may suppose that all types of atoms will be present in greater or less degree, excited to various energy levels, some with only a few quantized orbits and others with a greater number. The complete radiation which is emitted, or absorbed, as in the case of a bright back-

[8] Wood, Astrophys. J. **29**, 97 (1909).

[9] Bevan, Proc. Roy. Soc. **85**, 54 (1910).

[10] Holtsmark, Phys. Zeits. **20**, 88 (1919).

[11] Wright, Nature **109**, 810 (1922); see also Nicholson, Roy. Ast. Soc. Monthly Notices **85**, 253 (1925).

ground spectrum transmitted through the hydrogen, will be made up of the contributions of the Balmer lines and the continuous spectra from the various types of atoms. It is assumed that the hydrogen gas is in thermo-dynamic equilibrium and that the distribution of energy among the free electrons may be calculated from the usual formula of the kinetic theory. The number of electrons of energy $mv^2/2$ is then proportional to

$$\tfrac{1}{2}mv^2\epsilon^{-mv^2/2KT} \tag{3}$$

where T is the absolute temperature and K is the molecular gas constant, 1.372×10^{-16} ergs per degree Kelvin. We shall assume that (3) dictates the distribution of energy among the electrons which plunge into the second orbit of the hydrogen atoms giving rise to radiations. The intensity I_ν' of radiation of frequency ν is also proportional to expression (3), and upon introducing (2) we obtain

$$I_\nu' = a_n h(\nu-\nu_n)\epsilon^{-h(\nu-\nu_n)/KT}. \tag{4}$$

a_n is constant with respect to ν, but in general varies with n. Eq. (4) gives the intensity across the continuous spectrum for each value of n. We note that the curves of I_ν' plotted against wave-length descend to zero at each Balmer line; see, for example, Fig. 1. The complete continuous

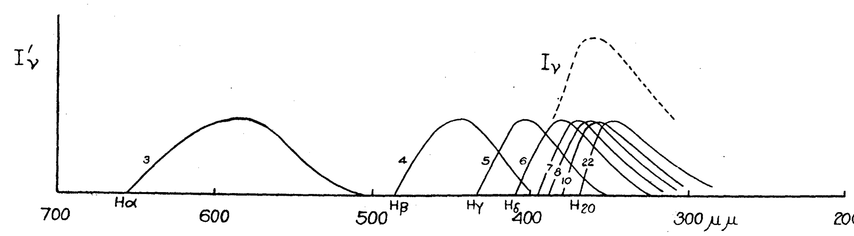

Fig. 1. Theoretical curves of I_ν' and I_ν for hydrogen at 2500°K, as in the reversing layers of the stars.

spectrum is the sum of the separate spectra, and the resultant intensity I_ν of radiation ν of the complete spectrum is

$$I_\nu = \sum_{n=2}^{n=\infty} a_n h(\nu-\nu_n)\epsilon^{-h(\nu-\nu_n)/KT}. \tag{5}$$

The relative intensity of the separate continuous spectra of the summation of (5) is given by a_n. This quantity is equal to the product of two factors a_n' and a_n'', a_n' being the probability of the existence of orbits out to and including the nth, and a_n'' the probability of the non-existence of orbits beyond the nth. (We must remember that the geometrical manner of speaking is perhaps only figurative, what is really in mind is an interplay of energy transfers.) It would seem possible to evaluate a_n' and a_n'' from the observed intensities of the Balmer lines. An attempt to do this, however, by the use of Einstein's probability coefficients after the manner of Milne[12] was unsuccessful because of a welter of unknown quantities and uncertainties of assumption. At any rate, a_n' obviously decreases rapidly with n. a_n'' increases rapidly with n, for the chance that an atom exists with all its orbits removed beyond the third, for example, is certainly small, whereas an atom with orbits absent beyond the fifteenth, say, may exist more readily. The product $a_n' \times a_n''$, or a_n, may from general physical considerations be expected to be small for small values of n, larger for intermediate values, and smaller again for high values of n.

