The Effect of an Electric Field on the Spectrum Lines of Hydrogen.

By

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(Received January 26, 1917.)

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§ 1. Introduction.

In 1913, the effect of an electric field on spectrum lines was investigated by Stark[1], and also by Lo Surdo[2] under different experimental conditions.

In a series of subsequent investigations undertaken by Stark and others, several elements beside hydrogen and helium were also examined. The results relating to these researches are collected in Stark's "Elektrische Spektralanalyse chemischer Atome."[3]

In the mean time, many researches were carried out by different workers after the method first employed by Lo Surdo. Among those we may cite Evans and Croxson[4] who have dealt with the helium line λ 4686 Å.U.

Quite recently, by adopting Lo Surdo's method, Howell[5] studied the manner of decomposition of certain spectrum lines of lithium and calcium in an electric field.

While Stark used canal rays as the source of light, Lo Surdo employed the glow in the region immediately in front of a cathode where the potential gradient is very large.

In Howell's paper, it is stated that the results obtained by Lo

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1 Sitz. Ber., Berlin 932 (1913).
2 Rendiconti d. Lincei, **22** 664 (1913).
3 Leipzig: S. Hirzel, (1914).
4 Phil. Mag., **32** 327 (1916).
5 Astrophys. J., **44** 87 (1916).

Surdo[1] and Puccianti[2] are somewhat different from those of Stark. In fact, instead of the many components observed by Stark, Lo Surdo found two parallel (p) components in all the hydrogen lines H_α, H_β, H_γ, and H_δ, and perpendicular (s) components agreeing in number with the term number of the series.

As further research relating to the effect of an electric field on spectrum lines seemed highly desirable, the present experiment was undertaken.

§ 2. Arrangement.

In the present experiment, making use of Lo Surdo's method, we examined the transverse effect relating to the spectrum lines of hydrogen.

The discharge-tube used as the source of light was prepared in the following way:—

One of the electrodes of a fused silica Geissler tube of an ordinary Plücker form was replaced by a long aluminium rod, which completely filled about the half length of the capillary portion whose diameter was 2 mm. This served as the cathode. The other electrode of the tube was taken away, and a glass bulb of nearly spherical form having a capacity of about 1 liter was attached to this end. A long aluminium rod, 2 mm. in diameter, which passed through the bulb and terminated in the broad part of the fused silica tube, was used as the anode. The attachment of the fused silica tube to accessory glass tubes was secured by means of sealing wax. Two side tubes were connected to the bulb, one of which served for the introduction of hydrogen gas and the other for the evacuation by a Gaede mercury pump. The hydrogen was generated by a Kipp's apparatus and was dried by passing it through concentrated sulphuric acid and a tube containing phosphorus pentoxide.

The discharge-tube was excited by an induction coil of 25 cm. spark length, the current in its primary being 3 or 5 amperes at 40 volts. For the interruption of the primary current, and for the rectification of the secondary one, a rotating rectifier attached to a mercury interrupter was employed. The current in the secondary circuit varied from 1·5 to 2·5 milliamperes. During the discharge, a spark gap was always inserted in parallel with the tube.

After repeated evacuation and refilling of the tube, the side tube leading to the Kipp's apparatus was sealed. The evacuation was then

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1 Rendiconti d. Lincei, **23** 82, 143, 252, 326 (1914).

2 Ibid., **23** 329, 331 (1914).

carried on under a continuous discharge, until the length of the Crookes dark space had increased to about 3 mm. or more; then the remaining side tube was also sealed. The length of the dark space of the tube thus produced showed a fluctuation amounting to a few tenths of a millimeter when the tube was newly excited; but usually it soon attained a steady state and afterward remained practically constant, even up to the end of 3 or 4 hours of continuous excitation.

Except a portion of about 4 mm. in front of the cathode, the capillary was covered with a thin asbestos paper. After several hours' excitation the inner wall of the capillary just in front of the cathode became coated with a thin film of some white substance due to the disintegration of the cathode, which considerably diminished the intensity of light. So it was found necessary to change the position of the cathode after one or two days' use of the tube.

For photographing the spectrum, we used the following four different instruments:

1. a four-prism spectrograph,
2. a single-prism spectrograph,
3. a spectrograph with a transparent replica grating,
4. a quartz spectrograph.

