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Determination of Ion Density and Temperature
of a Water-Stabilised Arc from Observations of
the Line Profiles of the Hydrogen Lines $H\beta$ and $H\gamma$

By

P. S. Pusey, B.Sc., K. C. Lapworth, M.Sc., Ph.D. and

*A. F. Metherell of the Aerodynamics Division,
National Physical Laboratory*

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of the Line Profiles of the Hydrogen Lines $H\beta$ and $H\gamma$ *

- By -

P. S. Pusey, B.Sc., K. C. Lapworth, M.Sc., Ph.D.
and A. F. Metherell

of the Aerodynamics Division,
National Physical Laboratory

SUMMARY

The ion density in the plasma of a water-stabilised arc has been determined by applying Holtsmark's theory to the observed profiles of $H\beta$ and $H\gamma$. The ion density so determined was used to compute the temperature of the arc.

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List of Symbols

N	=	number of perturbing particles per c.c. here taken to be equal to the number of ions per c.c.
n_e	=	number of electrons per c.c.
n_{H^+}	=	number of hydrogen ions per c.c.
n_{O^+}	=	number of oxygen ions per c.c.
n_H	=	number of neutral hydrogen atoms per c.c.
n_O	=	number of neutral oxygen atoms per c.c.
F	=	strength of electric field at a hydrogen atom due to the surrounding ions
F_0	=	normal electric field strength
β	=	F/F_0
$W(\beta)$	=	probability of F
I	=	intensity of a spectrum line
I_m	=	intensity of the m th Stark component
C_m	=	Stark coefficient
$\Delta\lambda$	=	wavelength displacement from undisturbed line centre
α	=	βC_m
$S(\alpha)$	=	a function of α
μ	=	a scaling factor
m	=	electron mass = 9.107×10^{-28} gm
e	=	charge on electron = 4.80×10^{-10} e.s.u.
k	=	Boltzmann's constant = 1.380×10^{-16} erg per degree
h	=	Planck's constant = 6.624×10^{-27} erg sec
T	=	absolute temperature in degrees Kelvin
B_{H^+}	=	partition function for the hydrogen ion
B_H	=	partition function for the neutral hydrogen atom
B_{O^+}	=	partition function for the oxygen ion
B_O	=	partition function for the neutral oxygen atom
χ_H	=	ionisation potential of the hydrogen atom
χ_O	=	first ionisation potential of the oxygen atom
$\Delta\chi$	=	depression of the ionisation potential due to ions
ψ_H ψ_O	=	functions defined by equations (4.3.7) and (4.3.8)
p	=	pressure (here taken to be 1 atmosphere = 1.013×10^8 dynes cm^{-2})
ϕ	=	function defined by equation (4.3.12)

1. Introduction

The profile of a spectrum line carries much information about the source from which it comes. This has led to theoretical and experimental work aimed at understanding the relationship between the properties of the radiating source and the spectrum line profiles. The causes leading to spectrum line broadening may be divided into two categories, namely, those effects which are associated with the radiating atom itself and those effects due to interference with a radiating atom by surrounding atoms, ions and electrons. These effects are summarised below:

I Broadening associated with the radiating atom alone.

- (a) Natural broadening
- (b) Doppler effect

II Broadening associated with interference by surrounding particles.

- (a) Impact broadening
- (b) Statistical broadening

In the cases of interest to us class I broadening is small compared with class II broadening and will be neglected. In class II broadening, interest centres on plasmas which are in thermodynamic equilibrium and a large fraction of the particles are ions and electrons. Ions and electrons have a larger effect on radiating atoms than neutral particles because of the strong, far reaching electric fields associated with ions and electrons. In the following, only the broadening effects of charged particles are taken into account.

A discussion and review of the phenomenon of spectrum line broadening is the subject of another paper in preparation and will not be dealt with in detail here. An excellent review has been given by Margenau and Lewis¹.

Spectrum line broadening has been of interest in astrophysics for many years and has recently become of interest in work with high temperature facilities such as welding arcs, high enthalpy hypersonic flow, strong shock waves and rapid electrical discharges.

The experiments described here have been conducted using a water-stabilised arc in which the arc is constricted and held steady by being struck inside the core of a water-vortex. The water in contact with the arc is decomposed to form hydrogen and oxygen at the high temperatures achieved with this device. The spectrum lines from the heated hydrogen are very broad and, in the observations described here, these broadened profiles have been used to find the ion density by treating the profiles according to Holtsmark's statistical theory of line broadening². Recent careful work carried out at Kiel has however shown that the statistical theory taking only the ions into account does not adequately describe the line profiles and strictly it is necessary to take account of the impact broadening due to electrons.

In the present work however the more simple approach of applying the statistical theory of line broadening has been adopted since the necessary computed data were available and reasonable accuracy for ion densities can be obtained with this more simple approach. The ion densities found using the profiles of H β and H γ were used to calculate the temperature of the plasma. The temperature is not very sensitive to the ion density and is given with good accuracy even when the ion density is in error.

This work is regarded as a starting point for line broadening studies in plasma spectroscopy. The case treated here has received considerable attention from other workers and has proved valuable in gaining experience in the experimental technique and in gaining better understanding of the theoretical work.

2. The water-stabilised Arc

This device, first developed by Maeker in 1951³ attains high current densities in the arc column by constructing the arc flame inside the core of a water-vortex. The arc is shown in Fig.1 and plate 1.

The arc is struck between hollow carbon electrodes by passing a carbon starting electrode along one hollow carbon electrode until it makes contact with the other electrode. The water vortex serves to constrict the arc flame and also prevents it wandering too much. The hollow electrodes make end-on viewing of the arc possible and all our ion density determinations were made using this configuration. An enlarged picture of the arc running inside the water vortex is shown in plate 2.

3. Experimental Procedure

3.1 Power supply and circuit

The arc was run from a 240 volt d.c. supply with a ballast resistance of 1 ohm made up from a series-parallel arrangement of nine 1 ohm heavy duty resistors. The arc current, determined by measuring the voltage across a low resistance was 66 amps.

3.2 Optical arrangement (Fig.2)

The arc discharge, viewed end on, was focused on the slit of a Littrow glass spectrograph. A mirror could be placed on the optical axis so as to focus on the slit either a tungsten strip lamp for intensity calibration of the plate or an iron arc for wavelength calibration. The iron arc could also be interchanged with a Guild hydrogen discharge tube to obtain the spectrum of unbroadened hydrogen lines.

The plate was calibrated for response to intensity by placing a six-step rhodium-on-quartz filter in front of the slit uniformly illuminated by the tungsten strip lamp.

3.3 Photographic procedure

The exposure time of the plate to the tungsten calibrating lamp was made not too different from the time of exposure to the water-stabilised arc so as to avoid reciprocity failure. The plates used were Ilford SR 20. These were developed in microphen (a fine grain developer) and were brushed with a very soft brush during development so as to reduce the Eberhard effect.

3.4 Densitometry

The blackening profiles were obtained using a Joyce-Loebl Mark III microdensitometer. Relative intensity was related to plate blackening by means of the stepped filter calibration.

4. Treatment of the Results

4.1 To obtain intensity profiles from the blackening profiles

A curve of densitometer reading against relative exposure as determined by each step of the stepped filter was obtained at the wavelengths of $H\beta$ and $H\gamma$. The densitometer deflections of the blackening profile could then be related to relative intensities to give the intensity profiles of the lines.

The wavelengths corresponding to different positions on the plate were found by plotting wavelength against position for the iron lines and using this graph to find the wavelength corresponding to any position on the plate.