The theory of Wright is the same as the foregoing theory in that the orbits below the nth are assumed to be quantized and those above unquantized, but differs in respect to the nth orbit. This is taken to be partially quantized. As a result the I_ν' curves will not drop to zero at each Balmer line but will extend to the red of the line. The experimental evidence may be represented equally well by either theory. As a matter of fact, it is hardly to be expected that either of these views is entirely correct. We recognize them to be special cases of the general retardation spectra which may occur when an electron loses energy in passing near an atom nucleus. And, quoting Sommerfeld,[13] "Everything still remains to be done for the proper theory of this retardation spectrum." There may be, as others have pointed out (for example, Stark[1]) more than one type of continuous spectrum emitted by luminous hydrogen, although the present experiments give no certain indication of this, one associated with the atoms, perhaps, one with the H_2 molecules, etc. These possibilities are included in a general way in the idea of the retardation spectrum. For, if the spectrum arises from the interaction of an electron and a hydrogen nucleus, the nucleus may be that of a free (i.e., undisturbed) atom, or that of an atom disturbed by surrounding atoms or ions which may or may not be attached to it sufficiently firmly to form molecules, or that of an atom disturbed in some other way. Indeed, the conception of the retardation spectrum is such a general one as to be almost unsatisfactory. It will now be apparent that although we have spoken of atoms in deriving the formulas, we have not meant necessarily the free partcles of a monatomic gas; the atom deprived of its outer orbits, as we put it, may very well be part of a molecule, or it just as well may not be. Therefore the explicit use of the Balmer orbits must be

[12] Milne, Phil. Mag. **47**, 209 (1924).

[13] Sommerfeld, Atomic Structure and Spectral Lines, 451 (1922).

regarded as illustrative, and the formulas as first, and perhaps distant, approximations.

Stellar Spectra

In the spectra of the stars and nebulae[14] which exhibit a well developed Balmer series, usually of absorption, a continuous spectrum is seen near the series limit. This appears to have a maximum of intensity in the region of the limit and to extend a short way to either side, 10 to 200A to the red of the limit and possibly 400A, or less, to the short wave side. With $T=2500°$K the curves of I_ν' against λ, where λ is the wave-length corresponding to the frequency ν, were calculated from (4) for each value of n and are plotted in the heavy line curves of Fig. 1. The value of n is written alongside each curve in the figure; for $n=3$, the curve corresponds to H_α, for $n=12$, to H_{10}, etc. The curve for $n=2$ is not drawn; its maximum is at $\lambda 5.76\mu$, and it makes a negligible contribution in the region of the spectrum under consideration. On the scale of Fig. 1 H_{30} is indistinguishable from H_{20}. The maximum ordinates of all the curves are made equal, this means that a_n was the same for all values of n. The final intensity curve I_ν, from (5), is obtained by adding the ordinates of the I_ν' curves of Fig. 1, assigning to each curve its value of a_n. In order to make the I_ν curve, sketched in the dotted line of Fig. 1, agree with the observed continuous spectra of the hydrogen stars, a_n must be small for the earlier and later values of n; so that only the I_ν' curves for n from, say, 9 to 22 make appreciable contributions to the I_ν curve. This type of variation of a_n with n is in reasonable accord with the physical notions of low temperatures and pressures in the reversing atmospheres of the stars and with the low decrement of the Balmer line intensities.

Experiments

A long hydrogen tube constructed after the manner of Wood[15] with the light coming end-on through a quartz window from the central portion only was operated in the "black stage," i.e., the Balmer lines strong and the molecular lines relatively weak. Moist hydrogen was introduced into the tube through a slender glass capillary and was excited by a 10 kv, 1 kw, 500 cycle transformer. The continuous spectrum always appeared in the spectrum of this tube. In general as the conditions of pressure, water vapor, current, etc., in the tube were changed so as to increase the purity of the atomic lines the continuous spectrum became

[14] Hartmann, Phys. Zeits. **18,** 429 (1917); see also Wright, loc. cit. 11, and Ch'ing-Sung Yü, Lick Observatory Bulletin, No. 375, 1926.

