OBSERVED
RELATIVE INTENSITIES
OF
STARK COMPONENTS
IN HYDROGEN

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Thesis.

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Introduction.

The structure of matter has long interested investigators in all branches of science. Only in comparatively recent years, however, has it been possible to formulate any theory giving a clear explanation of the observed facts. Workers in chemistry have studied the interaction of atoms and molecules, and have brought to light considerable information regarding molecular structure: but to the physicist has been left the problem of determining the structure of the atom and the nature of radiation. A close relationship exists between these two problems and a number of methods of approach have been employed by different investigators.

The first step forward in the recent advance in atoms research came with the discovery of radioactivity by Rutherford. The study of radioactive transformations led to thenuclear theory of the atom and the consequent explanation of the periodic properties of the elements. Spectroscopy and X-ray analysis have also contributed a great deal to our knowledge of atomic phenomena. Spectral series have been worked out for a large number of the elements, and the effect on the energy levels in the atom due to perturbing external fields has been investigated.

The splitting of lines in the Balmer series of hydrogen by an electric field was discovered by Stark. This effect, named after the discoverer, has been investigated by Stark and his co-workers in order to obtain both displacements and relative intensities of the components in the case of hydrogen. Because of several outstanding discrepancies between the observations of Stark and those of more recent experimenters, and also between obsefvation and theory, the present re-determination of intensities was carried out.

Measurements have been made on the strong components of the first four members of the Balmer series. Very good agreement with the calculations of Schrödinger, based on wave mechanics, has been obtained; whereas there are some very marked variations from the values obtained by Stark.

Theoretical Survey.

Theoretical interpretations of the Stark-effect possessing anything resembling a satisfactory character have ~~been~~ essential connections with the quantum theory. Indeed, the discovery itself was doubtless delayed by the fact that the classical theory of radiation failed to suggest an observable displacement of the spectral lines. It was very fortunate, therefore, that the foundation of the quantum theory of line spectra was laid by Neils Bohr in a series of papers published just prior to the discoveries of Stark and Lo Sardo. Thus the theoretical interpretations and experimental facts have developed simultaneously and with very great mutual benefit. While the theory has supplied what has grown to be an entirely adequate formal interpretation of all essential details of the experiments in hydrogen, it is also true that many theoretical points were either suggested or given a practical test through contact with observations on the Stark effect. For some years, in fact, this effect has served as a leading exercise in the development of quantum methods.

In his early papers Bohr gave a generalization, applicable to all simply periodic atomic systems, of the condition

$$E_n = nh\nu \qquad n = 0, 1, 2 \cdots$$

employed by Planck only in the case of the linear oscillator. A further generalization of the quantum conditions to include those suitable for multiply periodic systems was made independently by Sommerfeld and Wilson in 1915, and in the following year Epstein and Schwarzschild, also independently, gave a further development of the quantum theory through an ~~application~~ explanation of the Stark-effect. Guided by the solution of the problem of two centres given by Jacobi, who used elliptic coordinates, Epstein removed one of the centres to infinity to give the uniform electric field and retained the other with its Coulomb field. The coordinates then became parabolic and confocal; a third coordinate is the angle turned round an axis through the nucleus and parallel to the applied field. The variables are found to be separable in the Hamilton-Jacobi partial differential equation. The momenta derived therefrom are used in the quantum conditions :

$$\oint p_k \, dq_k = n_k h \qquad k = \xi, \eta, \varphi$$

where ξ, η are the parabolic coordinates and φ is the angle just mentioned. The evaluation of these elliptic integrals gives to stated approximations the energy of the system i.e. the values of the spectral terms in the presence of the external field. In his first paper Epstein made his results accurate to the first power of the applied field, and later included very small terms proportional to the square of the field (second order effect).*

The next advance in theoretical views of the Stark-effect was made by Bohr and consisted in an attempt to give a more definite picture of the hydrogen atom under the influence of an external field together with some general conclusions regarding polarization and intensities of Stark components which were based on this more definite study of the motion of the electron. The behaviour of the mechanical system was determined by Bohr through an application of perturbation theory borrowed from astronomy. The conclusions regarding the details of polarization and intensity which failed to appear in Epstein's treatment were then sketched on the basis of his Correspondence Principle. In essence this principle merely claims that in the limit of high quantum numbers the classical theory must give correct results.

For Newtonian mechanics a single electron moving

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* The method apparently allows any degree of accuracy, but in reality neglects from the beginning the observed fine structure of the Balmer lines.

about a nucleus gives a degenerate system. For relativity mechanics we have two incommensurate frequencies so that the electron will never get back to its starting point.

Under the classical theory the frequency of the electron in its orbit is equal to the frequency of the emitted radiation, and all frequencies are emitted at the same time.

If we define J, the periodicity modulus of the action function, or the phase integral $\oint p_s dq_s$ where the p's and q's are those arising in the Hamilton-Jacobi differential equation, we have the frequency ν given by

$\nu = k \frac{\partial E}{\partial J_s}$ where k = 1 gives the fundamental frequency and k = 2, 3, 4----- gives overtones.

and $\nu = \sum_s \left(k_s \frac{\partial E}{\partial J_s} \right)$ gives the combination tones.

For the quantum theory we have :

$$J_s = n_s h = \oint p_s \, dq_s \tag{1}$$

$$h\nu = E' - E = \Delta E . \tag{2}$$

Applying this to the hydrogen atom

$$\nu = \frac{2\pi^2 m e^4}{h} \left[\frac{1}{J^2} - \frac{\lambda}{(J + \Delta J)^2} \right]$$

where J and ΔJ both satisfy condition (1). Thus in the quantum theory there is a different ΔE for the overtones which are no longer integral multiples of the fundamental.

Any quantum theory frequency can exist only in case it approaches a classical theory frequency for high quantum numbers. This is Bohr's correspondence principle. Overtones can exist only if they exist in the classical theory. For this reason the simple Bohr theory of the atom with circular orbits is invalidated, there being only one possible frequency in the corresponding classical case.

In the limit the amplitude in emitted radiation must correspond statistically to that of classical theory. Thus the electric moment may be expressed in a Fourier series; and for a large number of atoms which are radiating, the amplitude of the electric vector will be proportional to the coefficient in the Fourier series of the particular term expressing this frequency. When a transition occurs between orbits in which the difference in frequency of revolution is appreciable the problem arises as to how the amplitude of the emitted radiation depends on the amplitudes in the initial and final states. Thus in practice different methods of averaging between the allied Fourier coefficients in the initial and final states are tried, and when the correct experimental intensities are obtained it is assumed that the method of averaging is correct. The energy actually emitted for any transition is proportional to the number of atoms undergoing this transition. Thus the coefficient in the Fourier expansion is a measure of the probability of a single atom emitting this ffequency.

The application of the correspondence principle to the problem of calculating relative intensities of Stark components has been carried out by Kramers for the Balmer series of hydragen and for ionized helium. In order to do this it was necessary to make a Fourier series analysis for the transitions considered, and to compute the coefficients. A discussion of his results is included in a later section of the paper.

Epstein formulated empirical laws governing the polarizations of the emitted lines. Bohr explains these empirical laws on the basis of the correspondence principle which implies that a line can be polarized in a given direction only if the Fourier series for the corresponding electric vector contains the frequency of the emitted line. He then states the polarization laws in the following form:-

If n_φ is the quantum number associated with the Epstein phase integral for the variable φ mentioned above, then for a transition between any two states if n_φ changes by zero the emitted line is polarized with its electric nector parallel to the electric field, while if n_φ changes by ± 1 the emitted line is polarized with its electric vector perpendicular to the field.

A more complete physical interpretation of the atom in a field is given by Kramers[*] in a paper correlating fine structure and the Stark-effect for the Balmer series in hydrogen and the ionized helium line λ 4686.

Sommerfeld,[▽] applying the quantum theory to elliptic orbits in which the variation of mass with velocity was taken into account, was able to account for the fine structure of the Balmer lines. Observations in hydrogen are very imperfect, but the fine structure of ionized helium series as observed by Paschen[†] confirm Sommerfeld's results. Sommerfeld then tried to solve the problem of the hydrogen atom in an electric field in which the variation of mass was taken into account, but the equations arising in the case cannot be solved by a separation of the variables. Thus the question arises as to whether these are continous sharply defined

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[*] H.A.Kramers - zeits. . Phys.3. 199, 1920.

[▽] A.Sommerfeld. - Ann.d.Phys. 51. 1, 1916

[†] F.Paschen - Ann.d. Phys. 50, 901, 1916.

lines connecting the Stark components with the fine structure.

The treatment of the problem by Kramers is carried out by a method of approximation using angle variables in the Hamilton-Jacobi partial differential equations, and based on the perturbation theory as used by Bohr.[*] In the absence of an electric field he obtains the fine structure in the same form as was previously given by Sommerfeld. In this case the motion is characterized by the quantum numbers which specify the axes of the orbital ellipse, and by two frequencies, - one the frequency of revolution of the electron and the other the precession frequency of the orbit. When an electric field is applied, a third quantum number is introduced which determines the angular momentum about an axis parallel to the field, and thereby the inclination of the orbital plane to the direction of the field. Since the value zero for this quantum number corresponds to motion through the nucleus, we are led to Bohr's earlier assumption that this value is not possible.

With increasing field the motion no longer remains in a plane; and the angular momentum together with the minor axis of the orbit, oscillate between fixed limits, thereby introducing a new frequency into the motion. In high fields

[*] N.Bohr D.K.D.Vidensk. Selsk. Skr. Afd. 8. R.IV,1, 1919.

this frequency is shown to become double that of the frequency of the rotation of the plane of the orbit about the axis of the electric field.

From his calculations he finds that in the presence of weak fields the components of fine structure split with one or more sharp polarized components which are displaced by amounts proportional to the square of the electric force. As the electric field is increased new components appear; and in strong fields all these components coincide with those given by the theory as given by Epstein.

A new field of investigation of the Stark-effect problem was opened up with the introduction of the Heisenberg-Born-Jordan matrix mechanics. According to this theory no continous picture of what occurs in the atom during radiation is required. The Heisenberg matrix is formed, the elements of which are merely made up of the amplitude and phase connected with any jump. ~~Using~~ A special form of the quantum condition for change in energy, together with a complete matrix mechanics is used which is analagous to the Hamiltonian mechanics used in the earlier work. Using operator methods the Stark-effect displacements were worked out for hydrogen by Pauli[°] and Dirac. By an application of perturbation theory

[°] W.Pauli Jr. Zs. f. Phys. 36, 336 1926.

to quantum mechanics, the Stark-effect was calculated by Foster[▽] for helium. Moreover, by determining the matrices required to give the analagous transformation to the canonical transformation in classical mechanics, Foster calculated the intensities of the helium components. In doing this he employed the general principle referred to later of assuming that the intensities are proportional to the square of the amplitudes of the associated vibrations. In order to get the relative intensities of the components, these values are multiplied by the Krönig[†] probability factors.

A further advance was made by the introduction of wave mechanics by Schrödinger.[°] This theory resulted from some earlier work by de Broglie[*] in which a material point is associated with a group of waves. According to wave mechanics, the solution of a problem in quantum mechanics is made to depend on the solution of a differential equation, known as the wave equation , in which the energy of the system appears. In solving such a problem the energy is calculated on classical grounds as in the old theory, and the only solutions of the wave equation admitted are those which are finite, single-valued and bounded in the phase space, for the special values of the energy corresponding to the ststionary

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[▽] J.S.Foster - Proc.Roy. Soc. 117, 137, 1927.

[°] E Schrodinger - Abhandlungen zur Wellenmechanik, Barth, Leipzig (1927.

[*] L.de Broglie - Ann d. Phys. 10, 22, 1925.

states of the system.

By calculating the energy for the hydrogen atom in a constant field of force, the displacements produced in the Stark-effect were thus calculated. Schrödinger does this both by a method of separation of the variables such as was employed by Epstein in his early work, and also by means of perturbation theory in a manner analagous to that of Bohr. The extension of this work to the calculation of intensities is given in a later section.

Experimental Survey.

The observations of Stark[*] were made using for the transverse effect a canal ray tube of the type shown in figure (1a). An electromotive force of from 5000 to 10000 volts, produced by a large induction coil, is used to operate the tube. This is applied between the anode (A) and the perforated cathode (C). A second electromotive force of from 1000 to 6000 volts supplies the field required to produce the Stark analysis between (C) and the auxiliary electrode (F) placed a few mm. away. The light is taken from a section midway between (C) and (F) where the field is constant. A reproduction of Stark's analysis is shown in figure (1.b.) Longitudinal observations were also made, but these led only to the result that the p-components were invisible and the s-components unpolarized.

Lo Surdo[†] made some independent investigations

[*] J. Stark - Elecktrische Spektralanalyse, Leipzig (Hirzel) 1914.

[†] Lo Surdo - Rend d, Linc 22, 664, 1913.

using a tube in which the discharge was constricted near the cathode. The field causing the splitting of the lines was produced in the Crookes dark space in which the total fall of potential of the tube takes place. This type of source has been used by many workers in the study of the Stark-effect, and a number of variations in the method have been employed in order to obtain a sharp analysis. The most successful modification has been that designed by Foster whose general procedure has been followed in all the tubes used in the present work.

The general features of the Stark effect which have been observed may be summarized as follows:

(1) Asymmetric displacements of the individual lines are observed for all elements.

(2) New combination lines appearing in the field, which produce group symmetry.

(3) Change in relative intensity of components at different field strengths; including the phenomenon of vanishing components observed by Foster (1) for helium.

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(1) J.S. Foster - Proc. Roy Soc. A. 114, 47, 1927.

(4) Displacements showing a non-linear relation with field strength in low fields. (In hydrogen this becomes evident from the fine structure theory.(2)

(5) A second order shift towards the red in strong fields. This has been observed in hydrogen by Takamine and N. Kokubu(3) and by Foster.(4)

(6) Single spectral series shows the same Stark patterns throughout.

(7) The direction in which a displacement takes place may change from one line to another in the same series.

(8) In the case of neon where the terms are multiplets an analogue to the Paschen-Back effect has recently been observed in the laboratory.* It is found that in high fields the displacements of the lines in the normal group tend to fuse. Those of the groups coming in in the electric field are effected in like manner, the whole structure forming a normal pattern such as is found in the case of simple spectra.

(2) H.A. Kramers Zs f. Phys. 3. 199, 1920.
(3(T.Takamine and N.Kokubu,Mem.Coll.Sci.Kyoto 3,271,1919.
(4) J.S.Foster Astraphys.Journ. 63 191,1926.
* W. Rowles.

Experimental Arrangements.