Between the source and the slit of the collimator of each spectrograph, excepting No. 4, an achromatic lens and a double image prism were placed so that the separated images of the two components of the source of light polarised parallel and perpendicular to the electric field were formed on the same vertical line of the slit.

Now we shall describe each of the instruments mentioned above.

(1). The four-prism spectrograph was constructed by slightly modifying the wave-length spectrometer of Hilger. In addition to a constant deviation prism (height 34 mm., long face 65 mm.), three 60° prisms of dense flint made by Hilger, ($n_D = 1{\cdot}6392$, height 45 mm., length of the base 64 mm.), were each placed in the position of the minimum deviation for $H\gamma$. The spectrum was photographed with a Zeiss Tessar having a relative aperture of 4·5 and a focal length of 18 cm. The dispersion on the photographic plate was 15·7 Å.U. per mm. at $H\gamma$. For this line and also for the lines belonging to the secondary spectrum of hydrogen lying between $H\beta$ and $H\gamma$, this instrument was specially adapted.

(2). The single-prism spectrograph was made by modifying a large spectrometer of Krüss. For photographing the spectrum, a Zeiss lens having a relative aperture of 6·5 and a focal length of 40 cm. was used. This instrument was employed for examining the decomposition of H_δ.

3. To examine the decomposition of H_α, a plane grating spectrograph was desirable, but as we had no good plane grating at hand, a transparent replica grating of Hilger was used. The arrangement was, however, far from being satisfactory, and only served for a rough comparison of the separation of H_α, H_β and H_γ.

4. It is stated in Howell's paper before cited that, in the spectrum of the glow in the Crookes dark space, beside the hydrogen lines, he observed a number of spectrum lines of the metal used as the cathode, and that he searched for the effect of an electric field on these lines, but with a negative result. In our experiment, we also noticed the appearance of the intense aluminium lines λ 3962 and 3944 Å.U. To ascertain the results arrived at by Howell, a quartz spectrograph of Hilger provided with a Cornu prism having a base of 65 mm. was employed. But, in the ultra-violet region, we could find no line which would be affected by the electric field.

For the measurement, we used a photo-measuring instrument of Hilger of 15 cm. travel. The ordinary eye-piece was replaced by a micrometer eye-piece having a screw of ½ mm. pitch, so that we could measure the plate in two directions perpendicular to each other.

The photographic plates we used were the panchromatic plate and the double-instantaneous plate of Wratten and Wainwright, and the Ilford special rapid plate. The exposure varied from 1 to 5 hours. In the present experiment, about 40 photographs were taken in all.

§ 3. Results.

The results obtained by the present experiment mainly relate to the mode of separation of H_γ, and the effect produced on some of the lines of the secondary spectrum of hydrogen.

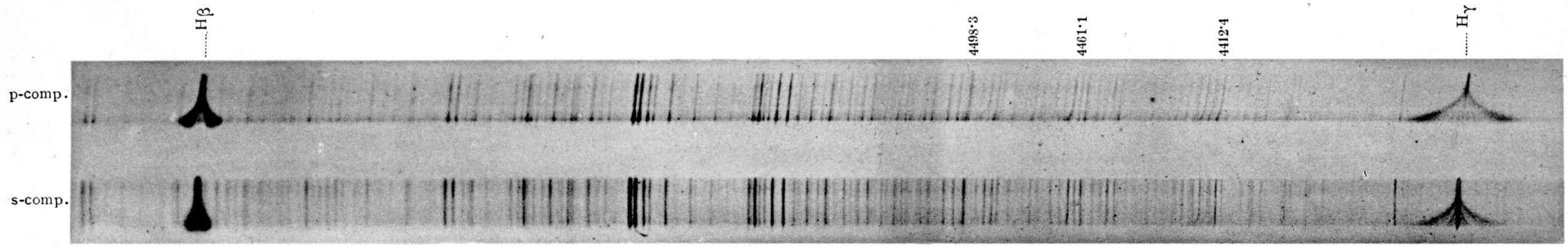
a). Lines belonging to the Balmer series.