[15] Wood, Proc. Roy. Soc. **97,** 455 (1920).

weaker throughout its entire extent. With exposures sufficiently long to bring out sixteen of the Balmer lines the continuous spectrum began somewhere near H_α and extended smoothly to the ultra-violet limit of observation λ230μμ. None of these spectrograms are reproduced here.

With dry hydrogen in the tube at a pressure of 6 to 8 mm of mercury, the continuous spectrum was of the same general character as that of the Wood tube. It was, however, vastly more intense and could be followed visually into the red easily as far as H_α, and perhaps beyond. The spectrum is shown in the two strips *a* and *b* of Fig. 2, for the longer and shorter wave-length regions, respectively. On strip *b* is an iron com-

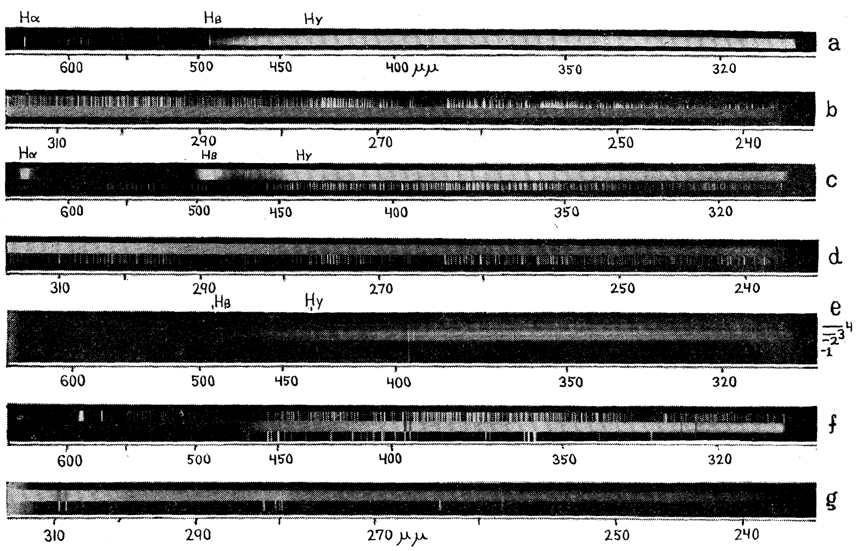

Fig. 2. Continuous spectrum of hydrogen from various sources; *a* and *b*, ordinary discharge tube, pressure 8 mm of mercury; *c* and *d*, condensed spark in hydrogen at one and a half atmospheres; *e*, striations of the positive column; *f* and *g*, condensed spark between aluminum terminals in water.

parison spectrum. As seen in the visual spectrograph the continuous spectrum fell off to the red above H_β much less slowly than strip *a* would indicate; the rapid decline there is due to the insensitiveness of the panchromatic plate in the yellow-green. The slow decline in intensity towards the ultraviolet in the region λ3000 to 2300A of strip *b* is really less rapid than it appears to be, for the dispersion of the spectrograph is increasing to the shorter wave-lengths. We may conclude that the continuous spectrum began in the red, rose gradually to a mild maximum of intensity in the near ultra-violet, and then fell off slowly in the region

[16] Lewis, Phys. Rev. **16,** 367 (1920).

λ3000 to 2300A. We may supplement this with a statement from Lewis[16] that the spectrum falls to a very low intensity at about λ1750A.

The spectrum of strips *a* and *b*, Fig. 2, is the spectrum of the "ordinary" hydrogen tube. Such a tube is a relatively weak source of visible light, but a very powerful source of ultra-violet light. When the conditions in in the tube are changed to bring out the Balmer spectrum the reverse is true, the tube gives a very brilliant visible light and but little ultra-violet light. Sensible evidence of this is obtained by sniffing the ozone in front of the tube.