In carrying out the measurements of intensities of the Stark compononents a Lo Surdo source was employed in conjunction with a vacuum system. A high potential apparatus supplied from 5000 to 10,000 volts to the tube, the current drawn varying from 4 to 12 mil.amps. The time of exposure varied from 30 minutes to 4 hours. Spectrograms of the light from the Crookes dark space were obtained, and by means of a wedge method using a Moll microphotometer, quantitative measurements were made which show marked agreement with the calculations of Schrodinger based on Wave mechanics.

The gases used in these experiments were hydrogen, helium and neon. The hydrogen was prepared in the laboratory, and was used alone and with varying proportions of helium. The helium was introduced in order to enhance the Balmer series. Water vapour was also tried for this purpose, but at the pressures required to operate the tubes, it did not appear to have the desired effect. Both the hydrogen and the helium were kept over water, and were purified by passing over charcoal immersed in liquid air. The neon was admitted to the system through a mercury trap, and was used practically pure, the whole tube being thoroughly roasted and evacuated before admitting the gas. H_α, however, always appeared stronger in the tube under these circumstances than when ~~a noticeable preparation~~ an appreciable proportion of hydrogen was added. Neon was therefore used in obtaining the H_α photographs.

The vacuum system (Fig.2) consists of a large capacity for keeping the pressure constant, a pyrex charcoal bulb through which the gas is forced to pass before entering the discharge tube, and a McLeod gauge constructed so as to read pressures up to five millimeters of mercury. The seals from the pyrex to the glass are in all cases made with wax.

The principle underlying the Lo Surdo type of tube is that extremely high fields may be produced by the fall of potential in the Crookes dark space by constricting the discharge at this portion of the tube. This method does away with the necessity of having two sources of high potential as required with the canal ray tube, and also gives very much better light intensity. In order to have this field large enough to give a measureable Stark-effect the constriction is made from 1 to 2.5 mm in diameter in the neighbourhood of the cathode. The constriction of the discharge has been effected in a number of ways by different experimenters, the method employed by the writer being illustrated in (Fig.3.a)

A heavy aluminium anode A is sealed into the main section of the tube which is made of pyrex. A lead to the vacuum system is made from near the anode, and is bent in line with the axis of the tube so as to allow rotary adjustment at the ground glass joint used in making connection. At a distance of about 10 cms. from the anode the tube narrows down to 1.3cms. internal diameter. Into this part is fitted a lavite block(L) which has previously been made in the required shape and then hardened by heating. The lavite is then sealed into the pyrex as firmly as is possible without using sufficient heating to cause adhesion between the two. Because of the nearly equal coefficients of expansion of the pyrex and the lavite, such a tube will stand considerable heating without cracking. Care should be taken, however, to allow the heat to distribute itself slowly by running the tube for a few seconds at a time at the beginning of a run.

The cathode (C) is an aluminium rod fitting into the lavite. This is held in position by a brass sleeve (S) which fits against the lower edge of the lavite block. The electrode may be rotated by means of a ground glass joint, to one portion of which is attached a flexible steel wire. A brass plug at the free end of the wire slides into the sleeve already mentioned, and the pin(P) holds the parts together. The pin moves within limiting slots in the brass sleeve. A compressed spring between the plug and the electrode serves to hold the cathode in position. Connections to the electrical apparatus are made by tungsten wires which are sealed into the pyrex with 702-P glass.

The general type of lavite section is shown in fig.(3.~~6~~b). A 6 mm. hole with flat ends is cut into the lavite at each end as indicated. A small hole is then drilled off centre, varying from 1.5 to 2.5 mm. in diameter, the lower edge of which is rounded slightly in order to prevent heating. A slit from .5 to .75 mm. in width is cut in the lavite in order to allow the light to pass out through the window to the spectrograph. The cathode in such a tube is a cylindrical rod which fits into the lower large hole in the lanite. With this arrangement pressures up to 2 or 3 mm. may be employed, and the fall of potential produced by the electrical apparatus described later takes place in from 1 to 3 mm. according to the length of the Crookes dark space. An intense light exists in the dark space when the tube is operated, and the conditions are excellent for studying the Stark-effect. In order to produce a convenient field distribution the cathode surface is drawn back about .3 mm. from the lavite. This makes the field decrease slightly at the cathode, whereas a steadily increasing field is produced if the lavite and aluminium are in contact. The former distribution is especially good for the study of the Stark-effect. Another advantage lies in the fact that in this way the cathode is kept insulated from the walls. This is very important when a metal coating is produced by sputtering from the cathode. In order to further control the trouble due to sputtering the end of the aluminium rod forming the electrode is turned to a slightly smaller diameter than that of the lavite over the 3 cms. of its length nearest its face.

During an exposure of three hours the bombardment of positive ions produces a small conical hole in the cathode surface which varies in depth from about 1 to 3 mm. according to the conditions under which the tube is operated. In cases when a very deep hole is produced, it is of extremely small diameter, and in no case does the hole seem to effect the field distribution during an exposure. If for any reason a fresh surface is required, the cathode may be rotated by the ground glass joint. After a long run, however, the tube has to be taken down, the lavite cleaned, and the cathode re-surfaced before it will run steadily again.

Various modifications of the type of tube were employed in the present work, the changes in design being made in an attempt to get field distributions which would produce lines suitable for intensity measurements.

(1) A ribbon - shaped hole (1.5 X 7 mm.) is cut through the central part of the lavite section. The end of the cathode is cut down to fit tightly into this hole, and the slit is cut parallel to the cathode face and in the direction of the long side of the hole at a distance of .2 mm. from the cathode. Fig. (4.a.). This tube was used in a horizontal position, and using a narrow slit and good focus, the Stark components were obtained parallel to one another on the photographic plate. Preliminary photographs showed that the light intensity was constant across the central 4 mm. of the discharge. This type of source permitted the use of the wedge in line with the source of light giving the Stark components, but gave no means of detecting secondary lines which might be superposed and thereby spoil intensity measurements.

(11) A tube was made as shown in fig. (4.b) which would give lines nearly parallel over a portion of their length, but curved at the ends so that secondary lines could be detected. The lavite section is sealed into a tube at right angles to the direction of the discharge. The cathode is

cylindrical and fits into a hole in the lavite which is cut slightly off centre. The discharge passes from the anode through a hole (1 X 3 mm.) in the lavite to the curved surface of the aluminium. The central section of the lavite is made about 5 mm. thick. Through this a very narrow slit is cut to the hole through which the discharge passes, the centre of the slit being almost tangential to the curved surface of the cathode. The light was observed with the tube in a horizontal position. This tube gave lines which could easily be measured on the microphotometer, the intensities to be found from an accompanying wedge pictures as described later, but overheating of the cathode made it impossible to use it with the high current density required to bring out the higher members of the series.

(111) A tube similar to (1) was used in which the end of the ribbon cathode was made with its outer edges curved, the intensity measurements to be made as ~~unit~~ in (11). Insufficient light intensity made this design useless for the higher series members.

(1V) In order to be able to use a higher current density, tubes were built with ribbon shaped holes of various sizes in the lavite. The discharge passed to a solid cylindrical cathode as in the general type, a Geissler tube with the same gas pressure being attached by ground glass joints, so that a normal gas spectrum could be obtained on the same plate to be used as a comparison.

(V) Due to the simplicity of design and superiority of light intensity available in tubes of the normal type, running in a vertical position with high current density over a very small area, attempts were made to modify this type so as to give a distribution suitable for obtaining Moll photometer curves giving a correct record of the blackening of the lines. Tubes were made in which the small hole constricting the discharge was modified in the following ways:

(a) A hole 1 mm. in diameter was drilled and tapered at the lower end with a 10° taper beginning about 2 mm. from its lower end. Fig. (4.c)

(b) A hole similar to the above was made using a 20° taper.

(c) A hole 1.5 mm. in diameter was cut straight through and widened slightly, over a length of about 4 mm. at a distance of about ½ mm. from the lower edge. In this case the cathode was placed flush with the end of the hole. Fig. (4.d)

(d) A hole 1.5 mm. in diameter was cut and widened to about twice this diameter by means of a large drill at its lower end. Fig. (4.e)

All these designs improved the distribution, but the best results were obtained using type (d) in which the cathode was drawn back through at least .3 mm. from the lower end of the hole. This is the type of tube used in obtaining the plates from which measurements were taken.

The electrical apparatus operating the tubes is made from parts obtained from the General Electric Company as shown in Fig. (5). A transformer rated to give 100 mil.amps. at 10,000 volts supplies the required high potential. Sixty-cycle alternating current passes through the primary and a controlling rheostat R_2. The centre of the secondary is grounded and the two half waves are rectified by kenotrons (K). The filament current of the kenotrons is controlled by the rheostat R_1 which is in series with the kenotrons primary, the voltage across which is readfrom the voltmeter. The pulses resulting in the direct current so produced are greatly reduced by two 1.4 condensers (C) connected in series, parallel with the tube. Further reduction is effected and the discharge is steadied by the 400 henry inductance (L)and water resistance (R_3)in series with the tube.

The voltage across the tube is read on an electrostatic voltmeter, (V_2) while a small Weston direct current ammater (A) gives the current. The applied voltage is kept constant during a run by small adjustments of the rheostat(R_2).

Two spectrographs were employed, one a Hilger quartz model E.I. and the other a glass spectrograph built at the Laboratory.

(1) The glass spectrograph is equipped with six prisms ground by Fecker and having faces (6 X 10) cms. These are mounted on a plane iron table which is boxed in, and the whole is kept at constant temperature by means of heating elements placed underneath and a tolnene expansion thermostat in the centre. The collimator and camera lenses are similar doublets of 115 cm. focal length, ground by MacDowell.

The spectrograph is built in two sections, raised to a convenient height from the floor by an iron framework. The camera section can thus be moved to any desired position. The plate holder is made to hold (1¼" X 8") plates, and by means of a bellows extension both adjustments in height and tilt are made possible. All the photographs from which measurements have been taken were obtained using this instrument. The dispersion for six prisms varies from 15 A° per.mm. in the red at H_α to 2.2 A° per ~~12~~ mm.at 4000 A°

(2) The Hilger spectrograph is an E.1. modèl and is equipped with both quartz and glass dispersive systems. This was used only during some preliminary experiments on tube design because of its relatively low resolving and dispersive power over the visible range.

The optical train used to produce sharp images on the slit of the spectrograph consists of a lens and Wollaston double image prism. Very good focussing is required in order to eliminate overlapping of the light emitted at different field strengths. In order to have the focus equally good for both the p - and the s - component images, the double image prism is used at a small angle to the horizontal. The lenses used were a Zeiss Tessar f 6.5 camera lens and a Zeiss f 2.7 camera lens, the latter being required with the glass spectrograph in order to fill the collimator lens with light.

Eastman 40 plates were employed for all the lines except H_α. For this line Eastman panchromatic cinematograph film was found very satisfactory, it being fast and very free from grain. A hydrochinone developer was used, made up according to a formula of L.E.Jewell. which is rather slow in its action, and very good for spectroscopic work.

Intensity Measurements.

The problem of making intensity measurements on spectral lines is a very difficult one, and only in recent years have such measurements reached any degree of accuracy. Direct measurements of radiation intensities are impracticable, so that photographic records have to be used. Thus the problem resolves itself into that of determining the relation between the blackening of the plate and the absolute intensity of the light falling on it, or, as is more generally the case in spectroscopic work, the relative amount of blackening produced by two sources of known relative intensities. The laws of blackening having been accurately found, it is then possible to compare intensities of lines provided some standard of comparison is used on each plate.

The difficulty arises on account of the complex relations involved in the plate calibration. It has been found that the blackening is a function of the following variables:-

(1) The exposure.
(2) The time of development.
(3) The developer.
(4) The type of plate.
(5) The sensitivity curve of the plate.
(6) The type of source (intermittent or steady)
(7) The intensity and wave length of the light.
(8) The dispersion of the spectrograph.

The intensities determined from such a calibration are photographic intensities only. In order to determine absolute intensities a standard source whose energy distribution is known is required, and the widths of the lines have to be taken into account as described later.

The problem of determining relative intensities of lines which appear on the same plate differing only slightly in wave length is free from many of these difficulties. Such is the case in measuring relative intensities of Stark components. Here the dispersion of the spectrograph and the sensitivity of the plate may be assumed constant over any set of components, and in all cases this time of exposure and plate treatment are the same for the lines considered.

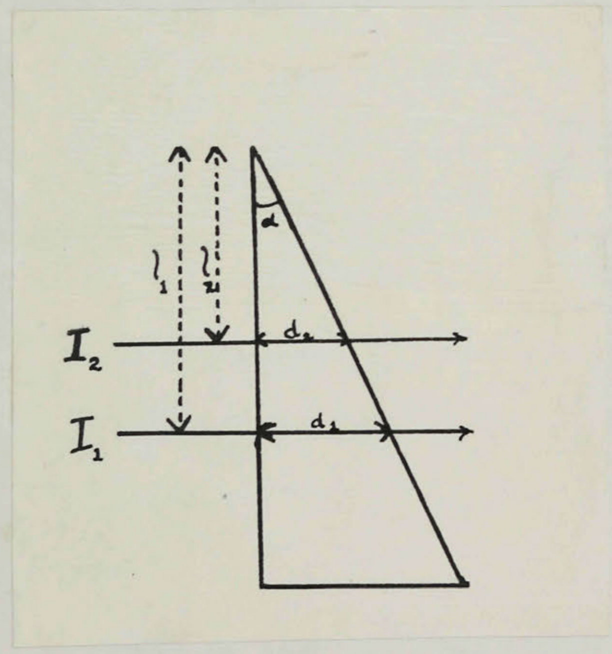
Stark measured the photographic relative intensities for the Stark components of the first four members of the Balmer series of hydrogen. As has already been pointed out these measurements have been found incorrect in several instances and a new determination was required.

The determination of intensities by means of a neutral glass wedge has been carried out with considerable success by * Merton and Nicholson and other experimenters. This general method was therefore employed in the present problem.

Merton and Nicholson - Phil.Trans A <u>216</u>,459, 1916.
and <u>217</u>,237, 1917.

A "neutral" tinted glass wedge is one which shows no absorption of a selective character throughout the region over which it is employed. In practice such a wedge is compensated by a similar wedge of colourless glass which is cemented to it so as to form a plane parallel plate. This wedge is placed in front of the slit of the spectrograph causing the lines at the photographic plate to fade away towards the dense end of the wedge. Thus the length of the lines on the plate correspond to intensities.

The simple theory of the wedge showing the relation between intensity and length of line follows from a consideration of the diagram in the margin.