4.2 Method of obtaining ion densities from the line profiles

The line profile is the result of all the Stark components of the line which are broadened by the random microfields and overlap to give the whole broadened line contour. It can be shown that the probability $W(\beta)$ of a field F occurring at the atom is given by

$$W(\beta) = \frac{4\beta}{3\pi} \int_0^\infty e^{-u} u^{\frac{1}{3}} \sin(\beta u^{2/3}) du \quad \dots (4.2.1)$$

where $\beta = F/F_0$. F_0 is called the "normal field" and is given by

$$F_0 = 2.61eN^{2/3} \quad \dots (4.2.2)$$

where N = number of ions per c.c.

Schmaljohann has found the value of this integral graphically for various β and tabulated the results in his report⁴. He also gives a graph of $W(\beta)$ against β . In a constant field F each line is split into a number of Stark components. For the m th component let the intensity be I_m and the displacement from the field free position be $\Delta\lambda$. Then,

$$\begin{aligned} \Delta\lambda &= C_m F \\ &= C_m \beta F_0 \end{aligned}$$

where C_m is the Stark coefficient.

In a field due to random distributions of ions, the intensity I_m must be modified by the probability of the field. The contribution from this component in the wavelength interval $\Delta\lambda, \Delta\lambda + d(\Delta\lambda)$ is given by

$$Id(\Delta\lambda) = I_m W\left(\frac{\Delta\lambda}{C_m F_0}\right) \frac{d(\Delta\lambda)}{C_m F_0} \quad \dots (4.2.3)$$

If we write $\Delta\lambda = \alpha F_0$ and sum over all Stark components, the intensity at displacement $\Delta\lambda$ in the interval $\Delta\lambda, \Delta\lambda + d(\Delta\lambda)$ is given by

$$\begin{aligned} I F_0 d\alpha &= \sum_m \frac{I_m}{C_m} W\left(\frac{\alpha}{C_m}\right) d\alpha \\ &= S(\alpha) d\alpha \quad \dots (4.2.4) \end{aligned}$$

The function $S(\alpha) = \sum_m \frac{I_m}{C_m} W\left(\frac{\alpha}{C_m}\right)$ can be calculated from

Stark data. This has been done by Schmaljohann for the lines H_α to H_δ . When $F_0 = 1$, $\alpha = \Delta\lambda$. Therefore, $S(\alpha)$ may be regarded as the line profile obtained when the normal field, F_0 , is 1 e.s.u. Schmaljohann's curves are normalised to give

$\int_{-\infty}^{+\infty} S(\alpha) d\alpha = 1$. According to the statistical theory of line broadening, the shape of the line profile is the same for all F_0 apart from a scaling factor. If the observed profile of one of the Balmer lines is normalised

to make $\int_{-\infty}^{+\infty} Id(\Delta\lambda) = 1$, and then plotted on a log-log graph, it will,

according/

according to the theory have the same shape as a plot of $\log S(\alpha)$ against $\log \alpha$ but will be displaced horizontally and vertically by an amount equal to the logarithm of the scaling factor. Hence the scaling factor may readily be derived and from this F_0 may be calculated and hence N determined⁵.

The procedure for the treatment of the results is set out below.

- (a) The line profile I v. $\Delta\lambda$ is obtained as described in 4.1.
- (b) The intensity scale is arbitrary. These relative intensity units are multiplied by a suitable factor to make

$$\int_{-\infty}^{+\infty} Id(\Delta\lambda) = 1.$$

- (c) From Schmaljohann's tabulated results of $S(\alpha)$ a plot of $\log_{10} S(\alpha)$ against $\log_{10} (\alpha)$ is prepared. On the same graph, $\log_{10} I$ against $\log_{10} (\Delta\lambda)$ is plotted, using the values of I adjusted to give the normalised profile. $\log_{10} I$ is plotted along the same axis as $\log_{10} S(\alpha)$. If Holtsmark's theory holds good, the two curves should be parallel to one another but displaced.

- (d) To obtain F_0

A curve of $S(\alpha)$ against α gives the line profile for $F_0 = 1$. If the statistical theory holds good, any line profile may be obtained by suitably scaling the profile of $S(\alpha)$.

Let

$$\left. \begin{aligned} I &= \mu S(\alpha) \\ \Delta\lambda &= \alpha F_0 \end{aligned} \right\} \quad \dots (4.2.5)$$

where μ is a scaling factor.

Since the profile has been normalised,

$$\int_{-\infty}^{+\infty} Id(\Delta\lambda) = \int_{-\infty}^{+\infty} S(\alpha) d\alpha = 1 \quad \dots (4.2.6)$$

From (4.2.5)

$$\int_{-\infty}^{+\infty} Id(\Delta\lambda) = \mu F_0 \int_{-\infty}^{+\infty} S(\alpha) d\alpha \quad \dots (4.2.7)$$

Comparing (4.2.6) and (4.2.7),

$$\mu F_0 = 1 \quad \dots (4.2.8)$$

From (4.2.5)

$$\left. \begin{aligned} \log_{10} I &= \log_{10} \mu + \log_{10} S(\alpha) \\ \log_{10} (\Delta\lambda) &= \log_{10} \alpha + \log_{10} F_0 \end{aligned} \right\} \quad \dots (4.2.9)$$

From (4.2.8) and (4.2.9),

$$\left. \begin{aligned} \log_{10} I &= -\log_{10} F_0 + \log_{10} S(\alpha) \\ \log_{10} (\Delta\lambda) &= \log_{10} F_0 + \log_{10} (\alpha) \end{aligned} \right\} \quad \dots (4.2.10)$$

From (4.2.10) it is seen that a plot of $\log_{10} I$ against $\log_{10} \Delta\lambda$ will give a curve parallel to that obtained by plotting $\log_{10} S(\alpha)$ against $\log_{10} \alpha$. The former curve however will be displaced downwards and to the right relative to the latter curve by $\log_{10} F_0$. This displacement is readily measured and hence $\log_{10} F_0$ is obtained. The ion density is then obtained from the relationship

$$\log_{10} N = \frac{3}{2} \log_{10} F_0 + 13.3536$$

4.3 Calculation of the temperature from the ion density*

In the plasma of the water-stabilised arc suppose that there are

- n_e electrons per c.c.
- n_{H^+} hydrogen ions per c.c.
- n_{O^+} oxygen ions per c.c.
- n_H neutral hydrogen atoms per c.c.
- n_O neutral oxygen atoms per c.c.
- N ions per c.c.

The plasma as a whole is electrically neutral. Therefore,

$$n_{H^+} + n_{O^+} = n_e \quad \dots (4.3.1)$$

$$n_e = N \quad \dots (4.3.2)$$

Using the fact that for every oxygen atom there must be two hydrogen atoms,

$$n_H + n_{H^+} = 2(n_O + n_{O^+}) \quad \dots (4.3.3)$$

The Law of Partial pressures gives

$$n_H + n_{H^+} + n_O + n_{O^+} + n_e = p/kT \quad \dots (4.3.4)$$

where p is the total pressure in the arc.