In applying the formulas to the vacuum tube continuous spectra a temperature of 20,000°K is assumed. The curves from (4) are given in Fig. 3 plotted with a_n constant, i.e., maximum ordinates equal. The maximum of the I_ν' curve for H_α ($n=3$) is at λ343μμ. If a temperature 10,000° had been chosen the maximum would have been at λ450μμ, and the curves would differ but little from those of Fig. 3. The I_ν' curve for $n=2$, which is a maximum at λ716μμ, drops off slowly across the visible and ultra-violet spectrum. It refers to the atom stripped of all its orbits down to the second. To obtain the I_ν curve, sketched in the dotted line of Fig. 3, in agreement with the vacuum tube continuous spectrum, we

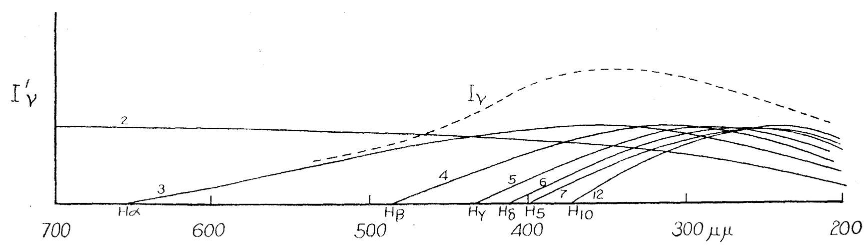

Fig. 3. Theoretical curves of I_ν' and I_ν for hydrogen at 20,000°K, as in a discharge tube.

must give greater importance to a_n for the earlier values of n. This is in keeping with the relatively high temperatures and pressures of the vacuum tube and the rapid decrease of the Balmer line intensities. Whether the I_ν' curve for $n=2$ should be considered at all is an open question. If the present view is correct one could perhaps decide this by observing whether the continuous spectrum extended to the red of H_α. This was attempted many times visually and photographically, with the result that a faint luminosity to the red of H_α was observed, so faint, however, that it may have been due to scattered light in the spectrograph. In this connection it may be mentioned that the ideas of this paper extended to the Lyman and infra-red levels of atomic hydrogen would lead to the possibility of continuous radiation, probably weak, veiling the visible and ultra-violet regions of the spectrum.

We may now pass to an examination of the continuous spectrum from hydrogen at higher pressures. A Pyrex bulb with a quartz window was fitted with two aluminum electrodes about 5 cm apart and was filled with dry hydrogen at a pressure of about one and a half atmospheres. The quartz window was arranged to view only the central portion of the discharge and not the electrodes. The spectrum of vigorous condensed discharges, about 7 amp., through the hydrogen was photographed and is shown in strips *c* and *d*, Fig. 2, for the longer and shorter wave-length regions respectively. In strip *c* the Balmer lines are greatly broadened, due to the Stark effect,[17] and soon fuse together in the march of the series to form a continuous spectrum, $H\gamma$ being the last line to appear separated from its neighbors. At the same time a continuous radiation extends throughout the entire spectrum. This has much the same characteristics as those of the lower pressure hydrogen of strips *a* and *b*, except that it declines more rapidly in intensity in the ultra-violet. Strip *d* is perhaps three times as strong as *b* at λ3100 and somewhat weaker than *b* at λ2400. Its maximum of intensity is apparently somewhere in the near ultra-violet. The molecular lines do not occur at all in this spectrum, and the more prominent aluminum lines but faintly. The spectrum of the high pressure hydrogen saturated with mercury vapor was much the same as that of strips *c* and *d* with the addition, of course, of the mercury lines. The line 2536A was reversed and broadened. There was no diminution of the continuous spectrum below λ2536A corresponding to the first resonance potential of mercury, as might be expected from the experiments of Schüler and Wolfe.[7]

For the hydrogen at the greater pressures, and possibly greater temperatures, the higher orbits may be expected to be even more unstable than for the lower pressure hydrogen of strips *a* and *b*, Fig. 2. Consequently, a_n for $n=2, 3, 4$, etc., must be given even greater weight over the later values than was done for the lower pressure hydrogen. This will yield an I_ν curve which drops off faster in the ultra-violet than the curve of Fig. 3, in entire conformity with the spectrum of strip *d*, Fig. 2.