If light of intensity I_1 penetrates a thickness d_1 of the wedge, and that of intensity I_2 penetrates a thickness d_2, then we have :

$$\frac{I_1}{I_2} = \frac{e^{-k_\lambda d_1}}{e^{-k_\lambda d_2}}$$

where k_λ is the coefficient of extinction per unit thickness of the wedge for a wave length λ.

$$\text{and } \log_e \frac{(I_1)}{(I_2)} = k\,(d_2 - d_1)$$
$$= K\,(l_1 - l_2) \text{ where } K = -k \tan\alpha \text{ and } l_1$$

and ℓ_2 are the lengths of wedge penetrated by the light of intensity I_1 and I_2 respectively.

We now define the density of the wedge D_λ for any wave - length λ by the relation:

$$\log_{10}\frac{(I_1)}{(I_2)} = D_\lambda(\ell_1 - \ell_2) \quad \text{i.e. } D_\lambda = .4343k \tan\alpha$$

From this formula the relative intensities of two lines of nearly the same wave length may be determined. For infinitely narrow lines this formula should give the true relative intensities, but in practice the lines are of finite width, and the relative energy content is given by

$$\frac{\int I_{\lambda_1}\, d\lambda_1}{\int I_{\lambda_2}\, d\lambda_2}$$

In order to evaluate these integrals an enlargement is made of the wedge photograph and the areas of the lines considered are determined by means of planimeter.

The intensities given by I_1/I_2 as obtained from the formula are known as the photographic intensities. If the lines are of nearly the same wave length, and are sharp in character, the photographic intensities will correspond very nearly to the absolute intensities. In the present investigation the photographic intensities only are measured.

In order to find the ratio $\frac{I_1}{I_2}$ it is first necessary to determine D_λ for the wedge used, and to obtain accurate measurements of the distance $(l_1 - l_2)$ on the photographic plate.

The wedge calibration for D_λ was made by using crossed nicols to reduce the light intensity in a known ratio and the wedge constant determined from the formula.

The optical system is shown in Fig. (6).
A Nernst glower is used as source. This is placed at the principal focus of the lens L thus producing a parallel beam in which the nicol prisms are placed. The lens (L) focussed the light at the slit of the spectrograph. The neutral wedge is mounted on the slit, and thus the image obtained on the photographic plate gives an exact record of the point in the wedge at which the light is completely cut off.

In practice two equal exposures are made on the same plate, different intensities being obtained by rotating the analyzing nicol. An iron arc comparison spectrum is added in order to determine the wave length accurately.
For convenience the ratio $I_1 : I_2$ are taken as 10 : I giving

$$D_\lambda = \frac{1}{l_1 - l_2}$$

Since the light transmitted by a pair of nicols varies with the square of the sine of the angle through which the analyzing nicol (A) is turned from extinction, the angles of rotation required are found to be 18° 26′ and 90° in order to give the correct intensity ratios. The angles are read on a fixed divided circle by means of a pointer attached to (A.)

The nicol prisms are cut with their end faces perpendicular to the beam of light so that no error arises due to variation in the angles of incidence of the polarized light when (A) is rotated. In order to eliminate error due to loss of light from the corners of the prisms when partially crossed, a diaphgragm (D) is inserted between (P) and (A) which restricts the light to a circular section through the centre of the prisms.

Considerable variation in the voltage operating the glower made it necessary to use a "floating battery" in order to keep the source constant during the calibration See Fig. (7).

The voltage of the 96 volt battery (B) is balanced against that from the 220 volt D.C. mains, the variable 390 ohms resistance being set so that a small charging current passes through the battery. Fluctuations in the applied voltage thus do not change the glower current, but simply vary the charging current. (V)is a voltmeter measuring the voltage across the glower. $(A_1)$is a milli-ammeter measuring the charging current And (A_2) an ammeter showing the current through the Nernst glower (G_2). The latter current was kept constant at .4amps. during exposures of twenty minutes each. The slit of the spectrograph was set at 0.1 mm.

The relative blackening of the wedge images was then determined at the desired wave length by means of a Moll self-recording microphotometer. Points of equal blackening were matched in the two curves, and, the magnification being known, the distance (l_1-l_2) could be measured. From this value, obtained from a number of plates in order to eliminate error in the prism settings, the value of D_λ was determined. (See Plate I (d) and (e))

	Line	D_λ
	H_α	.89
	H_β	.309
Values of D_λ	H_γ	.41
	H_δ	.564

In the present experiments the intensities were determined in two distinctly different ways.

(i) A source giving parallel components was used with sufficient magnification to produce images on the slit equal in length to the neutral wedge. Two similar wedges were mounted on the slit of the spectrograph, and the two sets of Stark-effect components were focussed so that the light from each passed through one of the wedges before reaching the spectrograph. An enlargement was made of the plate and the distance ($l_1 - l_2$) was found by measuring the difference in height of the lines. This value together with the known value for D_λ ,and the magnification of the enlargement, gave the relative intensities for any two lines in the region of wave-length, considered.

(ii) Stark photographs were taken with tubes giving a constant field over a short portion of the image. A wedge photograph of a continous source was then put on the same plate. In order to determine the intensities in this case, a Moll photometer curve was taken of the Stark components over the section in which the lines ran parallel, and without making any change in the adjustments of the instrument,a second curve was taken across the wedge photograph for the same region.

By matching deflections of the photometer for the lines considered with the corresponding deflections in the wedge curve, the blackening of the plate corresponding to known heights of the wedge could be found, and hence the required values of $(l_1 - l_2)$, the Moll magnification being known. The intensity calculations were then carried out just as in the previous method.

Discussion.

An outline has already been given of the methods employed in the theoretical determination of relative intensities for the Stark-components of the Balmer series of hydrogen. The values obtained by Kramers* using the correspondence princople, and by Schrödinger and Epstein using wave mechanics are plotted and compared with the experimental results of Stark and the writer in plates III , V, VII, and IX.

The estimates of intensities made by Kramers are based on application of the Bohr correspondence principle. According to this the relative intensities with which the Stark components appear should be intimately related to the values of the squares of the amplitudes of the corresponding harmonic vibrations occurring in the motion of the system within the limits considered. Accordingly Kramers calculates the intensities by finding the mean of the sum of the squares of the "relative amplitudes" of the vibrations occuring in the initial and final ststes. The "relative amplitudes" are the ratios of the coefficients arising in the Fourier expansion of the harmonic vibration of the system to the semi-major axis of the orbit which the electron is assumed to describe. In this way the values

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* H.A.Kramers - D.K.D. Vidensk. Selsk Skr. Naturv. og Mathem Afd.8, R 111, 3, 1919.

are brought to the same order of magnitude for the two states considered. It is pointed out that initially there is no way of knowing the relative importance of the two states in determining the intensities, and on this account the introduction of "relative amplitudes" is necessary. Bohr* predicted that for hydrogen both states would have to be taken into account, but that in the case of helium the initial state only would be considered. The latter has recently been shown to be the case by Foster in his treatment of helium displacements and intensities by quantum mechanics. In this work Foster finds admirable agreement between theory and experiment using fields as high as 1,00,000 volts per cm. It will be noticed, however, from the tables in Kramers' paper that much better agreement with the experimental results of Stark would be obtained if the intensities for hydrogen were calculated from the values of the relative amplitudes in the initial states only.

It is clear that any treatment of the problem based on the correspondence principle will become more accurate as the quantum numbers increase, since the motion in this case approaches the classical form. For this reason a study of the first few members of the Balmer series affords a very

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* N.Bohr D.K.D. Vidensk. Selsk. Skr.Naturv. og Mathem Afd.8, R 1V, 101, 1922.

godd test for the theory. The observations of Stark are in very good qualitative agreement with Kramers calculations; but several lines are reported which are forbidden by the theory, and in a few outstanding instances a reversal of intensities occurs between the observed and theoretical results. (e.g. H_β ± 4 : ± 6 s - components and H_δ ± 6 : ± 22 S - components.)

In a few cases Kramers finds that his calculated intensities are zero when the intensities are not actually zero. This is explained either on the grounds of a change in the Fourier coefficients caused by fine structure considerations which he neglects, or by supposing that while the amplitudes may be zero in the initial and final states of the atom, they need not be zero for all the mechanically possible positions between these states. Neglecting these states, the intensity may appear to be zero, while if they were taken into consideration the intensities would no longer vanish.

[*]Foster and [†]Kiuti have both obtained numerous plates confirming the theoretical calculations of displacements without any of the additional lines which Stark reports; and [▽]Foster has explained Stark's result on the basis of

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[*] J.S.Foster - Phys. Rev. 23,6, 668, 1924.
[†] M.Kiuti - Jap.Journal of Phys. 4, 13, 1925.
[▽] J.S.Foster - Astrophysical Journal 62 ,4, 229, 1925.

the effect produced on the lines by slight field variations during an exposure.

The present investigation was begun in order to obtain more accurate results than those of Stark with which to compare the estimates given by Kramers, and to use the results to determine the corrections in the theory required to make it agree with experiment. Some preliminary work was carried out in tube design, and results were obtained for H_β using the direct wedge method.[†]

Shortly after this work had been done there appeared a determination of intensities based on wave mechanics by Schrodinger which was strongly supported by the measurements on H_β.

Schrödinger[*] shows that the wave mechanics and quantum mechanics are equivalent and that for any problem he can write the terms of the corresponding Heisenberg matrix as known functions of the solutions of the wave equation. Therefore, in order to calculate the intensities of the Stark components, the wave equation is put into the Stark-effect form and solved. It is then possible to form a matrix, corresponding to that of Heisenberg, in which each of the elementsis a function of the solution obtained,

[†] J.S.Foster and M.L.Chalk. Nature 118, 592, 1926.
[*] E.Schrödinger - Ann. d. Phys. 4 80, 437, 1926.

the solutions being normalized beforehand. According to Heisenberg the square of the amplitude of an element in the matrix is a measure of the probability of transition between the two states considered. In order to determine the energy emitted at that frequency, the square of the amplitude is multiplied by the coefficient of the fourth power of the frequency of emission as required on the classical theory.

Following Heisenberg, Schrödinger determines the relative intensities by calculating the values of the terms in his new matrix, and performing the above operations. Actually in determining the relative intensities in the case of the Stark components, the multiplication by the term containing the frequency is of comparatively small importance, since the difference in frequencies for the lines considered is always small. The effect of this term would be, however, to make the intensities slightly weaker for components lying towards the red.

The selection and polarization rules for the Stark-effect are included in the solution of the wave equation, and agree with the results already obtained by experiment and from the calculations of Schrödinger.

*Epstein independently calculated the intensities of the Stark components for the first four Balmer series lines using the Schrödinger wave equation. The equation is solved by a method of successive approximations, and applying the above method,the amplitude and the polarization rules are determined.

These amplitudes are compared with the results obtained by Stark and are plotted in plates 111, V, V11, and 1X. The agreement with Stark's results is much better than is obtained by Kramers from the correspondence principle. In using the amplitudes insted of their squares, (as is done by both Kramers and Schrödinger), Epstein quotes from a paper on the intensities of multiplets by H.N.Russell in which it is stated that the observed values, estimated by the experimental physicist from the blackening of the photographic plate, are not proportional to the intensities but to their square roots, i.e. to the amplitudes of the emitted waves.

On the other ahnd, Epstein's results are in total disagreement with the values obtained by Schrödinger though he considers the same problem and uses the same equation. The discrepancies are quite unaccouhted for by his neglecting

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* P.Epstein. Phys.Rev. 28 695, 1926.

to square the amplitudes. The results have not been checked by the writer but it is thought that an error has been introduced into the expression obtained for the amplitudes. From these results, moreover, there is no evidence of the sum of the intensities in the two polarizations being equal as predicted by Bohr, and demanded by the theory of Schrödinger. This latter condition is further to be expected from the theoretical results obtained by Foster* in the case of helium, which are qualitatively correct in the lines observed.

Finally it must be stated that for all the components observed by the writer, the intensities correspond to those calculated by Schrödinger. A description of the plates and the results obtained for the separate components are given in the following sections.

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* J.S.Foster. Proc. Roy. Soc. 117, 37, 1927.

Results.

The results obtained in the determination of the intensities may best be explained by reference to Plates I - IX. The results for each of the lines are tabulated and a general criticism of the observations follows. The observed values for different pairs of components are compared with the relative intensities as calculated from Schroedinger's values. The lines are designated in the usual way in terms of the unit of displacement.

Line	Polarization		Observed Rel.Ints.	Calc.Rel.Ints
H_α	p	$\frac{\pm 3}{\pm 4}$	1.38	1.37
		$\frac{\pm 3}{\pm 2}$	3.32	3.16
		$\frac{\pm 4}{\pm 2}$	2.40	2.31
		$\frac{\pm 0}{\pm 1}$	1.40	1.42

Line	Polarization		Observed Rel. Ints.		Calc. Rel. Ints. Schroedinger
H_β	p	$\frac{\pm 8}{\pm 10}$	1 1.02 1.11	1.04	1.06
		$\frac{\pm 8}{\pm 6}$	4.54 4.65	4.59	4.74
		$\frac{\pm 10}{\pm 6}$	4.45 4.03	4.24	4.46
	s	$\frac{\pm 4}{\pm 6}$	1.54 1.59	1.56	1.56
		$\frac{\pm 4}{\pm 2}$	9.06 3.42	6.24	6.35
		$\frac{\pm 6}{\pm 2}$		4.00	4.07

H_γ	p	$\frac{\pm 18}{\pm 15}$	1.18	1.14
		$\frac{\pm 5}{\pm 2}$	1.03	1.23
	s	$\frac{\pm 10}{\pm 13}$	$\left.\begin{matrix}1.11\\1.05\end{matrix}\right\}1.07$	1.063
H_δ	p	$\frac{\pm 28}{\pm 24}$	1.72	1.34
	s	$\frac{\pm 6}{\pm 10}$	1.77	2.02

The intensities of the components in the case of H_α were measured from the photograph shown in Plate II. An exposure of one hour was made using neon in the tube with an applied voltage of 8000 volts and a current of 4 mil.amps. No secondary spectrum lines appear. Visual observations and photometer curves from other photographs were obtained which gave good support to the measured intensities. The strong central p-component which appears in the photometer curve is due to the overlapping of the s-components, and does not indicate an undisplaced line in this polarization.

Measurements were made in H_β from four different plates using different proportions of hydrogen and helium in the tubes. Two of the plates (See plate lc) were taken using a tube of type (1) with a ribbon cathode and direct wedge photographs were obtained. The field distribution and light intensity were found to be constant from a preliminary exposure with the wedge removed from in front of the slit. This is shown in Plate I a. and the contact print Ib. The tube was operated at 7000 volts, drawing a current of 15 mil. amps. The other results were obtained using a tube of type (4.d.) such as was used for the other lines. One of the photographs is reproduced in plate IV.