Of the four lines ($H_\alpha, H_\beta, H_\gamma, H_\delta$) we have examined, the most satisfactory result was obtained for the H_γ line. A reproduction of the photograph obtained by the four-prism spectrograph is given in Fig. 1, Pl. I, and the portion near H_γ is shown more enlarged in Fig. 2, Pl. I.

For H_α we could only measure the *p*-components. For H_β, the resolution of our instrument was insufficient, and as shown in the

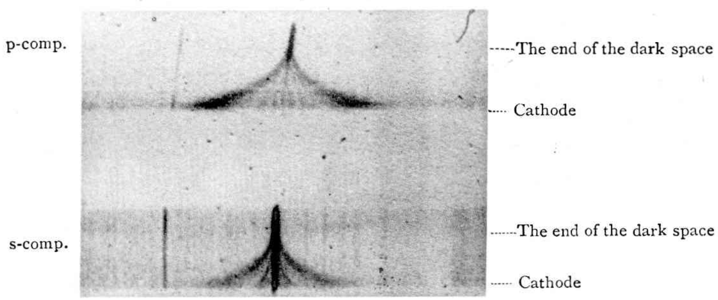
Plate I.

Fig. 1.



Magnification : 12

Fig. 2.



Magnification : 19

Exposure : $4^h\ 8^m$.

accompanying photogragh (Fig. 1, Pl. I) two *p*- and two *s*-components of H_β remain unresolved, although they are considerably broadened. For H_δ also, the result was far from being satisfactory. We noticed two *p*-components and four *s*-components on some of the photographs taken with the single-prism spectrograph, and also on those taken with the four-prism spectrograph. In the course of further experiments which are now in progress, we shall re-examine more closely the above three lines.

As shown in Fig. 2, Pl. I, the *p*-components of H_γ consist of two intense outer components and four inner components of weak intensity; so that there are six components on the whole. The presence of a weak central line which was also given by Stark, may be due to the incomplete rectification of the current in the secondary circuit. In the *s*-components we see, beside a strong central line, two outer and two inner components.

In his later work, Stark found a great number of *p*- and *s*-components for the lines H_β, H_γ and H_δ. But, as remarked by him in one of his papers, it is obvious that with Lo Surdo's method, the difficulty of obtaining a photograph showing such complicated decomposition is very great. Moreover, in Lo Surdo's method, it is not easy to know the intensity of the electric field. Therefore, to determine the field intensity we were obliged to use the following data for the outer components of H_γ given by Stark in the chapter entitled " Grobzerlegung " of the hydrogen lines.

4·6 Å.U. per 10^4 volt/cm. for the *p*-components,

3·2 Å.U. per 10^4 volt/cm. for the *s*-components.

In the first place, we measured the amount of separation of the outer *p*- and *s*-components of H_γ, shown on the photographic plate, at several different points just corresponding to the various distances from the cathode, and from these data, curves were drawn by taking the amount of separation and the distance from the cathode in *x*- and *y*- directions of the rectangular coordinate axes. It is to be remarked that as the appearance of these lines are by no means well defined, especially at the immediate neighbourhood of the cathode, a certain amount of error in determining the point of maximum density must certainly be allowed for.