An experiment by Horton and Davis[18] in which a continuous spectrum was obtained entirely free from atomic lines deserves a few remarks. They observed that hydrogen at a moderate pressure, less than 1 mm of mercury, excited by electrons of energy less than 15 volts became suffused with a blue glow which yielded a continuous spectrum with no traces of lines of the molecular or atomic spectra. The continuous

[17] Hulburt, Phys. Rev. **21,** 24 (1923).
[18] Horton and Davis, Phil. Mag. **46,** 872 (1923).

spectrum, although fading out towards the red, definitely extended to the long wave side of $\lambda 478\mu\mu$. This is the wave-length corresponding to 2.4 volts, which was the dissociation potential ascribed to H_2. It was therefore suggested that the continuous spectrum, in part at any rate, might possibly be attributed to the formation of aggregates such as H_3.

In the present instance we have obtained this low voltage spectrum in a slightly different way. A small straight glass discharge tube 15 cms long and 7 mm inside diameter with aluminum electrodes at either end was excited with 500 cycle alternating current rectified by a kenotron. (The rectified current was used merely because of convenience, direct current would have served as well.) The tube was connected permanently to a large bottle of about 10 liters capacity, in order to maintain the pressure steady, and the whole system was filled with dry hydrogen. At a pressure of about 1 mm of mercury the first striation of the positive column, the striation next to the Faraday dark space, appeared a vivid blue, whereas the other striations were pinker or whiter. The blue striation was usually narrower than its neighbors. The image of this tube was focussed broadside on the slit of the spectrograph, so that the spectra of several striations could be observed simultaneously. These are shown in strip *e*, Fig. 2. Region 1 of the strip is the Faraday dark space, 2 the blue striation, 3 the second striation, and so on. It is seen (as well as the reproduction will permit) that the spectrum of the blue striation is a continuous spectrum free from the Balmer and molecular lines, whereas the other striations of the positive column contain all three spectra. The continuous spectrum of the blue striation is evidently the same as that in the low voltage experiment of Horton and Davis. For Bramley[19] has found that at pressures of the order of 1 mm of mercury the electrons in the striation nearest the cathode have velocities of about 10 to 15 volts. Furthermore, at these pressures Smyth and Brasefield[20] in a positive ray analysis of the ions in the positive column of hydrogen have observed a large proportion of H_3^+ ions.

We regard this low voltage continuous spectrum as a retardation spectrum of much the same type as the other vacuum tube continuous spectra of Fig. 2. The strong concentration of H_3^+ ions in the regions where the spectrum arises is taken to mean that in these regions partially or completely unquantized atomic nuclei exist. An experiment in keeping with these general ideas is that of Lemon[21] who observed a continuous spectrum of unusual intensity from hydrogen excited by a one ampere current

[19] Bramley, Phys. Rev. **26,** 794 (1925).
[20] Smyth and Brasefield, Phys. Rev. **27,** 514(A) (1926).

of electrons from a hot cathode at 100 volts. These violent conditions are exactly suitable for the removal of the outer quantum orbits (always speaking geometrically) and therefore a strong retardation spectrum would be anticipated.