In determining the intensities for the components in H_γ considerable difficulty arose because of the superimposed secondary lines (Plate VI). With the field distribution employed, these could always be observed, however, and the measurements on the photometer curves were taken from section of the curve which was believed to be free from secondary lines. Although the inner components in the s-polarization were strong, no intensity measurements were made on these lines because of the overlapping of the p-components. The two sets of p-components ±18; ±15 and ±5; ±2 shown in the diagram Plate VII are not necessarily plotted on the same scale, because although relative intensities were obtained for the pair ±18: ±15 and for the pair ±5 : ±2 no measurement giving the ratio of the intensities of lines belonging to the different sets was obtained.

Measurements on H_γ were interfered with by secondary lines, but one photograph was sufficiently clear to yield the results shown in Plates VIII and IX.

Very good agreement with the calculations of Schroedinger is obtained for all the components of H_α and H_β which have been observed.

In the case of H_α, Kiuti[*] has obtained the weak components s-±5 and ±6 required by the theory and found a faint indication of p ±8 from the apparent relative intensities of these to the grating ghosts, he estimates their intensities to be a few thousandths of that of the strongest lines. No attempt was made to obtain these lines in the present investigation, since direct measurements between such weak components and the other lines could not be determined with any better degree of accuracy than has already been attained.

Estimates of the intensities for H_β have been made by both Foster* and Kiuti**. Both these writers report analyses varying considerably from the original results of Stark. From observations on H_β, H_γ and H_δ Kiuti paints out, however, that his results for intensities agree qualitatively with those of Stark, and he states that the theory (of Kramers) emphasizes the intensities of the outer components too much. Foster estimates the relative intensity of s ±4 to s ±6 as being 2; but no quantitative mesurements have been made by any experimenters since Stark published his results.

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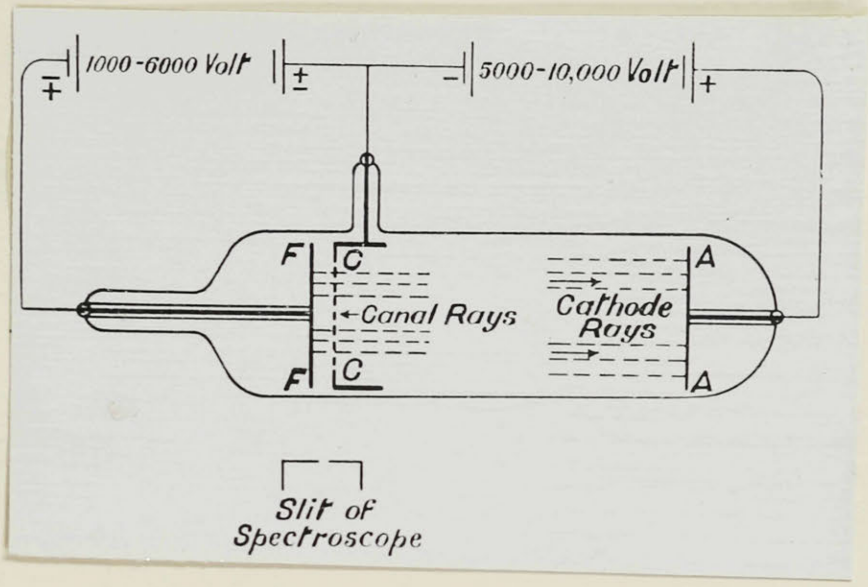
* J.S. Foster- Astrophys Journ. 62 229, 1925.

The results for H_γ show a reversal of the p ± 2 to p ± 5 intensities as observed by Stark; but otherwise no very great variations from his results are obtained. In H_δ p ± 28 to p ± 24 intensities may be affected by secondary lines. The agreement with the theory is not good, but is considerably better than that existing for Stark's observations on the same lines.

The diagram of intensities, shown in Plates III, V, VII and IX, gives a clear representation of the results obtained and their relation to all the theoretical and experimental work which has been done on the determination of intensities of Stark-components in hydrogen. It is not thought that the type of source could account for variations in intensity comparable with those existing between the results of Stark and those of the writer. No forbidden components are present in the new photographs, and a very clear analysis is obtained, this being very clearly demonstrated by the strong helium lines which appear on the plates. It is therefore thought that the measurements herein reported are considerably more accurate than any which were reported by Stark.

From the results obtained it may be stated that, within the limits of experimental error, the calculations of Schroedinger for the relative intensities of Stark components in the Balmer lines of hydrogen are correct.

(a)


1000-6000 Volt
±
5000-10,000 Volt
+
F
C
Canal Rays
Cathode Rays
A
Slit of Spectroscope

(b)

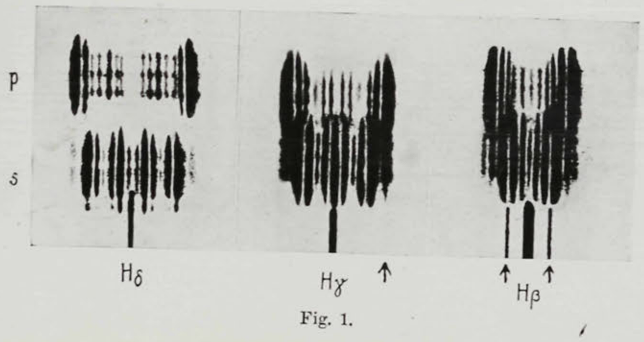

p
s
Hδ
Hγ
Hβ

Fig. 1.

FIG. 1.

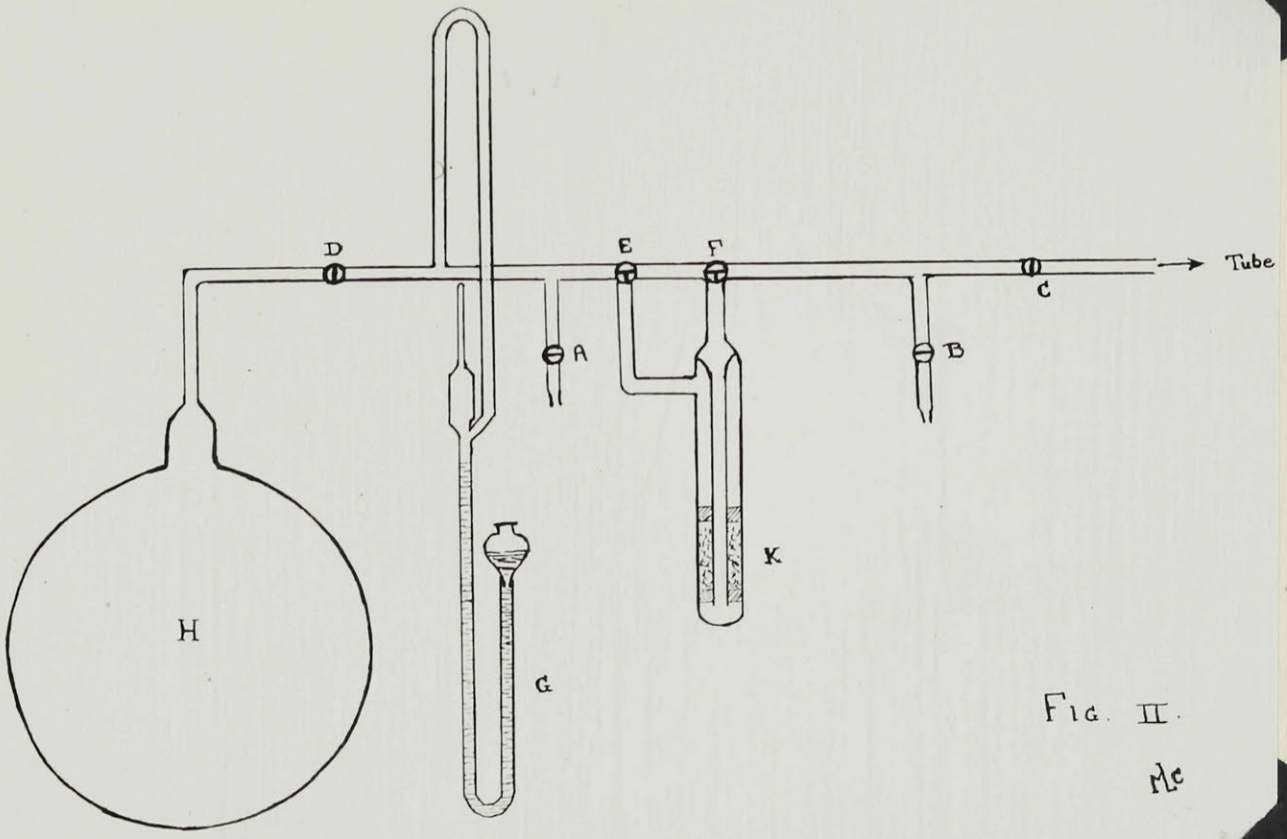


Fig. II.