The Saha formula gives

$$\frac{n_e n_{H^+}}{n_H} = \frac{(2\pi m k T)^{3/2}}{h^3} \cdot \frac{2 B_{H^+}}{B_H} \exp \left\{ - \frac{\chi_H - \Delta\chi}{kT} \right\} \quad \dots (4.3.5)$$

$$\frac{n_e n_{O^+}}{n_O} = \frac{(2\pi m k T)^{3/2}}{h^3} \cdot \frac{2 B_{O^+}}{B_O} \exp \left\{ - \frac{\chi_O - \Delta\chi}{kT} \right\} \quad \dots (4.3.6)$$

where/

* The treatment given here is substantially the same as that given by W. R. S. Garton in a course of lectures on "The Spectroscopy of Hot Gases" given at the Imperial College of Science and Technology in 1958.

where B is a partition function and χ is the first ionisation potential. The suffices H, H⁺ etc., indicate the atom or ion being considered. $\Delta\chi$ is the lowering of the ionisation potential due to surrounding ions⁶.

The ionisation potential of the hydrogen atom is 13.595eV and of the oxygen atom is 13.614eV and considerable simplification is achieved if χ_H and χ_O are both taken to be equal to 13.6eV. If we now

$$\text{let } \psi_H = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{2B_{H^+}}{B_H} \exp \left\{ -\frac{\chi - \Delta\chi}{kT} \right\} \quad \dots (4.3.7)$$

and

$$\psi_O = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{2B_{O^+}}{B_O} \exp \left\{ -\frac{\chi - \Delta\chi}{kT} \right\} \quad \dots (4.3.8)$$

then, the condition that equations may be solved for n_{H^+} , n_{O^+} , n_H and n_O is expressed by

$$\begin{vmatrix} \psi_H & -N & 0 & 0 & 0 \\ 0 & 0 & \psi_O & -N & 0 \\ 1 & 1 & 1 & 1 & -\left(\frac{P}{kT} - N\right) \\ 0 & 1 & 0 & 1 & -N \\ 1 & 1 & -2 & -2 & 0 \end{vmatrix} = 0 \quad \dots (4.3.9)$$

This reduces to

$$\left(\frac{P}{kT} - N \right) \left\{ 2\psi_H(\psi_O + N) + \psi_O(\psi_H + N) \right\} - 3N(\psi_H + N)(\psi_O + N) = 0 \quad \dots (4.3.10)$$

If now the following numerical values are inserted:

$$\frac{B_{H^+}}{B_H} = \frac{1}{2}$$

$$\frac{B_{O^+}}{B_O} = 0.445$$

$$\chi = 13.6 \text{ e.v}$$

$$\Delta\chi = 7 \times 10^{-7} N^{\frac{1}{3}} \text{ e.v}$$

$$k = 1.380 \times 10^{-16} \text{ erg per degree}$$

and the arc is assumed to run at a pressure of 1 atmosphere so that

$$p = 1 \text{ atmosphere} = 1.013 \times 10^6 \text{ dynes cm}^{-2}$$

equation/

6. Discussion of the Results

Although there is a difference of 20% between the ion densities obtained from the two lines, the temperature difference is only 3%. The temperature is not very sensitive to ion density for, as more heat is added to the plasma, most of this energy goes to forming more ions and the temperature does not increase very much. It may readily be shown from the equations that the uncertainty ΔT in the temperature is related to the uncertainty ΔN in ion concentration by

$$\frac{\Delta T}{T} \approx 0.15 \frac{\Delta N}{N}$$

Thus, quite good temperature values are obtained even when the ion density is subject to quite large uncertainties.

When the experimental errors have been taken into account there remains a real difference between the ion density determined from $H\beta$ and that determined from $H\gamma$. To understand how this difference arises it is instructive to compare our results with those of other workers. The lines of the Balmer series have been investigated very thoroughly by the group at Kiel working under Dr. Lochte-Holtgreven. Jürgens⁷, in 1952, measured the ion density and temperature in a water-stabilised arc in many different ways and obtained the same result, within the limits of experimental error, for each of the different methods. This indicated the existence of local thermodynamic equilibrium. The question of optical thickness of the spectrum lines was investigated experimentally and Jürgens found that $H\beta$ and the higher members of the Balmer series are optically thin for end-on observation of the arc. We did not make experimental observations of the optical thickness of $H\beta$ and $H\gamma$ but since the conditions under which our arc was run were very similar to the conditions in Jürgens work, it may be assumed that we were looking at optically thin lines. Therefore, the difference in ion density cannot be traced to distortion of the line profiles due to optical thickness effects.

In particular, Jürgens applied Holtsmark's theory to the wings of the line profiles of $H\alpha$, $H\beta$ and $H\gamma$ and obtained good agreement between these lines for the ion density. The ion density in his work turned out to be $(8.4 \pm 0.3) \times 10^{16} \text{ cm}^{-3}$ corresponding to a normal field strength, F_0 , of 250 e.s.u.

In 1954 Wolf-Dieter Henkel⁸ investigated Stark effect broadening of the higher members of the Balmer series and found on applying Holtsmark's theory that at small normal field strengths he obtained the same value of F_0 from all the Balmer lines and also, at very large normal field strengths he again obtained the same value of F_0 from all the Balmer lines. However, as the field strength increases from very small values, the higher members of the Balmer series yield values of F_0 which are greater than those given by the lower members. The smallest and largest values of F_0 measured in Dieter-Henkel's experiments were 22 e.s.u. and 151 e.s.u. respectively. Our results give values of F_0 of 197 e.s.u. for $H\beta$ and 221 e.s.u. for $H\gamma$. This may still be in the transition region described by Henkel whereas Jürgens results would correspond to the high field strengths giving the same value of F_0 for all Balmer lines. The greater broadening of the higher Balmer lines is attributed to the fields due to electrons. The higher members of the series are more sensitive to the Stark effect and therefore the influence of the electrons becomes more marked for these lines.

More recent work by Bögen⁹ (1957) has shown, from very careful determinations of the line profiles of $H\alpha$, $H\beta$ and $H\gamma$ that the effect of the electrons must be taken into account. He proves this by showing

that/

that the experimentally determined contour lies somewhere between the contour obtained by assuming $N = n_i$ and that obtained by assuming $N = N_i + N_e$. From these remarks it seems very likely that the discrepancy in our results between the ion density derived from $H\beta$ and $H\gamma$ separately can be explained by the broadening due to electrons, which we have not taken into account.

The asymmetry of $H\beta$ seen in Fig.3 has been discussed by Griem¹⁰. He attributes the asymmetry to three effects. These are (1) the quadratic Stark effect, (2) the dependence of the intensity on the fourth power of the frequency and (3) the distortion due to plotting the profile on a wavelength scale instead of a frequency scale.

The whole subject has recently been well reviewed by Margenau and Lewis who discuss the results of the workers mentioned above. Only a brief sketch has been given here to show that our results, although probably lacking the accuracy of the later Kiel work, do fall in line with the Kiel results. From this discussion, we may say that $H\beta$ probably gives a better result for ion density than $H\gamma$ when statistical broadening by ions alone is considered to influence the line profile.

This phenomenon has obvious applications to determination of electron densities under hypersonic re-entry conditions. Electron density and its relationship to spectrum line profile is the subject of a paper in preparation, in which some promising shock tube experiments will be discussed.