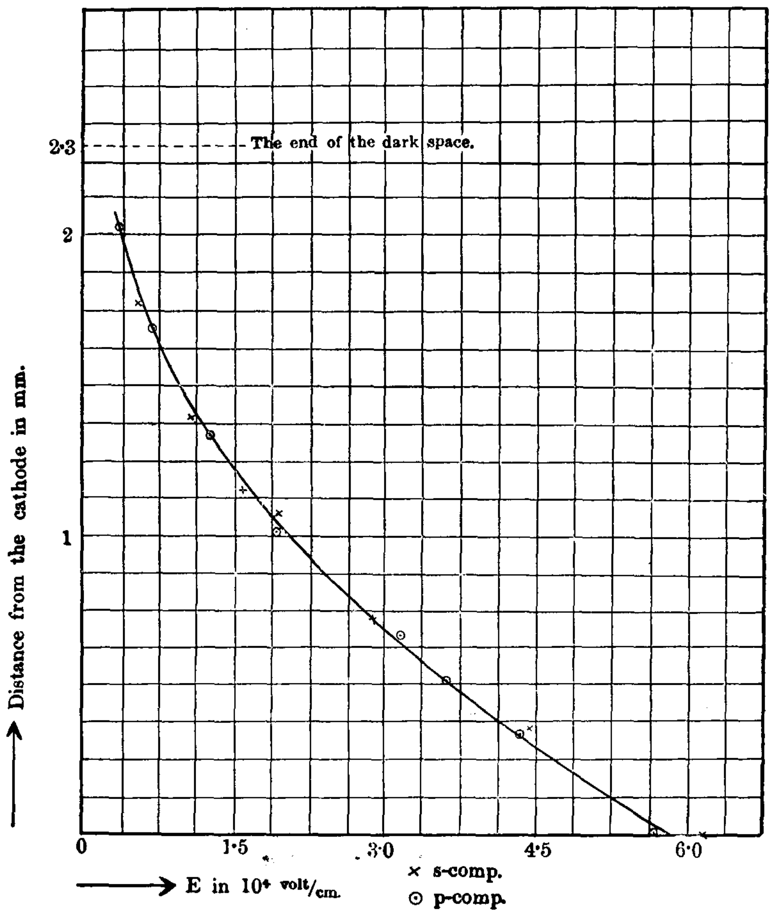
By using Stark's data given above, we are able to determine the distribution of the electric field in the region just in front of the cathode.

In the case shown in Fig. 1, Pl. I, where the length of the dark space was 2·3 mm., the results shown in Table I was obtained.

TABLE I.

p-component.		*s*-component.	
Distance from the cathode in mm.	E in 10^4 volt/cm.	Distance from the cathode in mm.	E in 10^4 volt/cm.
0	5·64	0	6·15
0·34	4·35	0·35	4·45
0·50	3·67	0·71	2·88
0·67	3·07	1·06	1·90
1·03	2·05	1·15	1·59
1·34	1·25	1·42	1·06
1·68	0·70	1·77	0 56
2·01	0·38		

Fig. 3.



By taking the field intensity E and the distance from the cathode as abscissa and ordinate respectively, and plotting the above results, the curve shown in Fig. 3 was obtained.

It will be seen that if we denote the field intensity at the end of the dark space by E_0, the quantity $E-E_0$, so far as the present experiment is concerned, seems to increase nearly proportional to the square of the distance from that end.

For the inner *s*-components of H_γ, similar measurements were carried out and it was found that, in addition to the fact that the separation is approximately symmetrical, it is proportional to the field strength.

The following table (Table II) gives the ralation between the field intensity E and the amount of displacement $\delta\lambda$ from the position of the undisturbed line.

TABLE II.

E in 10^4 volt/cm.	$\delta\lambda$ in Å.U.	$\delta\lambda/E$
1·68	0·76	0·45
1·92	0·82	0·43
2·96	1·19	0·40
4·25	1·89	0·44

It was at once evident that these components corresponded to (+1) and (−1) of Stark, given in the case of "Feinzerlegung" of hydrogen lines.

Quite a similar result was obtained also for the four inner *p*-components of the same line, but in this case, owing to the faintness of the photographic image, the accuracy was much less.

The amount of the displacement were again found to be nearly symmetrical; for $E=5{\cdot}83\times10^4$volt/cm, $\delta\lambda$ was 3·7 Å.U. for the one, and 1·7 Å.U. for the other pair of components. They corresponded almost exactly to (+2), (+1), (−1), (−2) of Stark, given in the case of "Feinzerlegung".

b). Secondary spectrum of hydrogen.

Besides the lines belonging to the Balmer series, Stark found that some of the lines belonging to the secondary spectrum of hydrogen were also affected by the electric field, but in a quite different manner.

The main results obtained on these lines by Stark may be summarized as follows:

(1). Many of the lines belonging to the secondary spectrum of hydrogen are not affected by the electric field.

(2). The effect on the affected lines are one-sided, that is, the lines are displaced either only toward the red, or only toward the violet.

(3). The amount of displacement is very small compared with that of the Balmer lines.

(4). The amount of displacement increases more rapidly than is proportional to the field intensity.

(5). As the type common to the affected lines, one *p*-component and two *s*-components are generally observed, the one of the latter being displaced nearly equal in the amount to the former, while the other is very slightly displaced in the same direction.