Mc

Fig. 2

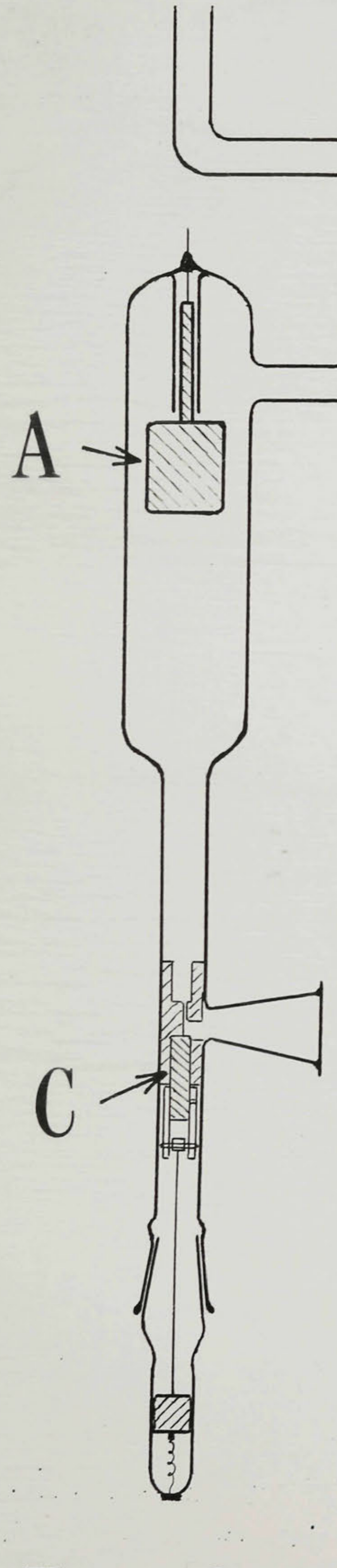


Fig. 3a

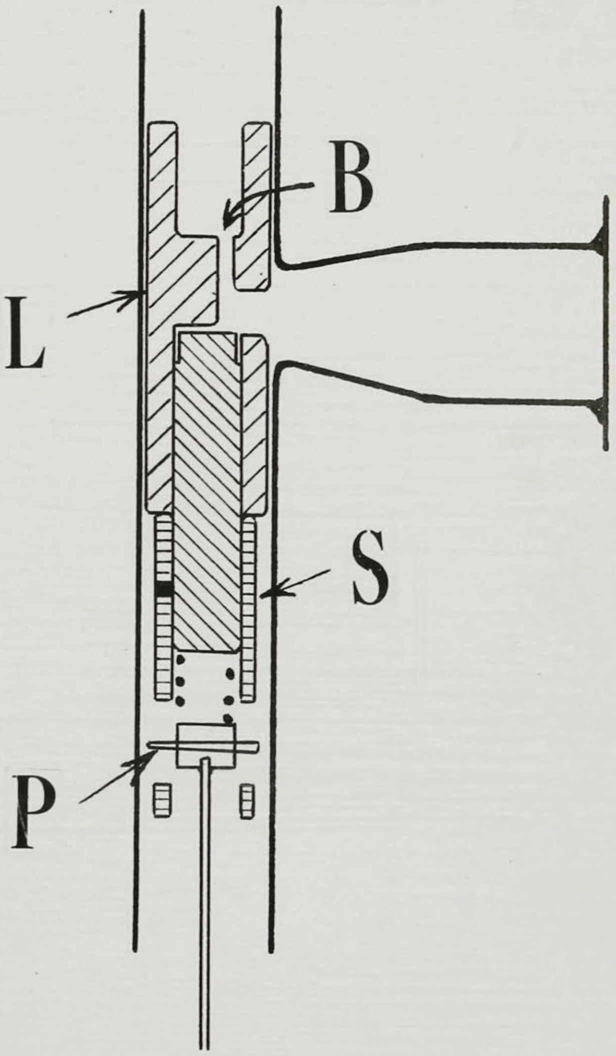


Fig. 3b

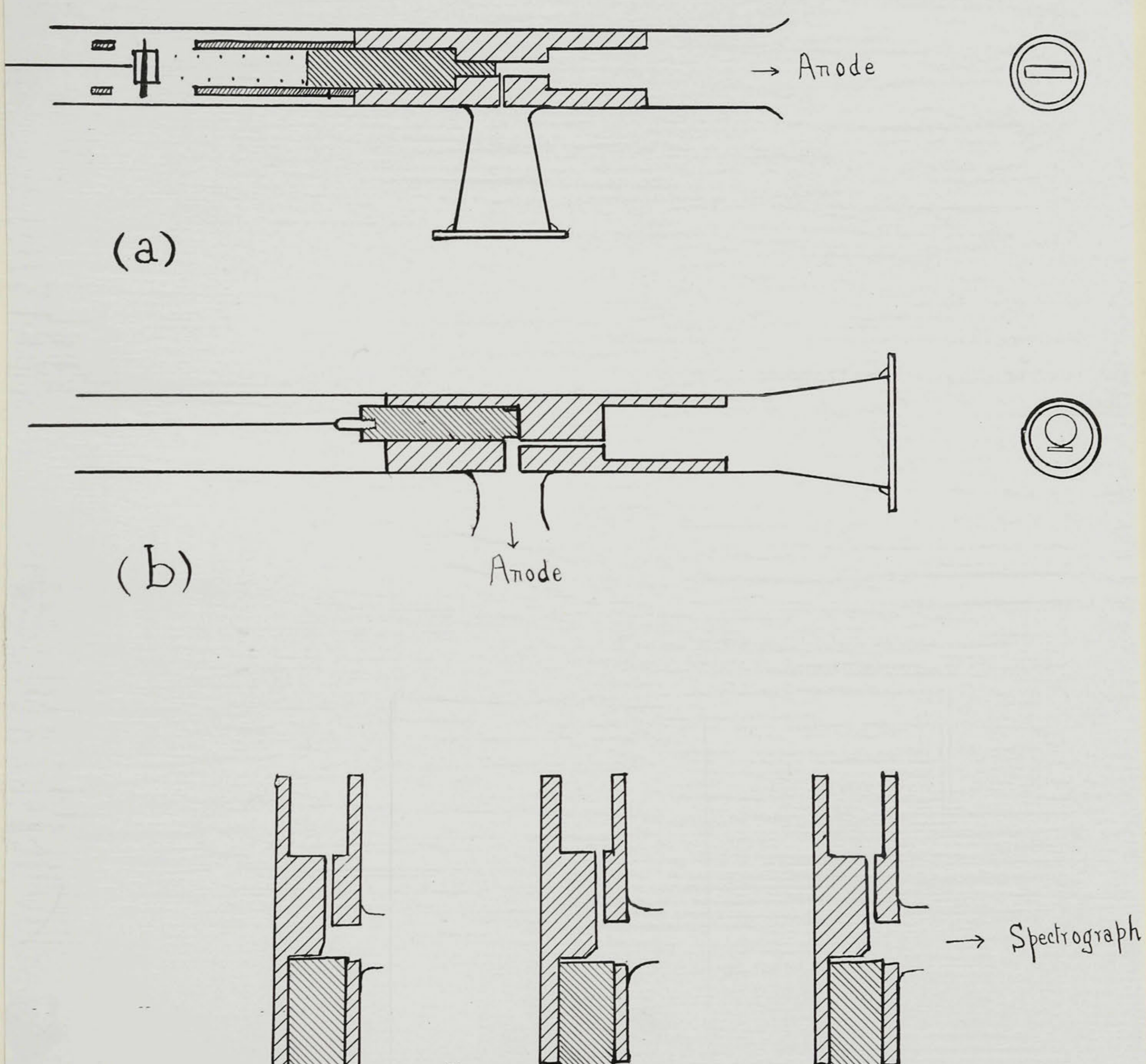


FIG. 4

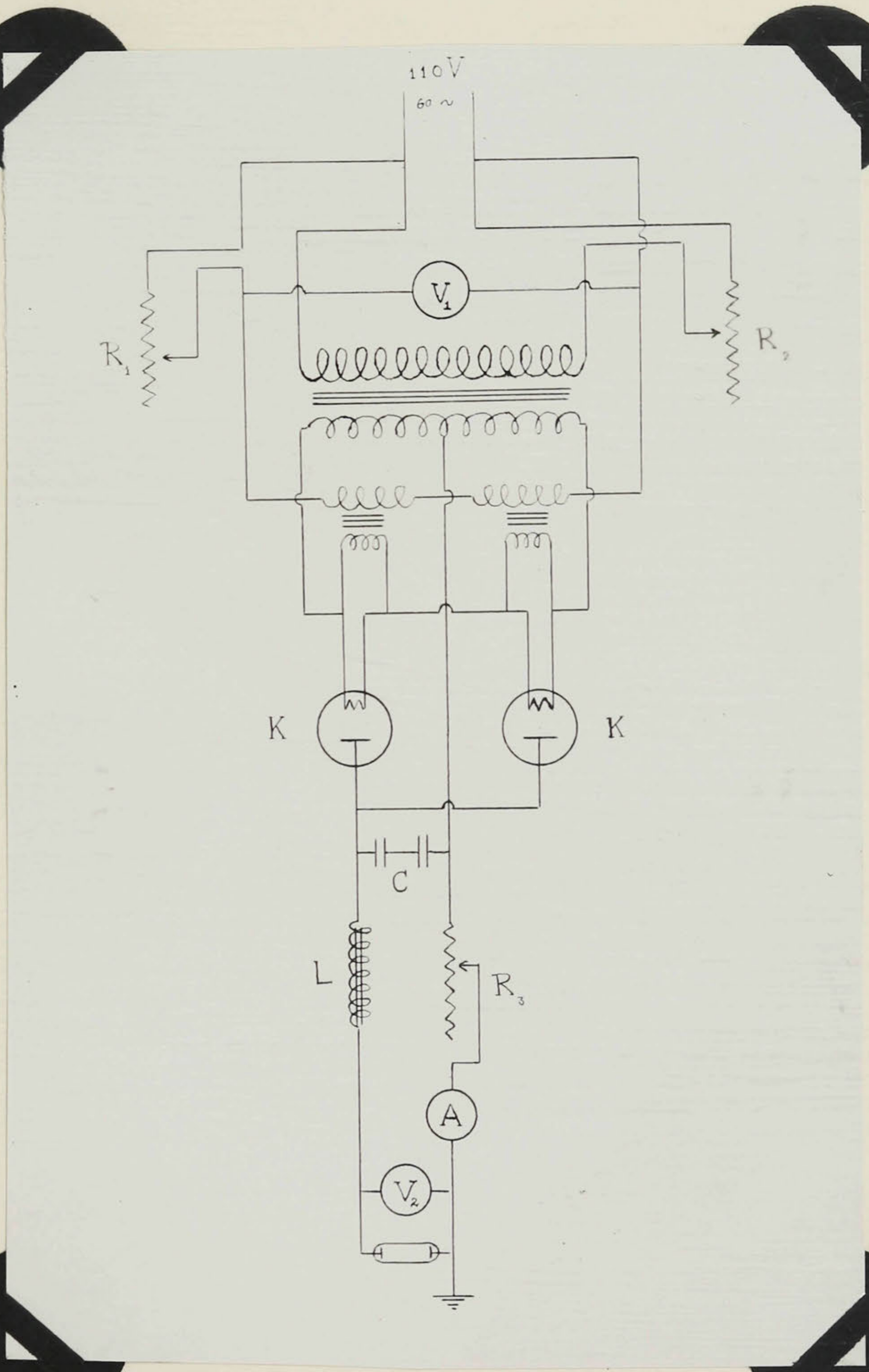


Fig. 5.

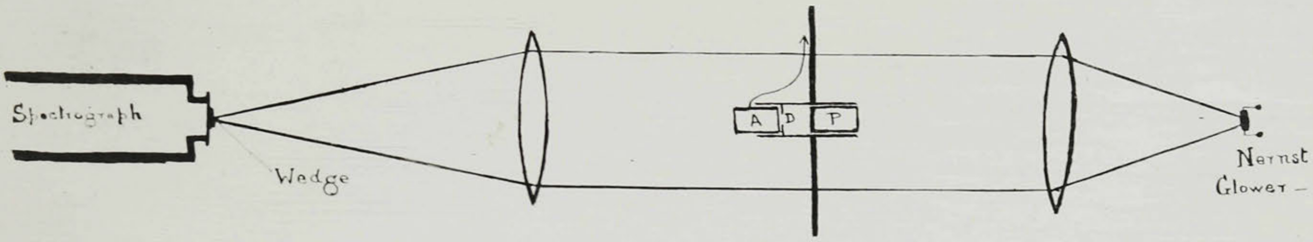

Spectrograph
Wedge
A
D
P
Nernst
Glower –

Fig. 6.

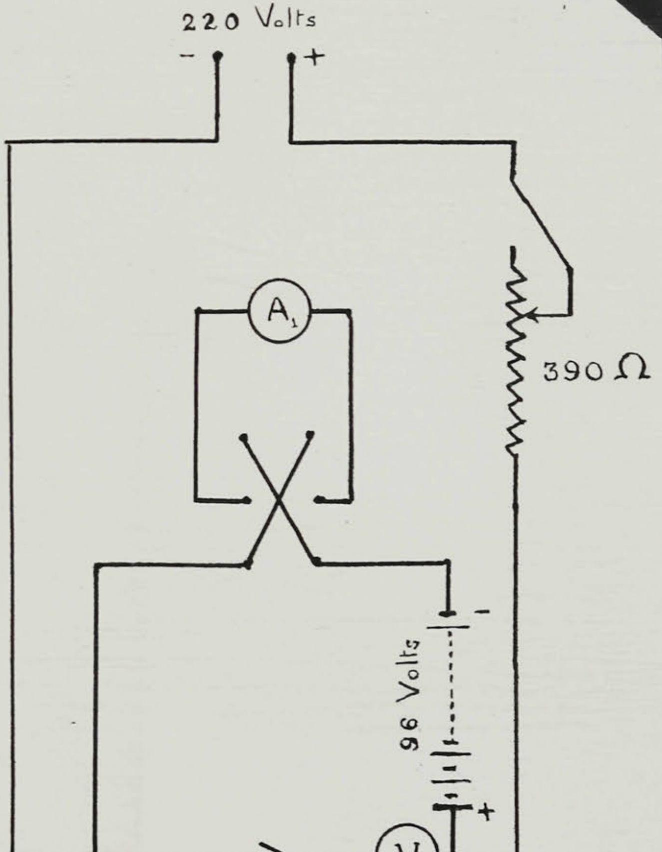
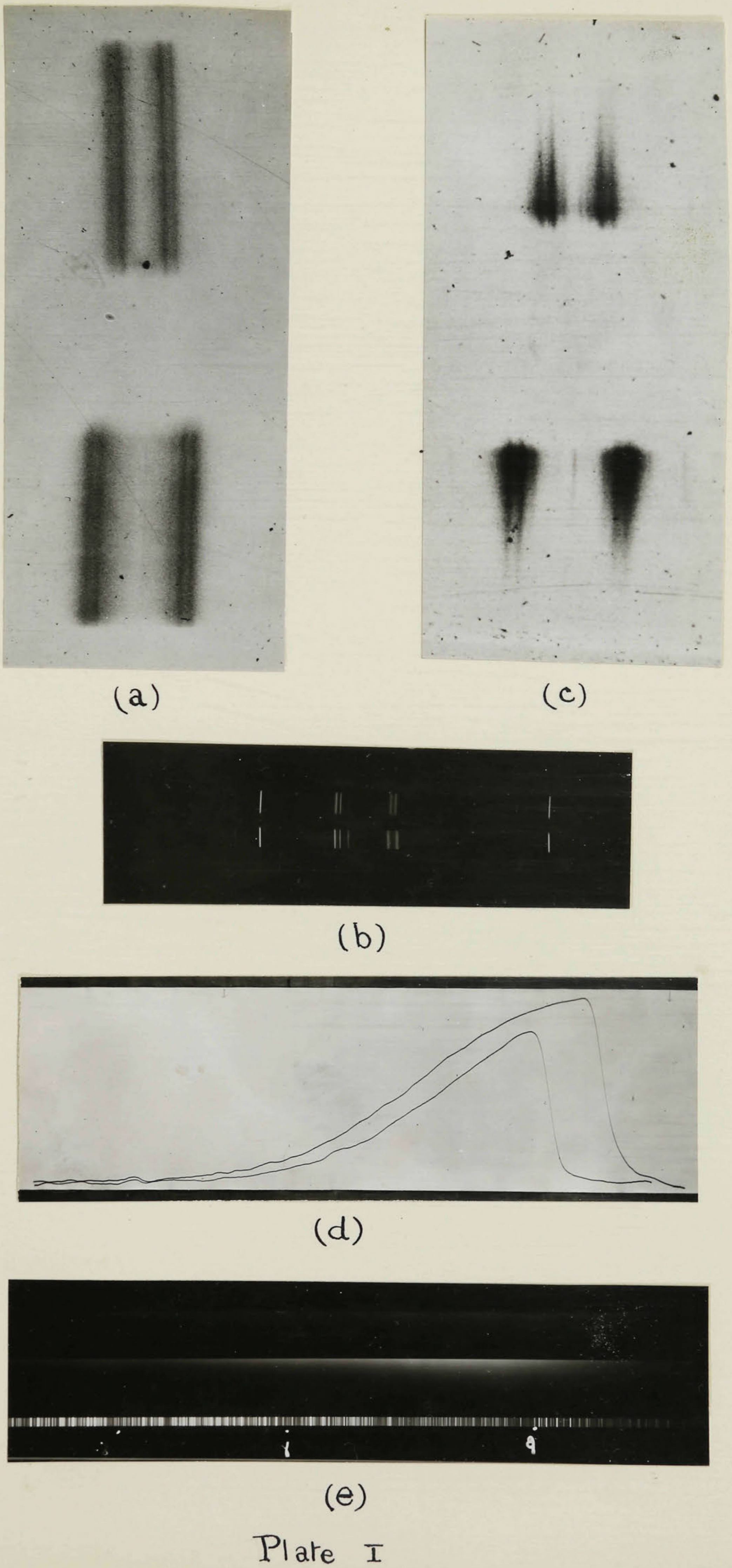

220 Volts
–
+
A_1
390 Ω
–
96 Volts
+
V
G
A_2

Fig. 7.



(a) (c)

(b)

(d)

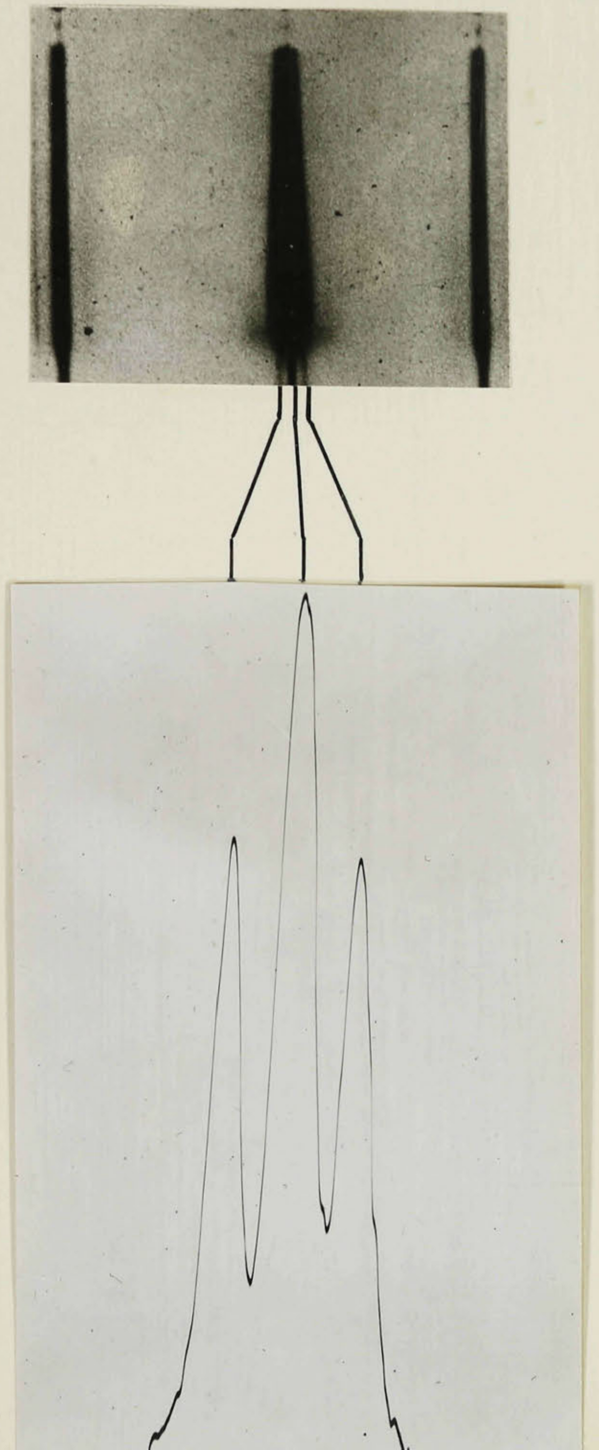
(e)