7. Conclusion

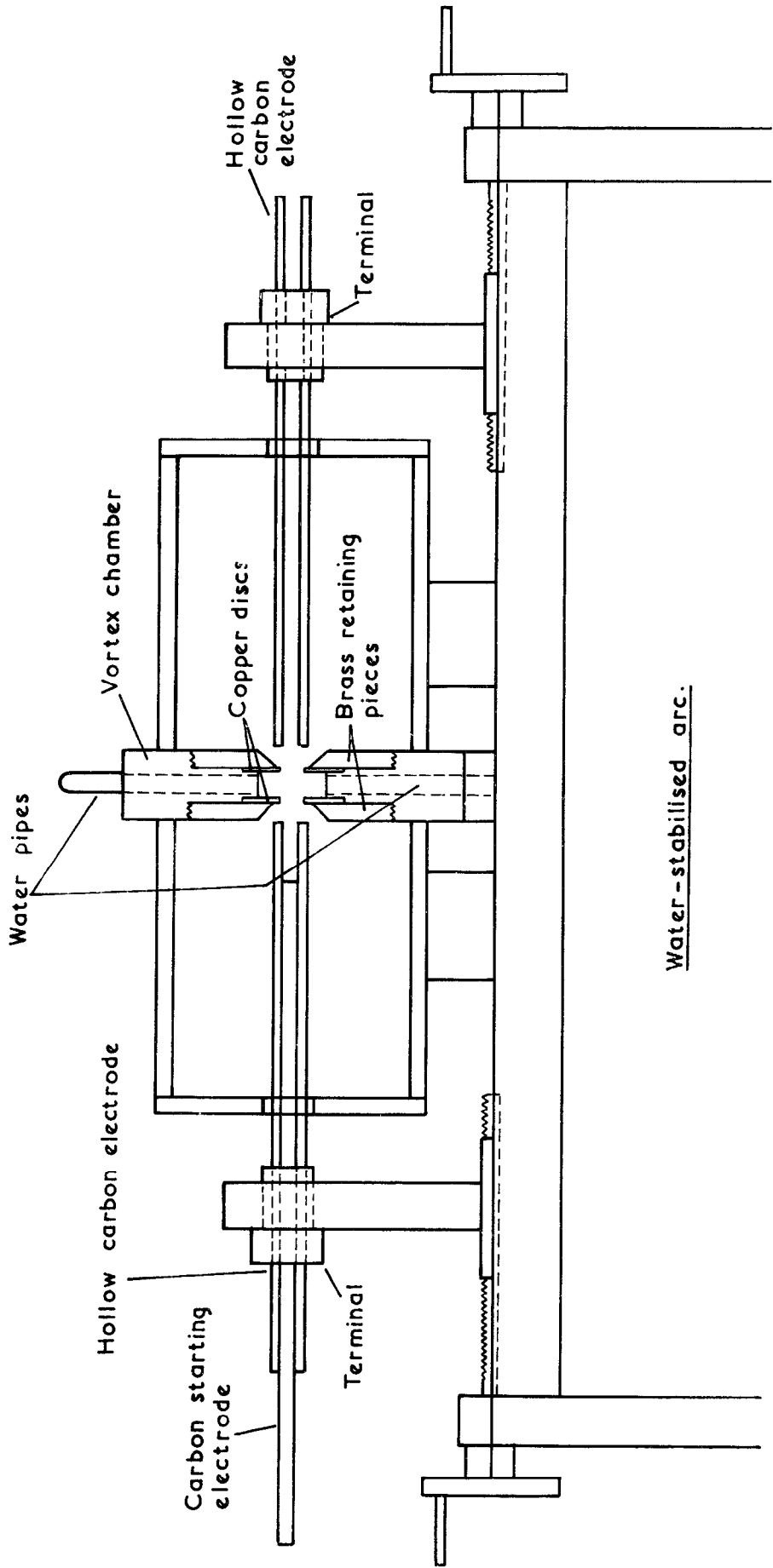
Ion densities have been measured in a water-stabilised arc by applying Holtsmark's statistical theory of broadening to the observed profiles of $H\beta$ and $H\gamma$. Temperatures have been deduced from these ion densities. The lack of agreement between ion densities is attributed to the greater effect of electrons in broadening $H\gamma$ than $H\beta$. Temperature, however, is not very sensitive to the ion density and a good measurement for temperature is obtained. Taking $H\beta$ as the more reliable result, the ion density is $(6.2 \pm 0.5) \times 10^{16} \text{ cm}^{-3}$ and the temperature computed from this is $(12,030 \pm 150)^\circ\text{K}$.

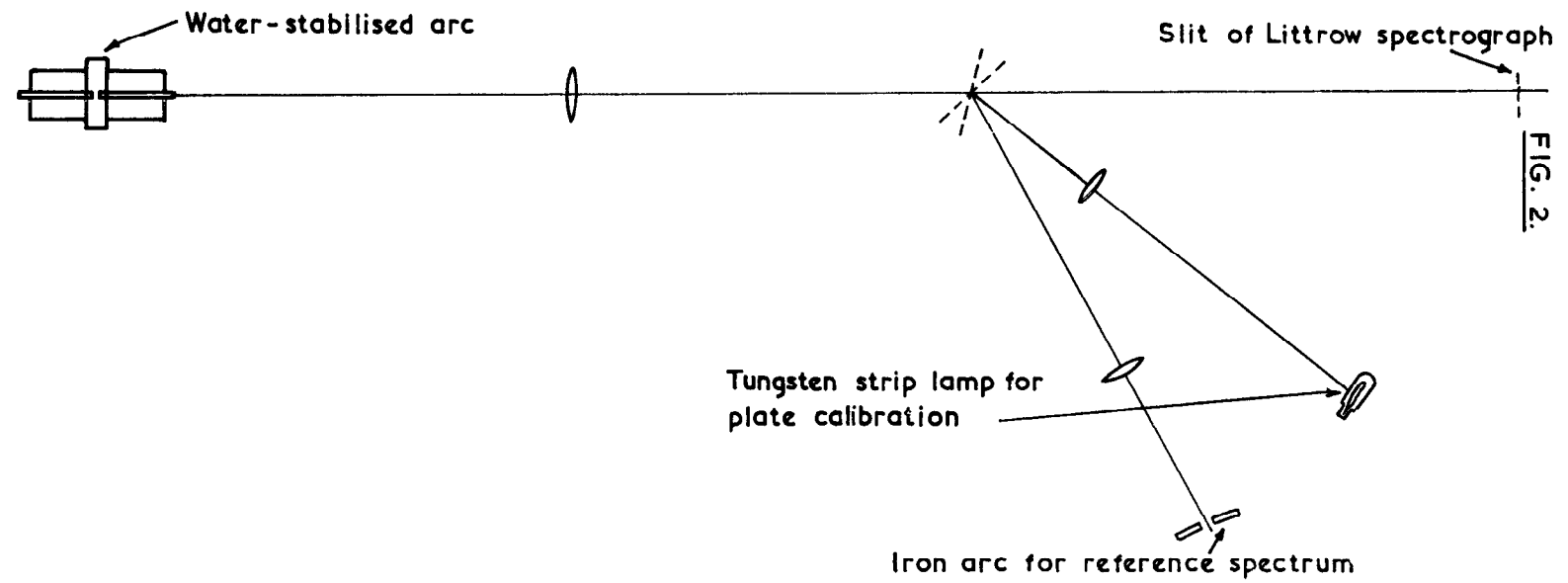
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FIG. 1.