In the present experiment, the region in which a number of affected lines were found, extended from λ 4390 to λ 4530 Å.U. The wave-lengths of the lines in this region, which were determined by photographing the spectrum of an iron arc in comparison, were found to agree fairly well with those obtained by Watson[1] and given in Kayser's Spectroscopie. In the following we have adopted Watson's values to the first decimal of an Å.U.

As the results obtained in the present experiment, we have to note the following facts.

(1). In most cases, the displacement is one sided, just as remarked by Stark; but there seems to be some exceptions. For instance, in the *s*-components of the line λ 4417·5, one component is displaced toward the violet, while the other two are displaced toward the red.

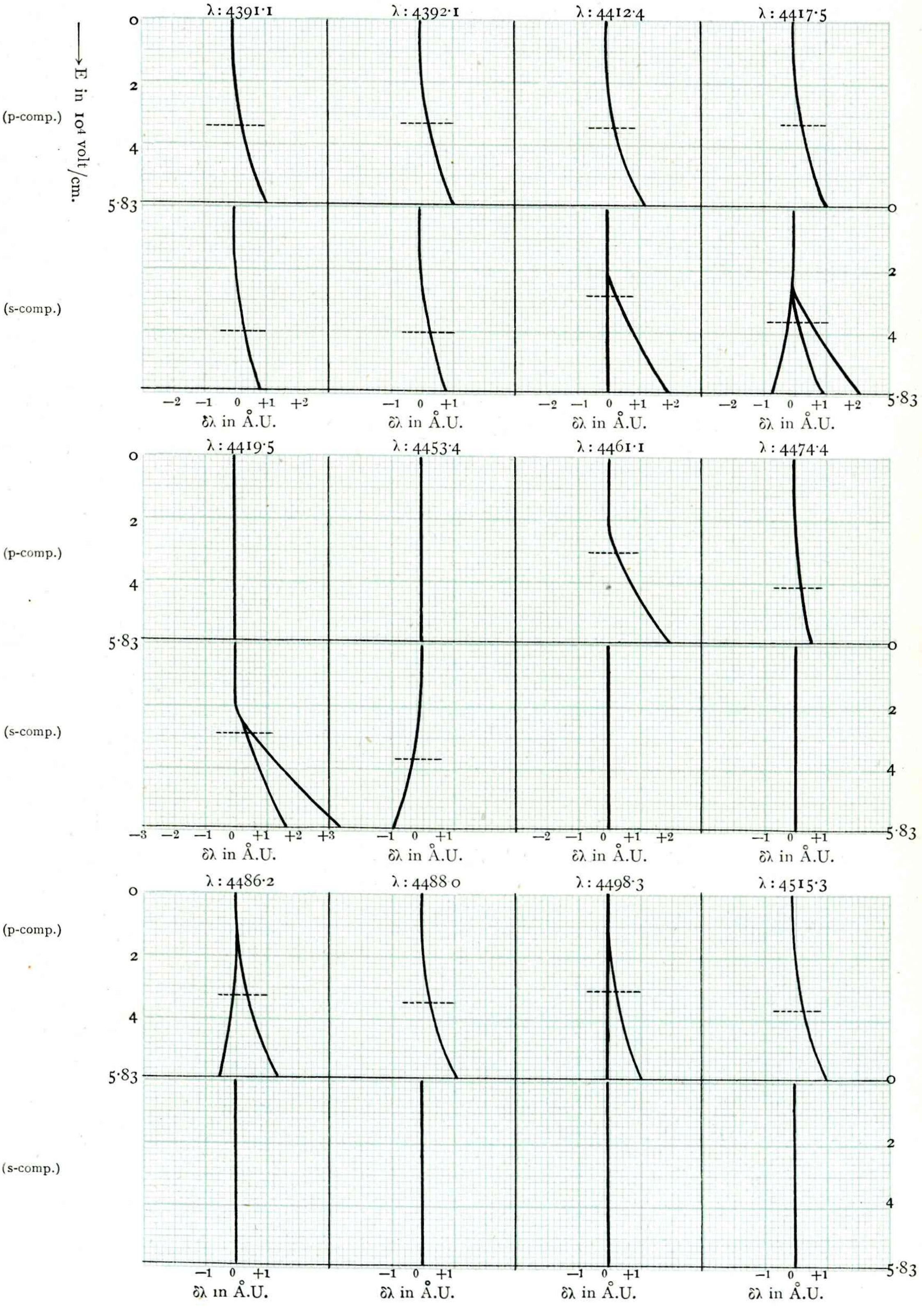
In the *p*-components of λ 4486·2, one is displaced toward the red, the other toward the violet.