Plate I

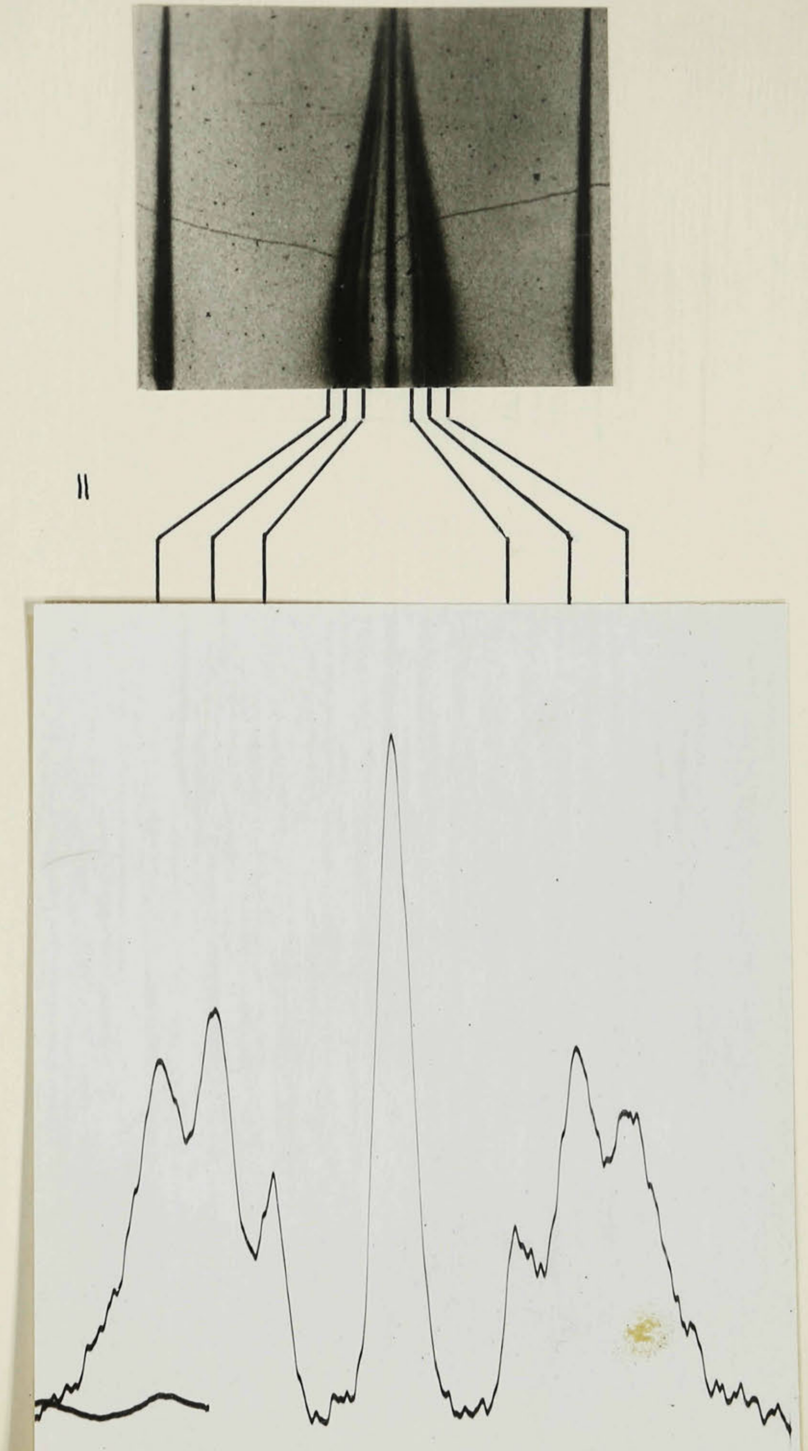
Plate II

H_α

$\perp$



$\parallel$



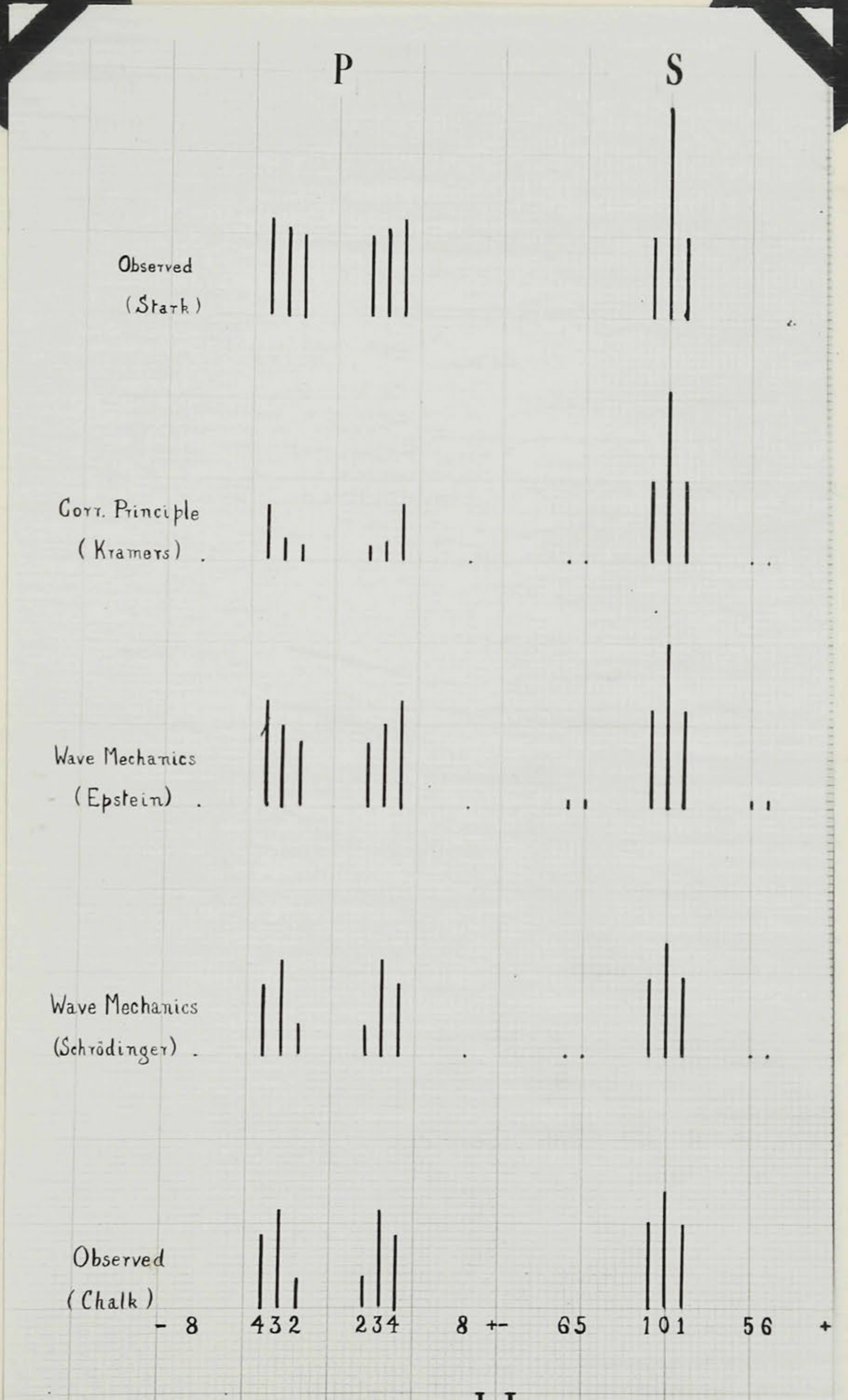
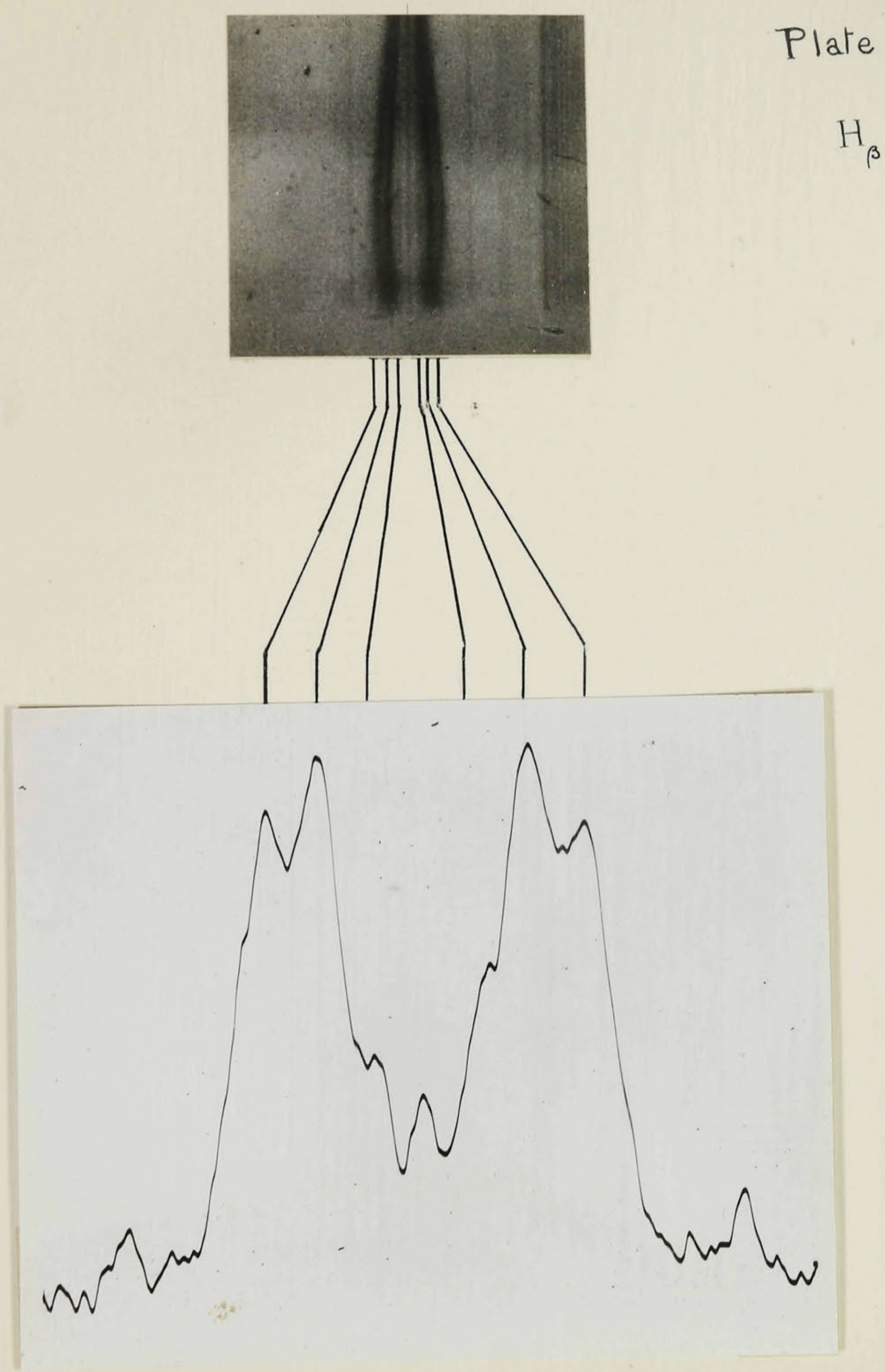

P
S
Observed
(Stark)
Corr. Principle
(Kramers)
Wave Mechanics
(Epstein)
Wave Mechanics
(Schrödinger)
Observed
(Chalk)
- 8
4 3 2
2 3 4
8 +-
6 5
1 0 1
5 6
+
H_α

Plate III.

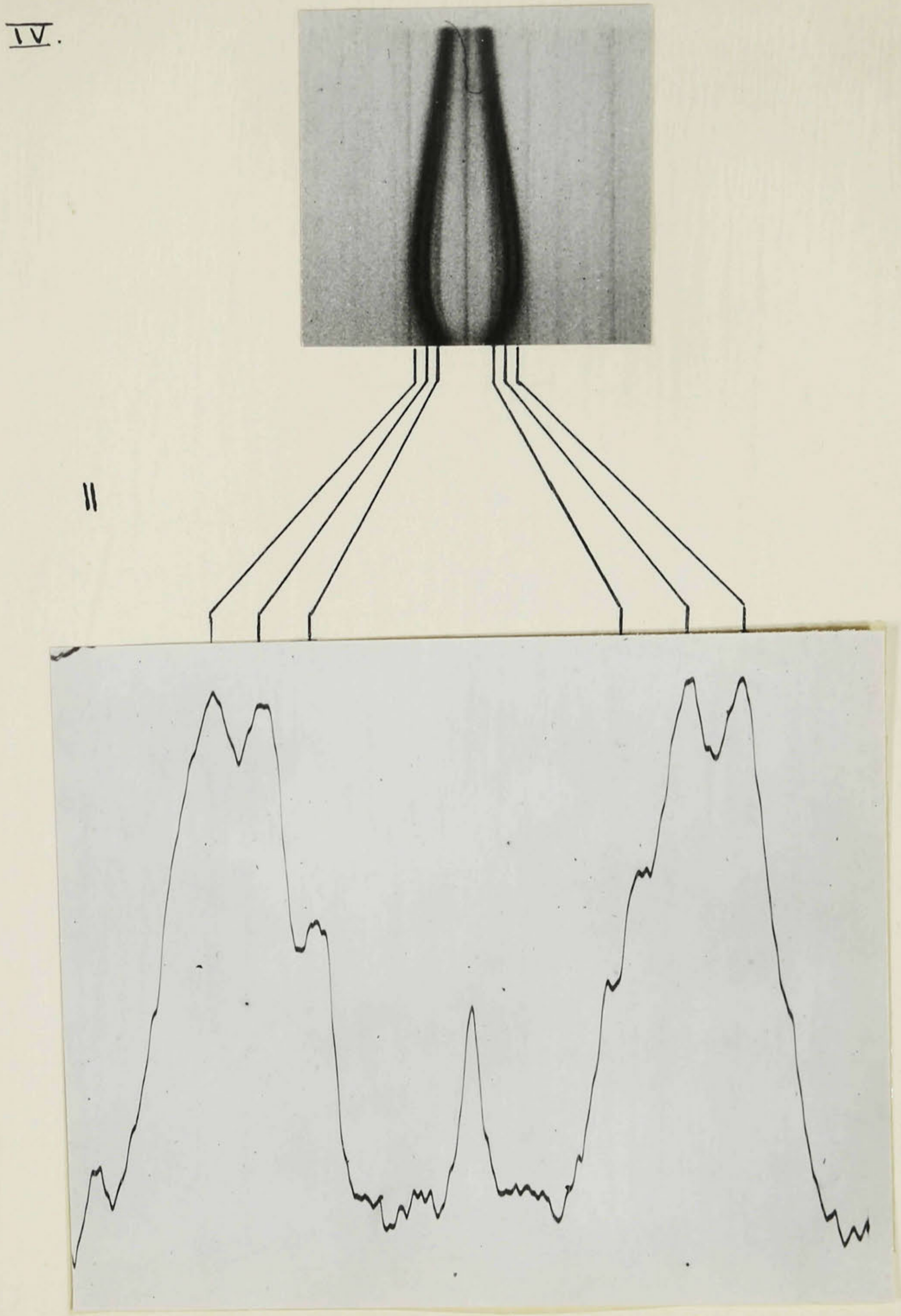
Plate IV.