Optical arrangement

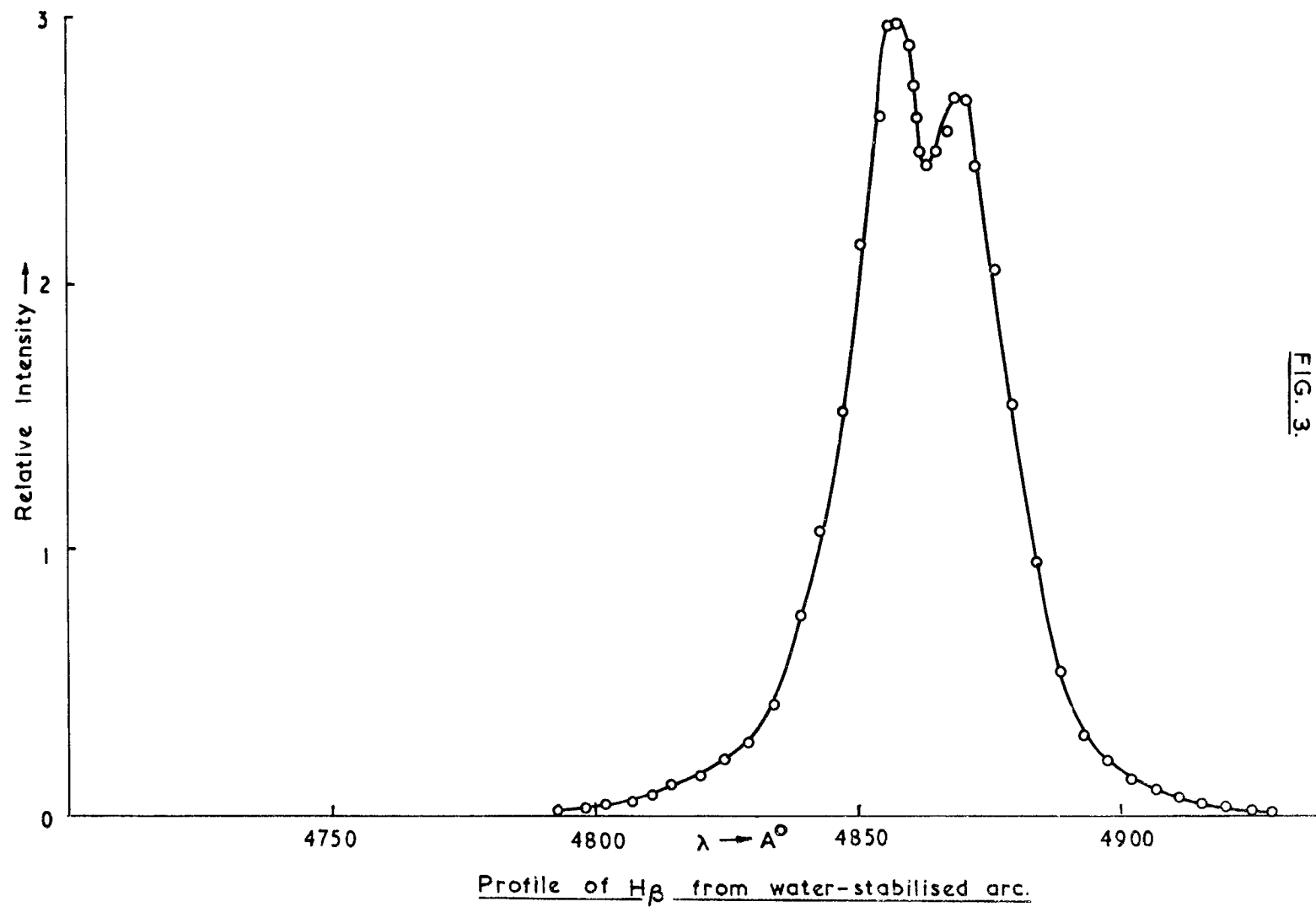
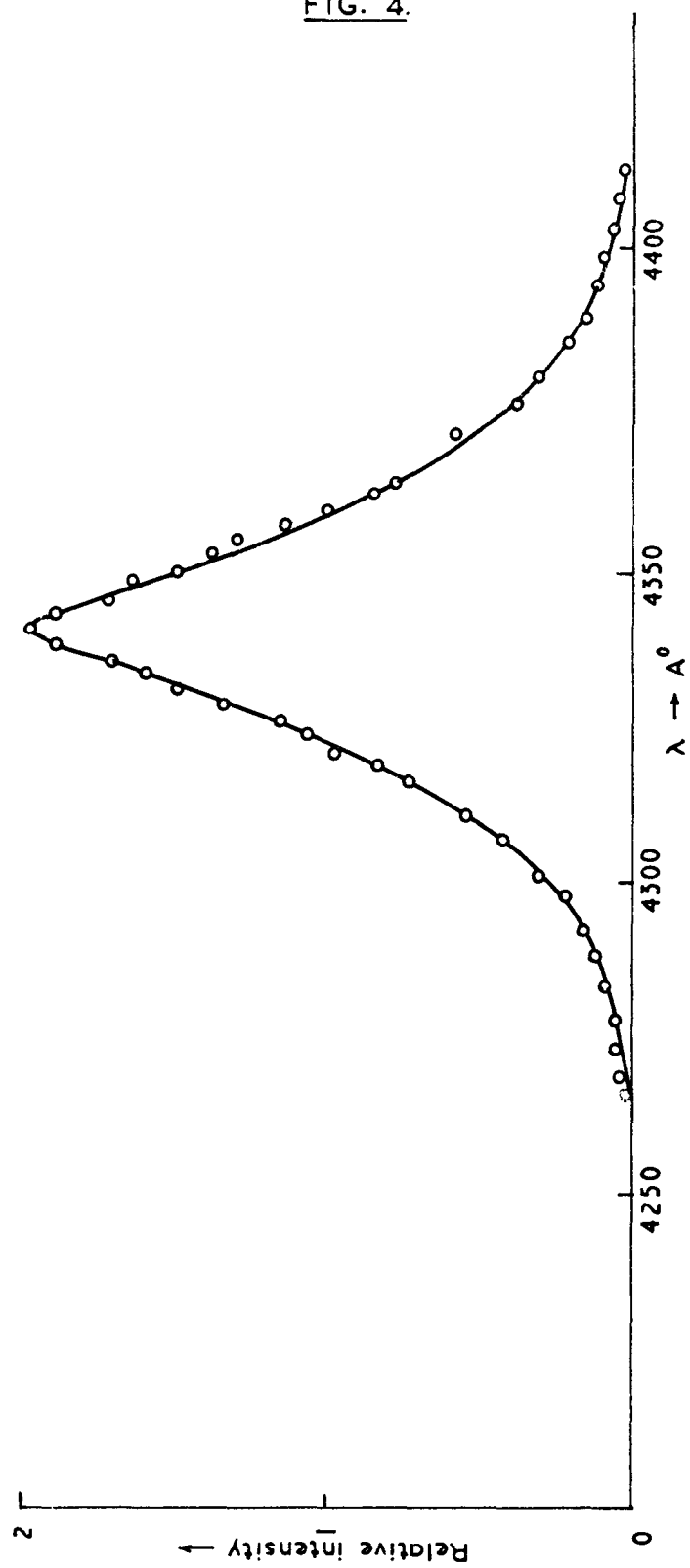


FIG. 3.



Profile of $H\gamma$ from water-stabilised arc.

FIG. 5.