The spectrum of the condensed spark between aluminum terminals in hydrogen at pressures above atmospheric, as in strips *c* and *d*, Fig. 2, is remarkably similar to the spectrum of the condensed spark between aluminum terminals under water[22] shown in strips *f* and *g*, Fig. 2. The type of electrical excitation and the current, 7 amp., were the same in each case. This suggests that the continuous spectrum of the water spark is a retardation spectrum arising from electrons plunging into or near hydrogen nuclei. This is supported by the fact that the character of the continuous spectra from the water spark is unaffected by the kind of metal used for the electrodes. It seems probable that the hydrogen nuclei are more important to the production of the continuous spectrum than other atoms. For a spark between aluminum terminals under carbon tetrachloride was found to yield a much weaker continuous spectrum, although otherwise like that in water. The carbon tetrachloride was the commercial material and may have contained hydrogen in the impurities; also, no effort was made to rid the electrodes of hydrogen. Further, the spectrum of the condensed spark between aluminum terminals in dry air at atmospheric pressure,under the same conditions as in hydrogen, possessed a much fainter background continuous spectrum than that from hydrogen. The fact that the continuous spectrum appears strongest in hydrogen, next strongest in helium, and less strong in other elements (the meager experimental data allow no certain estimates farther into the periodic table) suggests that the intensity of the continuous spectrum is a decreasing function of the mass of the atomic nucleus.

In conclusion we may call attention to the uses of the various sources of continuous spectra for investigations in the ultra-violet. The most intense source is the spark in water or in hydrogen at a high pressure, and is useful for qualitative experiments such as the observation of absorption lines, etc. It is not at all difficult to arrange and operate. Like any spark it is unsteady and therefore unsuited for quantitative spectrophotometry. Aluminum or copper are convenient metals for the electrodes of the water spark, the aluminum preferably in the form of duralumin and the copper in phosphor bronze, for these alloys splinter away less rapidly than the pure metals. As a source sufficiently steady for quantitative measure-

[21] Lemon, Nature **113,** 127 (1924).

[22] Hulburt, Phys. Rev. **24,** 129 (1924).

ments there seems to be nothing better than the ordinary hydrogen tube, 5 to 10 mm in diameter and at a pressure of 2 to 10 mm of mercury, used end-on. Its spectrum is very uniform throughout the entire region from $\lambda 500$ to $200 \mu\mu$, which is a great advantage. The most serious disadvantage is the weakness of its spectrum; this, however, may be overcome to some extent by allowing the tube to absorb considerable electrical energy.

NAVAL RESEARCH LABORATORY,
WASHINGTON, D. C.,
July 22, 1926.

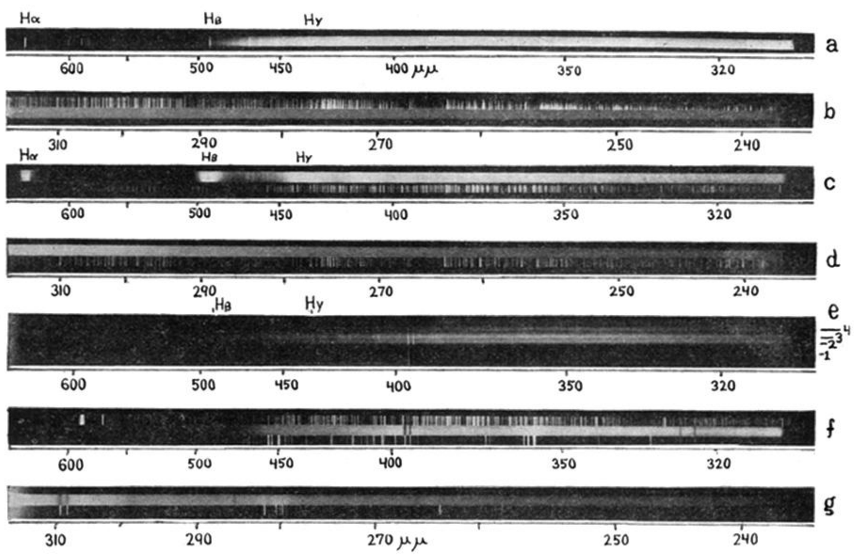

Fig. 2. Continuous spectrum of hydrogen from various sources; *a* and *b*, ordinary discharge tube, pressure 8 mm of mercury; *c* and *d*, condensed spark in hydrogen at one and a half atmospheres; *e*, striations of the positive column; *f* and *g*, condensed spark between aluminum terminals in water.