H_β

$\perp$



$\parallel$



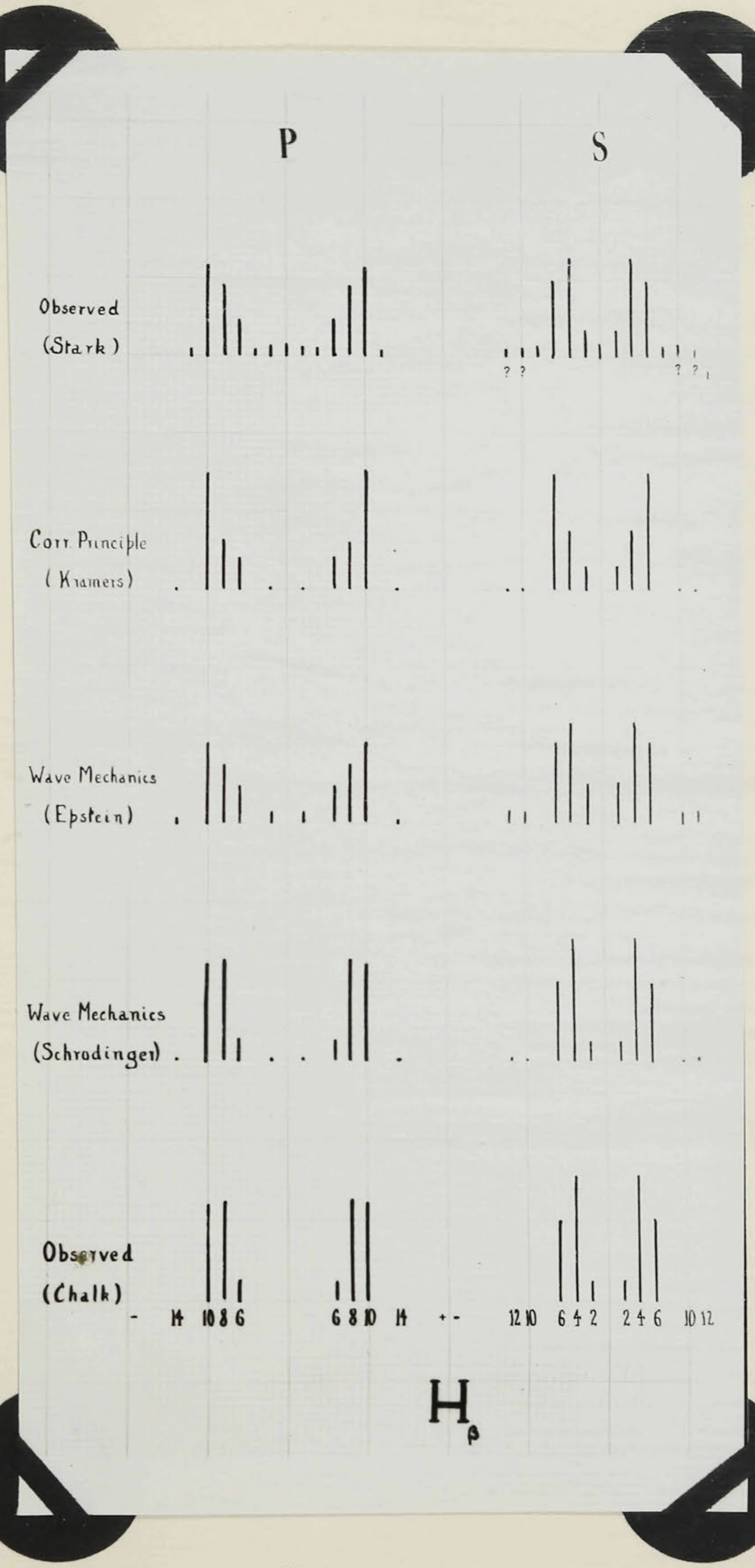
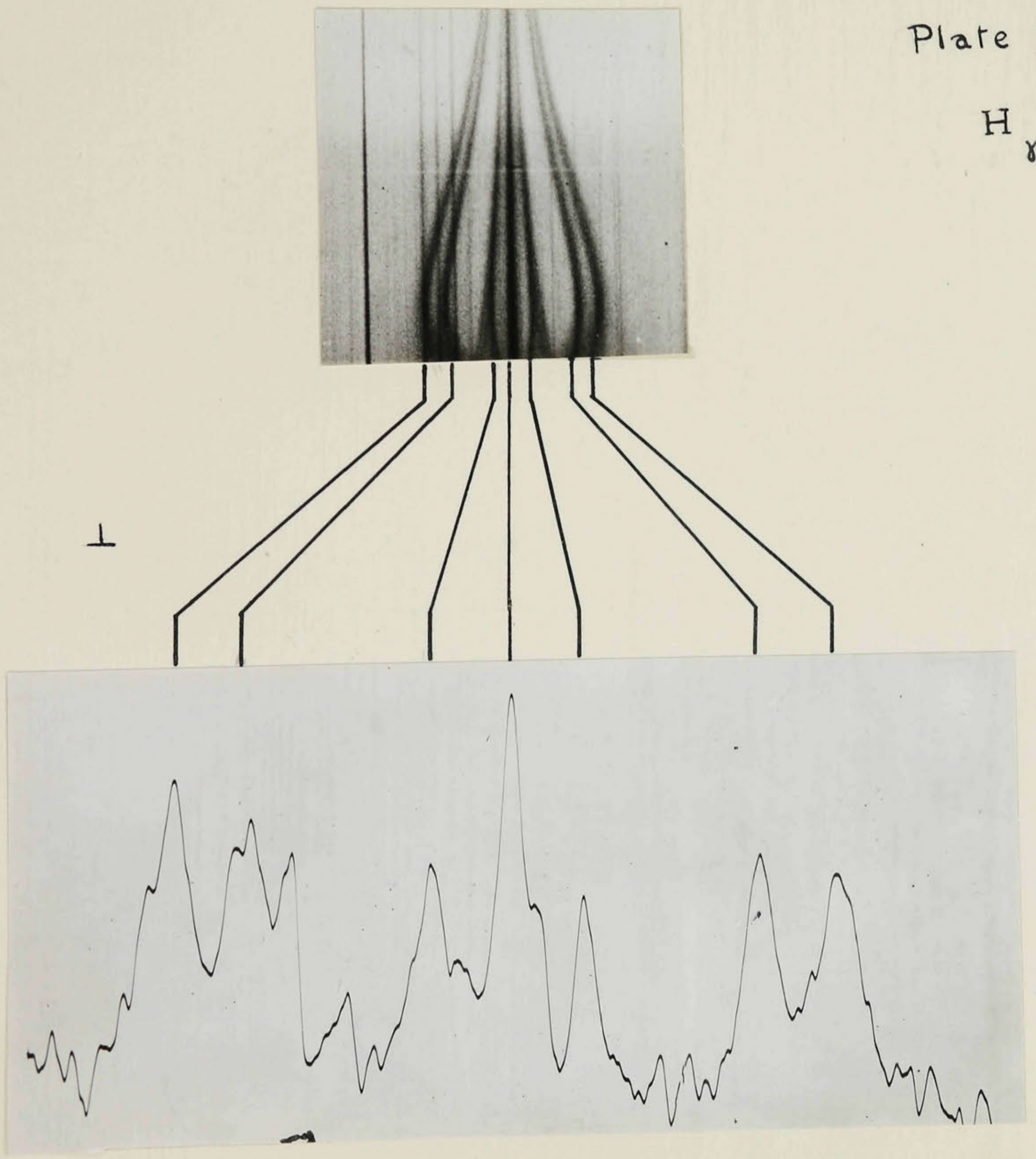
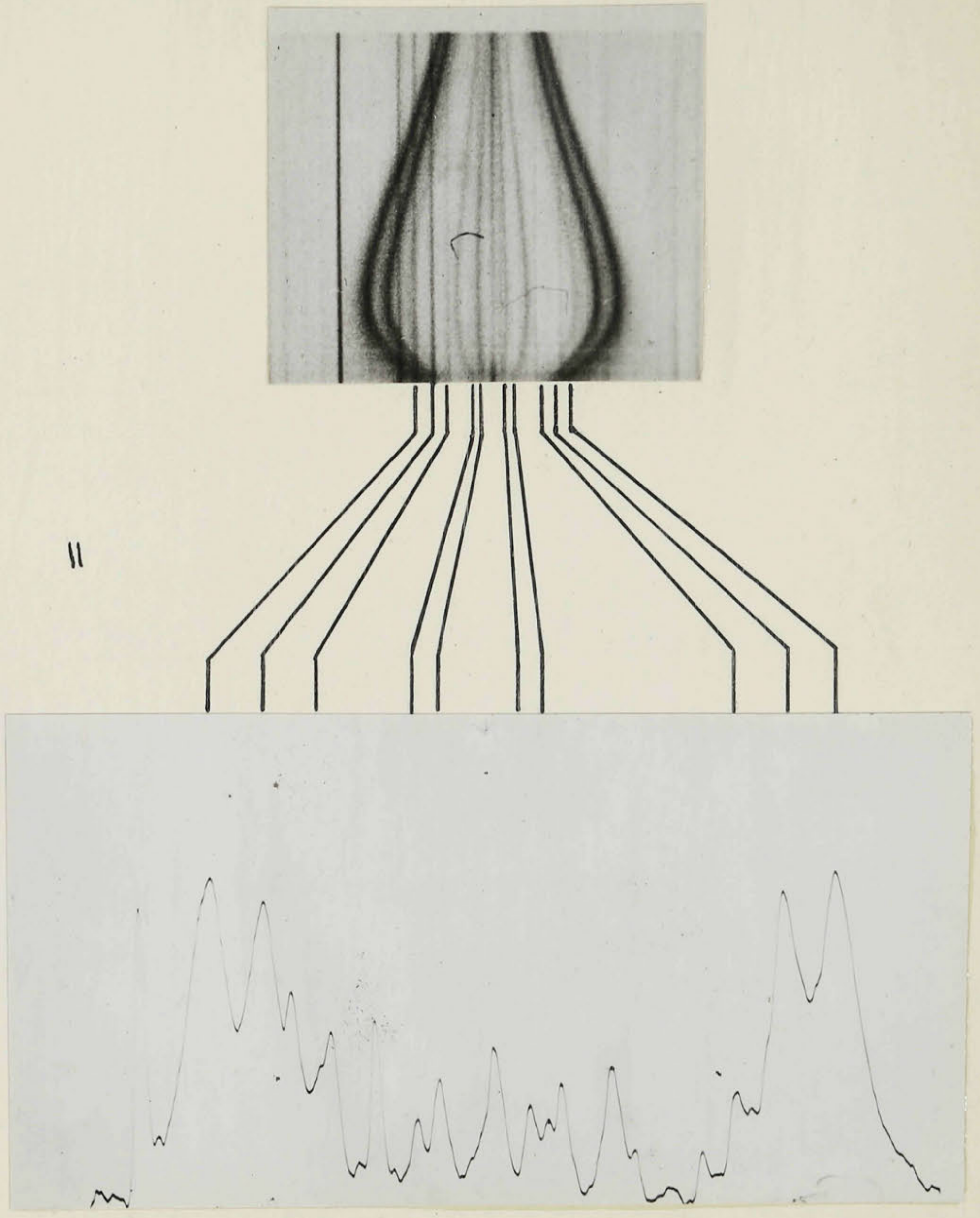

P
S
Observed
(Stark)
? ?
? ?
Corr. Principle
(Kramers)
Wave Mechanics
(Epstein)
Wave Mechanics
(Schrodinger)
Observed
(Chalk)
- 14 10 8 6
6 8 10 14
+ -
12 10 6 4 2
2 4 6 10 12
H_β

Plate V.