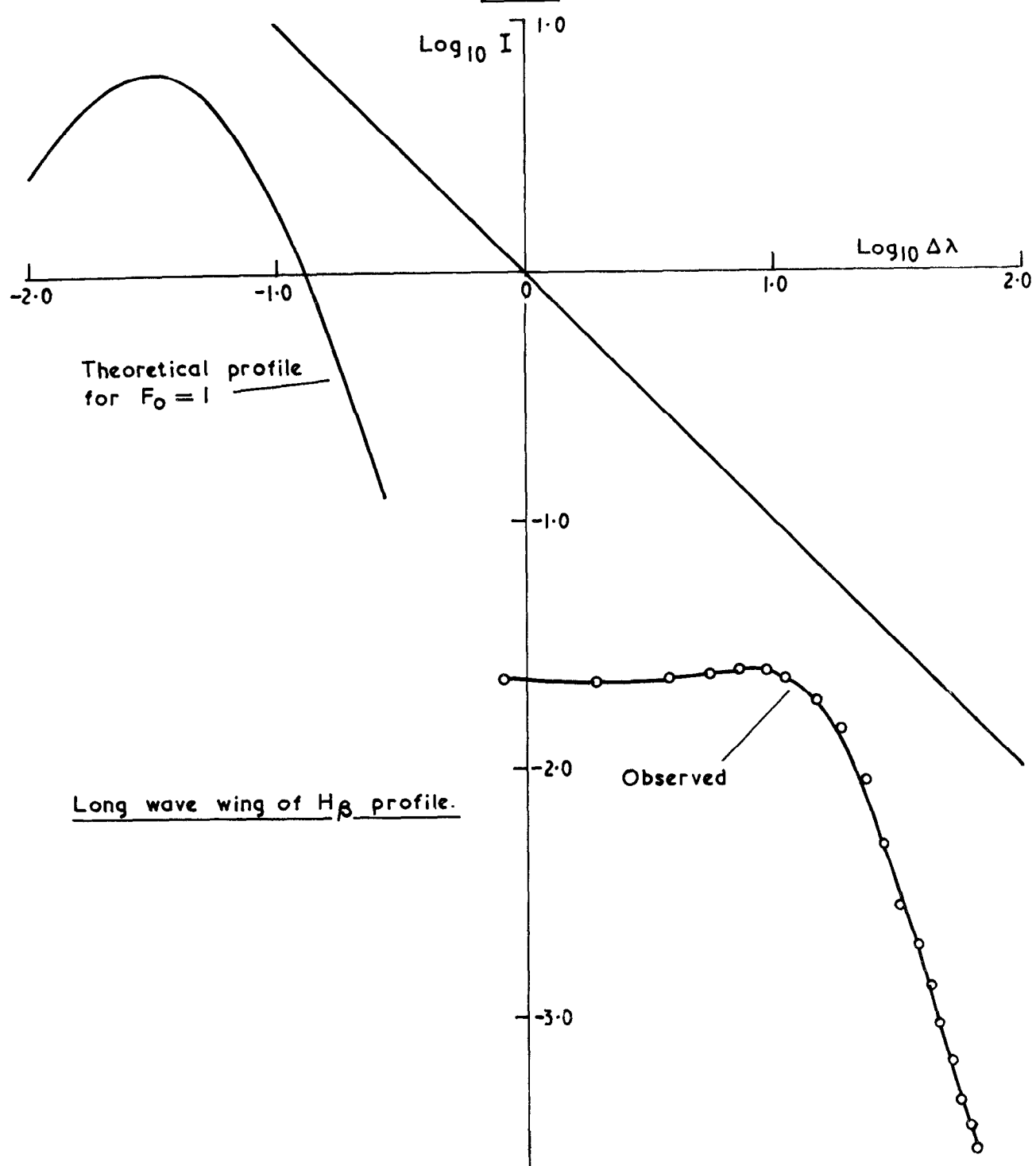


FIG. 6.
1.0

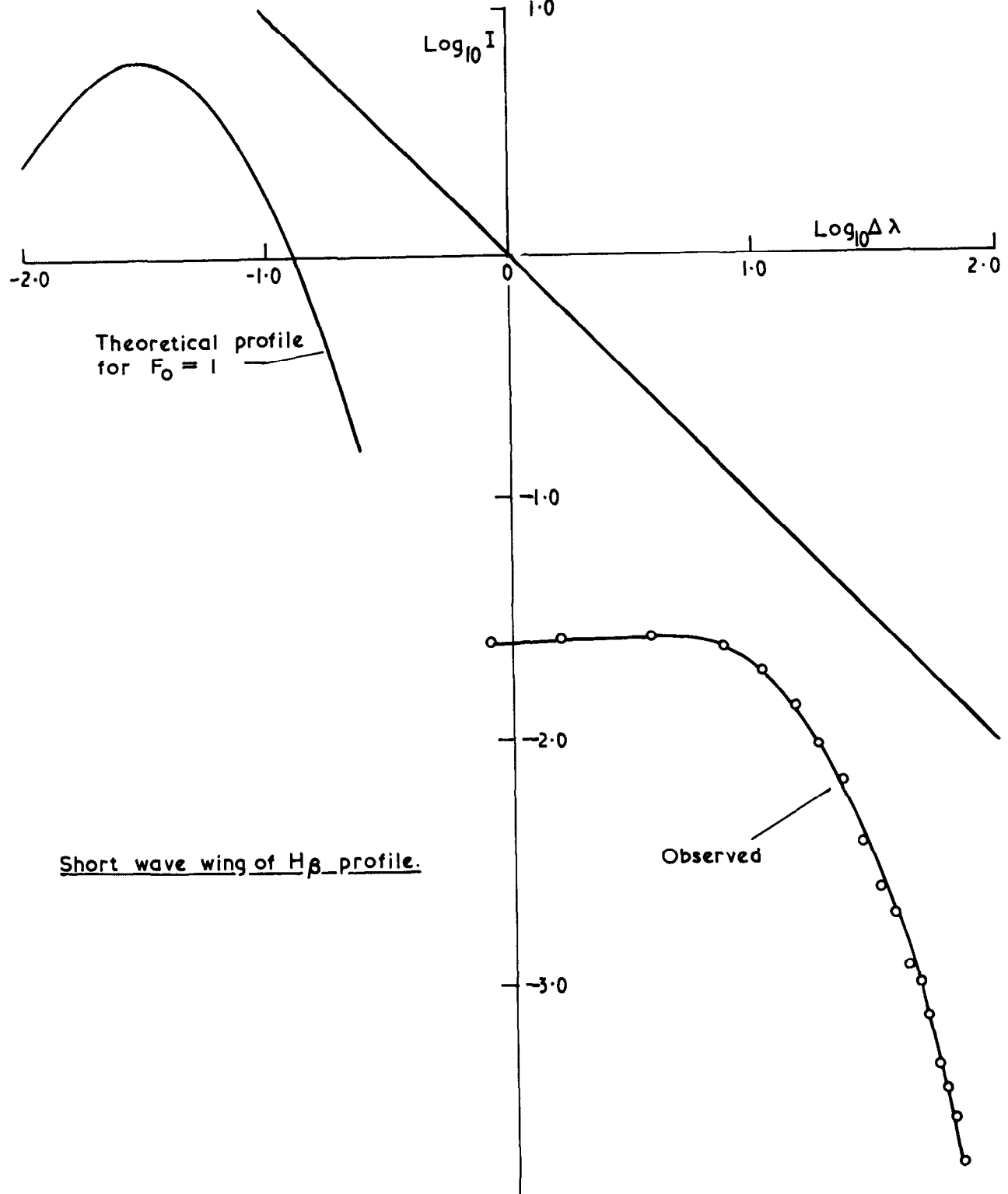


FIG. 7.