Plate $\overline{VI}$

H_γ





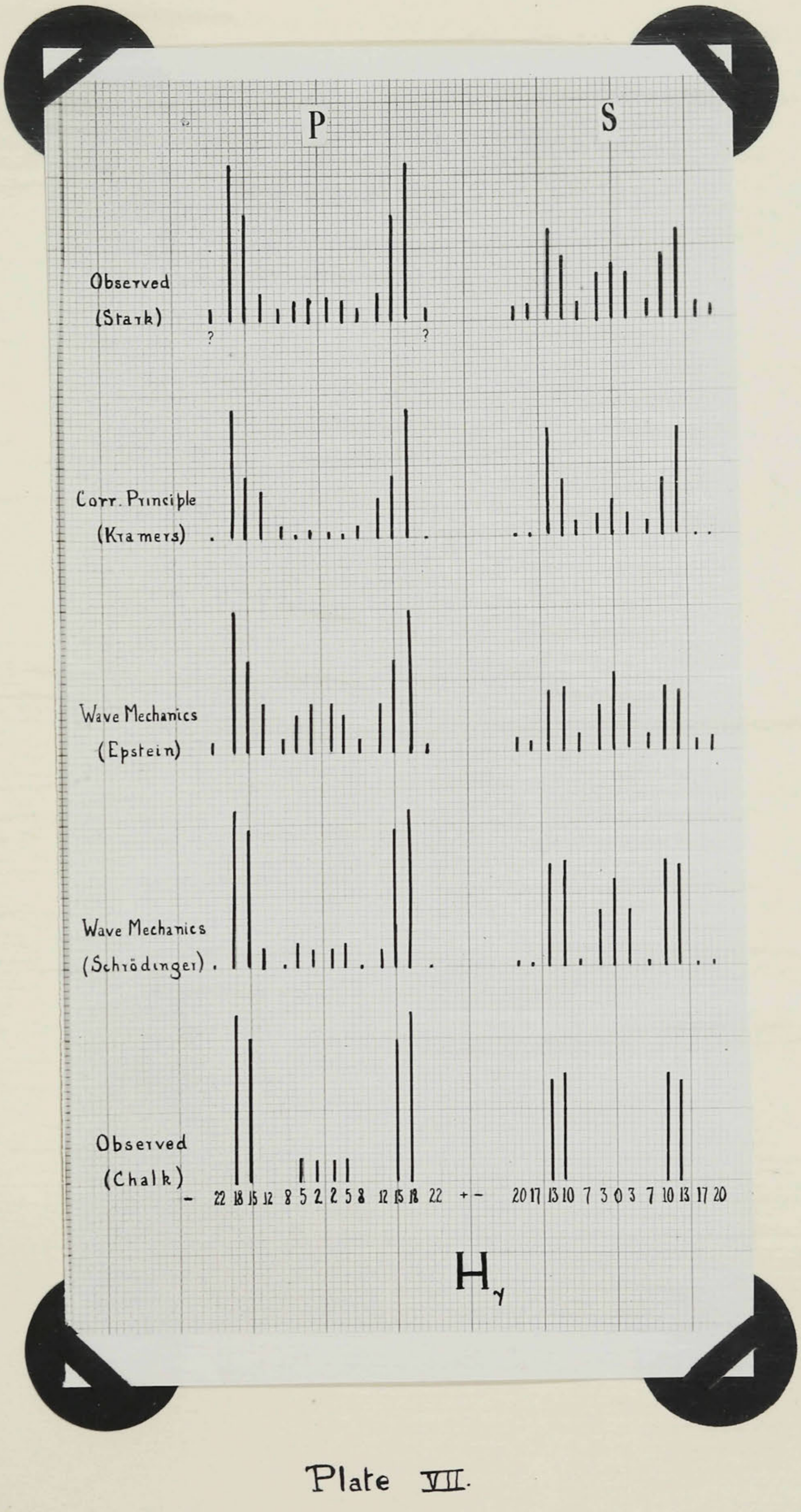
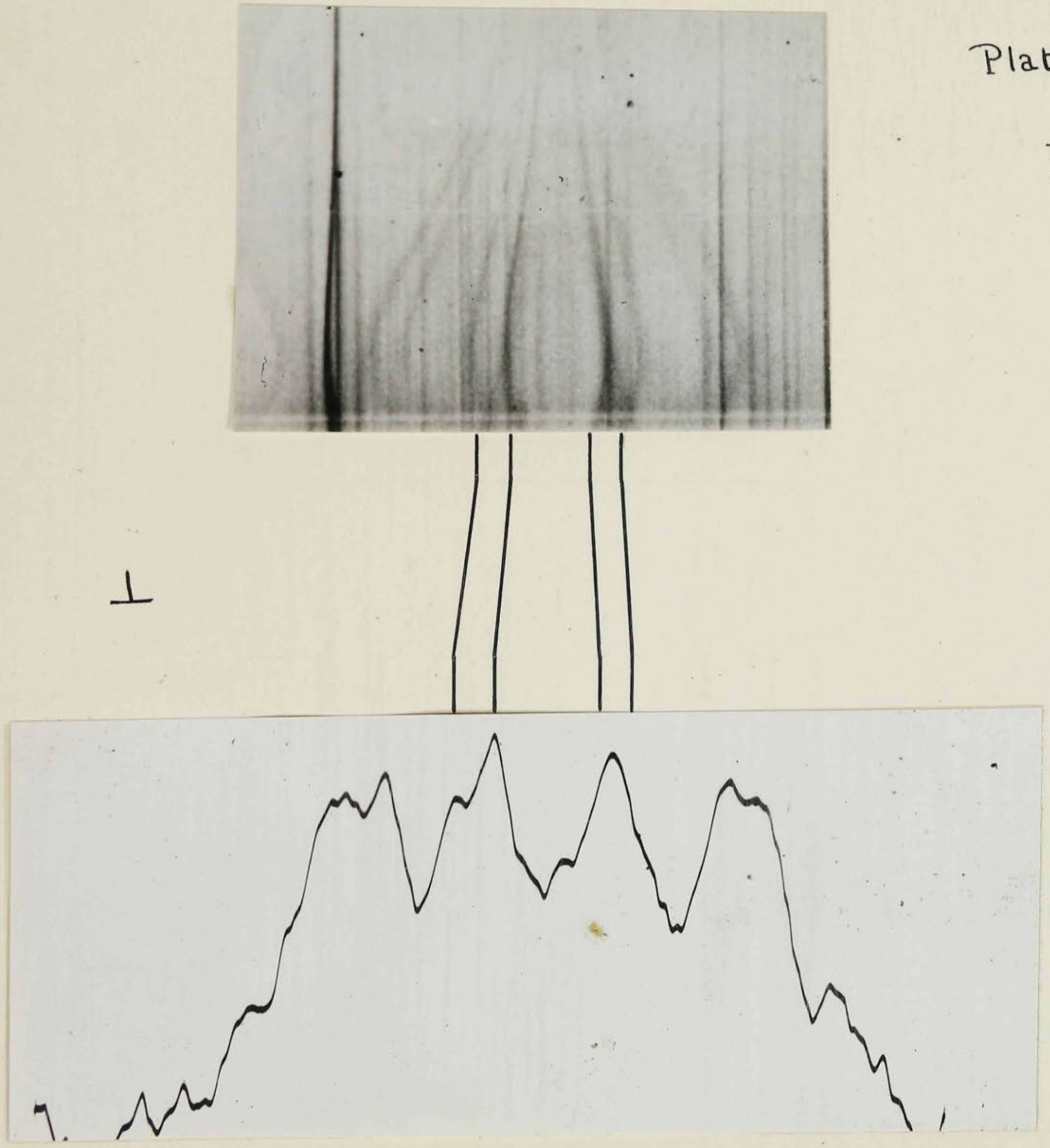

P
S
Observed
(Stark)
?
?
Corr. Principle
(Kramers)
Wave Mechanics
(Epstein)
Wave Mechanics
(Schrödinger)
Observed
(Chalk)
- 22 18 15 12 8 5 2 2 5 8 12 15 18 22 + -
20 17 13 10 7 3 0 3 7 10 13 17 20
H_γ

Plate VII.

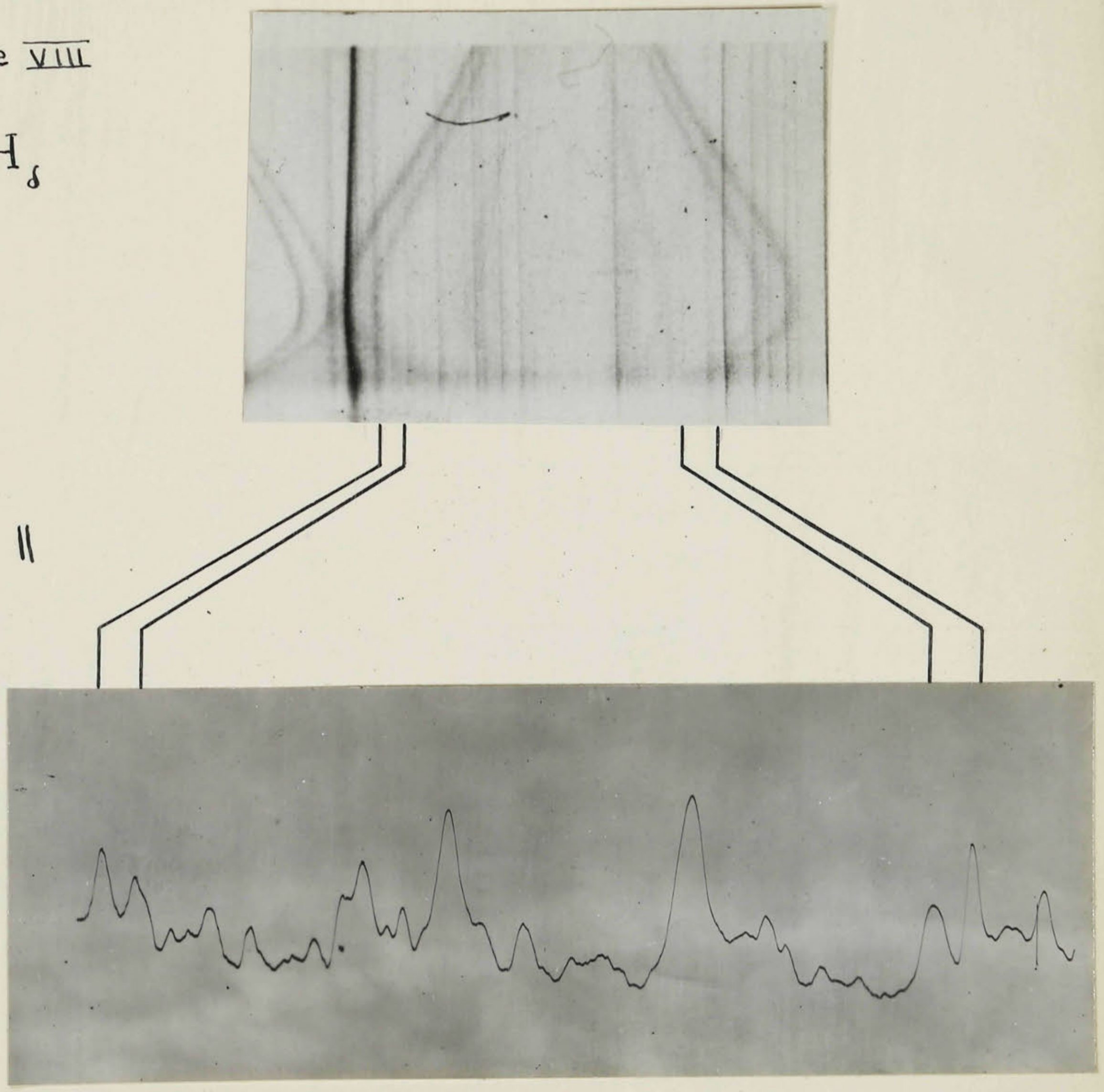
Plate VIII

H_δ

$\perp$



$\parallel$



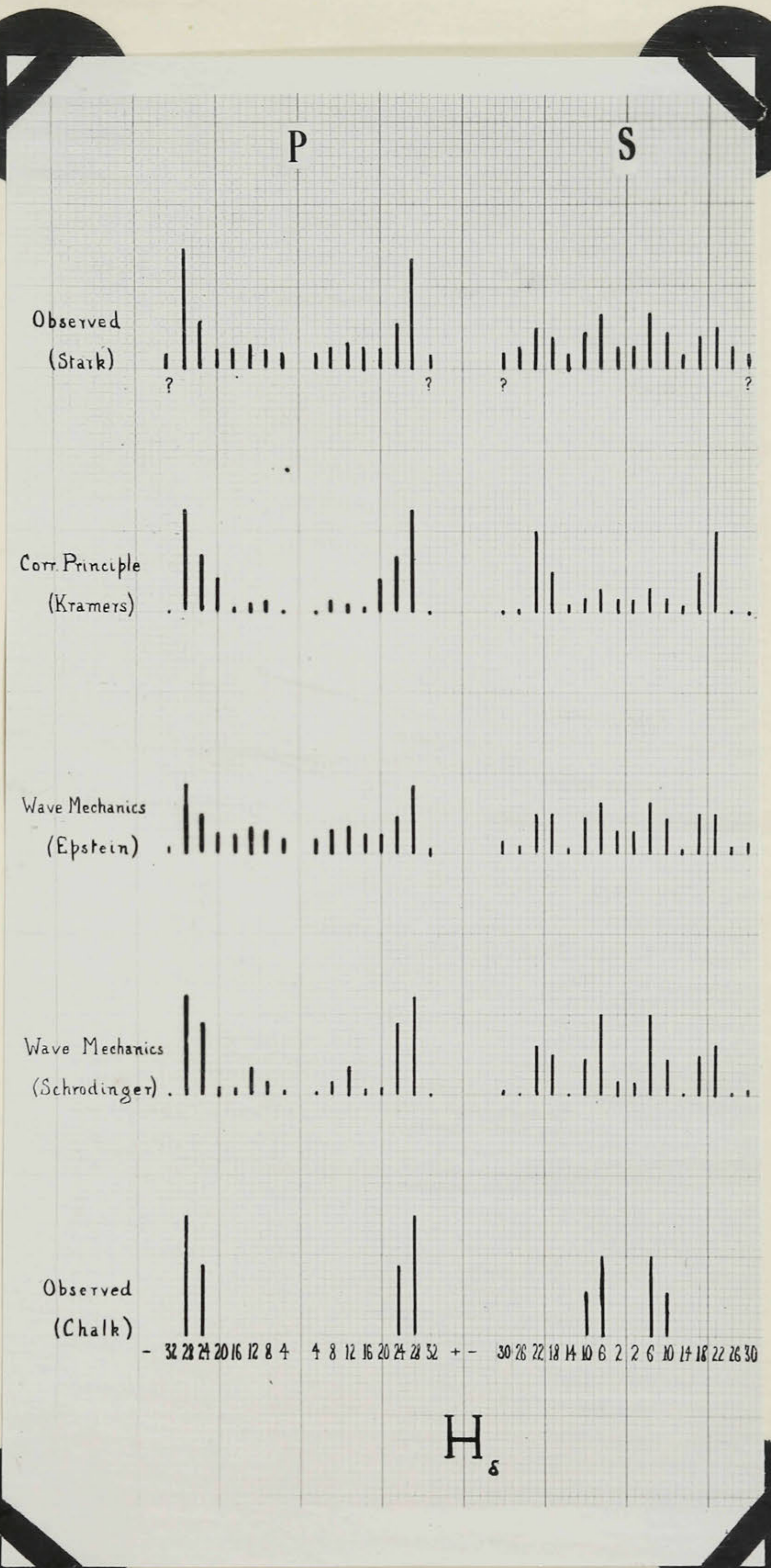

P
S
Observed
(Stark)
?
?
?
?
Corr. Principle
(Kramers)
Wave Mechanics
(Epstein)
Wave Mechanics
(Schrodinger)
Observed
(Chalk)
- 32 28 24 20 16 12 8 4 4 8 12 16 20 24 28 32 + - 30 26 22 18 14 10 6 2 2 6 10 14 18 22 26 30
H_δ

Plate IX