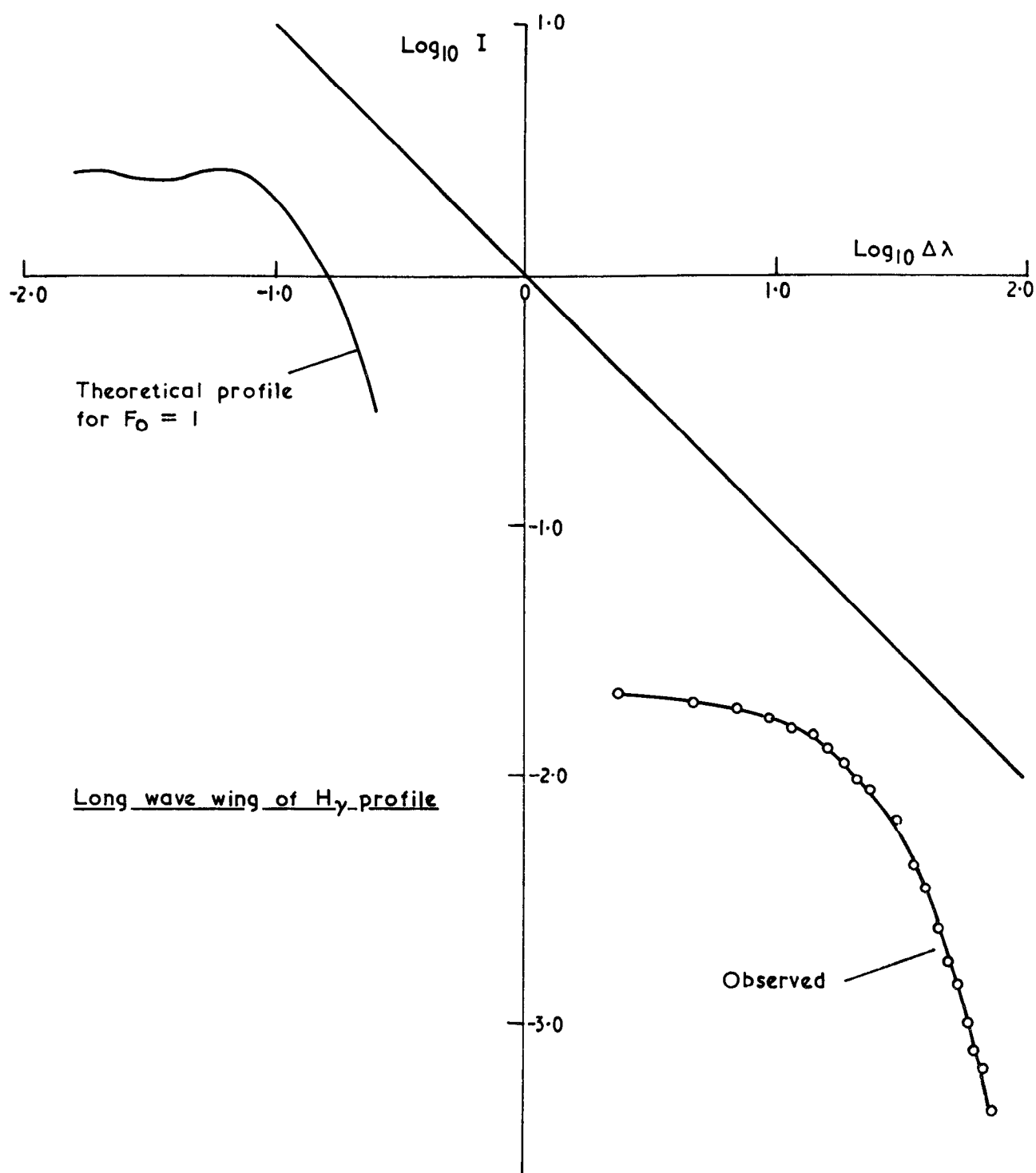
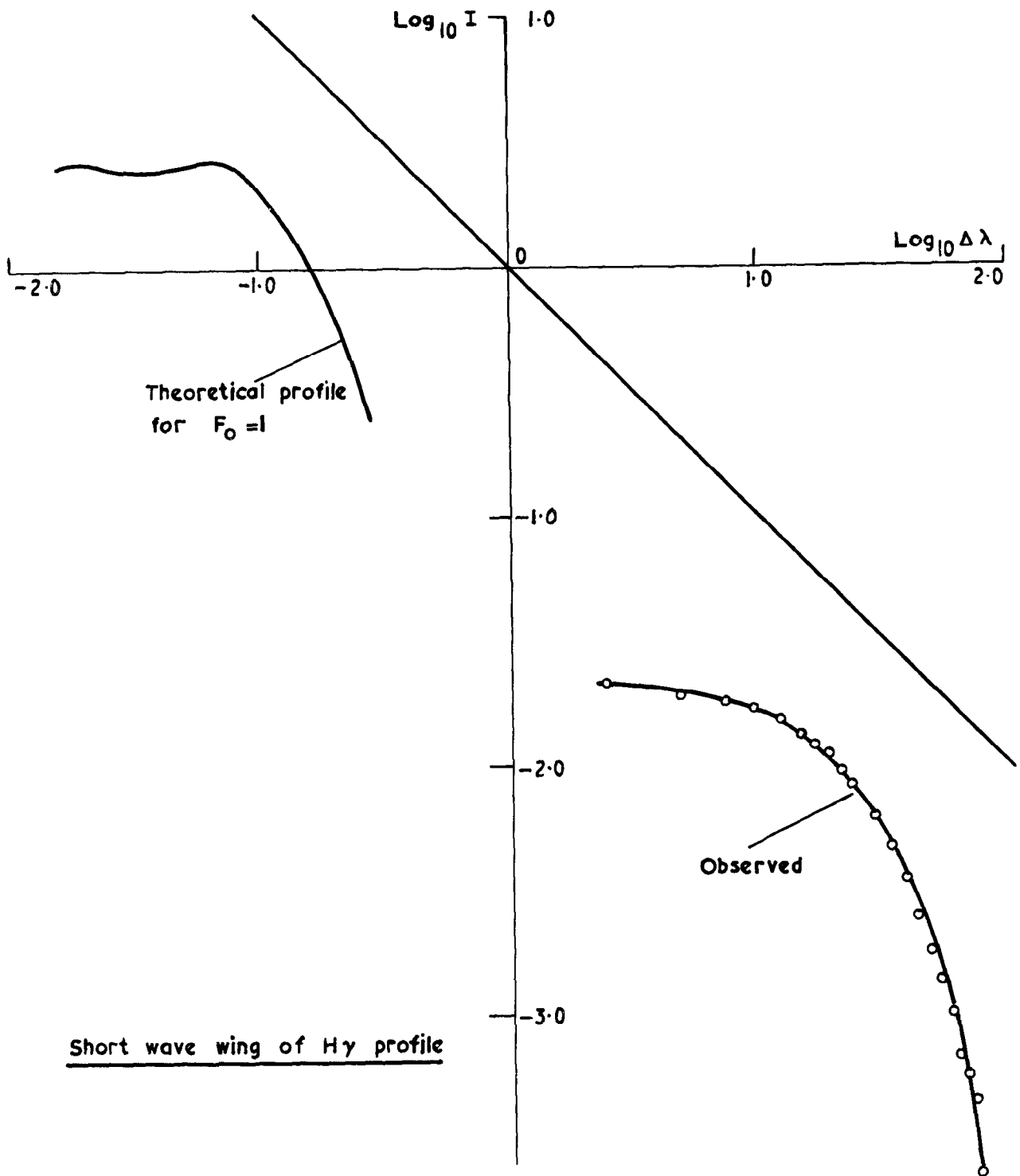


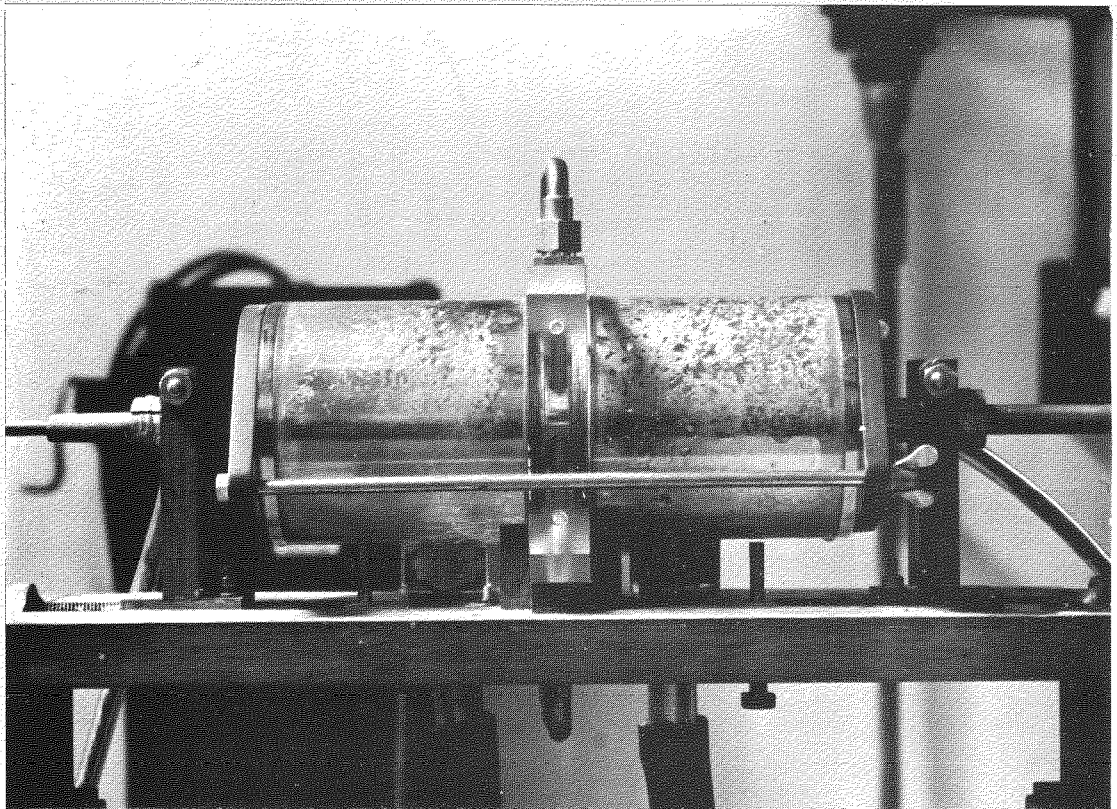
FIG. 8.



Short wave wing of $H\gamma$ profile

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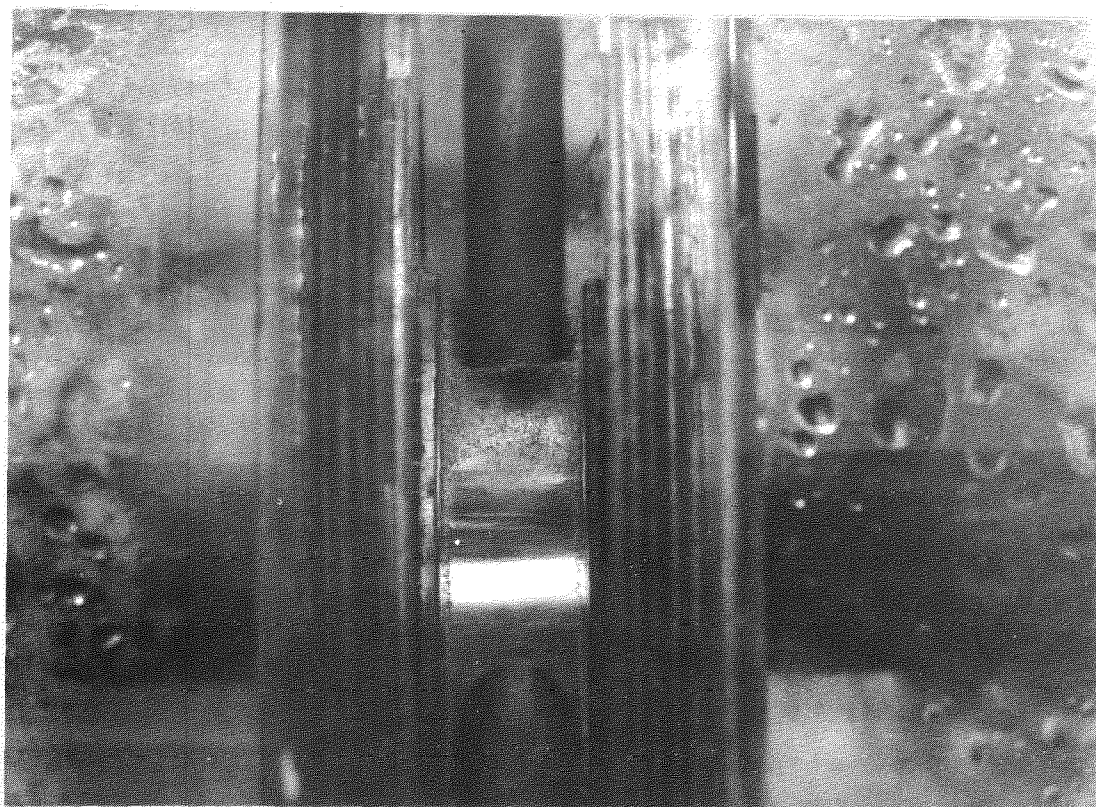
PLATE I



Water-stabilised arc .

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PLATE 2

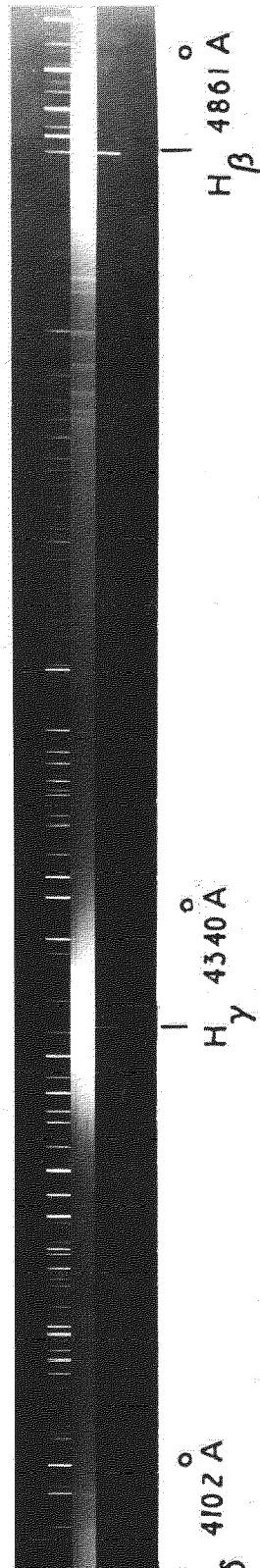


Arc constricted by water vortex

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PLATE 3

Iron arc reference
Water-stabilised arc
Hydrogen reference



Spectrum of broadened hydrogen lines.

A.R.C. C.P. No.614. June, 1961.
Pusey, P. S., Lapworth, K. C. and Metherell, A. F.

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