(2). The type described by Stark as common to most of the affected lines, namely, that consisting of one *p*- and two *s*-components, was not observed in the present experiment. But, as the maximum intensity of the electric field calculated from the photograph was about $5{\cdot}83 \times 10^4$volt/cm., and thus inferior to that of Stark ($7{\cdot}40 \times 10^4$volt/cm.), it seems probable that the smaller displacement in the *s*-component could not be detected in our case.

In Fig. 4, we have drawn roughly the curves to show various modes presented by the affected lines. Just as stated by Stark, the amounts of displacement observed were very small for these lines, so that, with the dispersion used in the present experiment, we were unable to measure the amounts of displacement in the region above the dotted line

1 Proc. Roy. Soc., A 82 189 (1909).

Fig. 4.



λ: 4391·1
λ: 4392·1
λ: 4412·4
λ: 4417·5
λ: 4419·5
λ: 4453·4
λ: 4461·1
λ: 4474·4
λ: 4486·2
λ: 4488 0
λ: 4498·3
λ: 4515·3
(p-comp.)
(s-comp.)
E in 10⁴ volt/cm.
5·83
δλ in Å.U.

The numerical values used for drawing the diagrams given in Fig. 4 are tabulated below:

TABLE III.

λ in Å.U.	δλ for *p*-comp.		δλ for *s*-comp.		Remarks.
	$E=5·8$	$E=4·6$	$E=5·8$	$E=4·6$	
4391·1	+1.1		+0·8	+0·5	Both the *p*- and *s*-components of the line λ: 4392·1 showed similar displacements.
4412·4	+1·2	+0·6	+2·1	+1·2	Stark gives for the *p*-comp. of this line: δλ = 1·1 at $E=4·8$ δλ = 1·8 at $E=7·4$ Both the *p*- and *s*-components of the lines λ: 4414·4, λ: 4415·3 showed similar displacements.
4417·5	+1·2		−0·6 +0·9 +2·2	— +0·4 +1·3	
4419·5			+1·5 +3·4	+1·0 +2·0	
4453·4			−0·8		
4461·1	+1·9				Stark gives for the *p*-comp. of this line: δλ = 1·4 at $E=4·8$ δλ = 2·8 at $E=7·4$
4474·4	+0·6				
4486·2	+1·2 −0·6	+0·9 —			
4488·0	+1.1	+0·5			
4498·3	+1·1	+0·8			
4515·3	+1·1	+0·5			In the *p*-comp. of the lines λ: 4519·3, λ: 4520·1 and λ: 4524·3, similar displacements were observed.

N.B. In this table, δλ is expressed in Å.U., and E in 10^4 volt/cm.
The + sign means a displacement toward the red, − toward the violet.

It is here to be remarked that in Stark's method we employ a uniform electric field, while in Lo Surdo's method we employ a heterogeneous field. In fact, each method has its own advantage. As a merit of Lo Surdo's method we may state that, in addition to its experimental simplicity, the use of a heterogeneous field has its peculiar advantage in allowing us to follow gradual changes brought on each spectrum line under investigation. The authors believe that this advantage is most highly appreciated when we examine the behaviour of the lines belonging to the secondary spectrum of hydrogen, in which many lines are clustered closely together. For in such a case, the superposition of one displaced line on the other unaffected one often takes place, just as shown in the photograph accompanying the monograph of Stark. (Fig. 2, Tafel III.)

§ 4. Summary.

1). Employing Lo Surdo's method, the effect of an electric field on the spectrum lines of hydrogen was investigated.

2). For H_γ, in addition to the two outer p-components and the three s-components, which were obtained by former investigators adopting Lo Surdo's method, four inner p-components and two inner s-components were obtained which were clearly identified with certain components obtained by Stark.

3). Relying on the data given by Stark for H_γ in the case of " Grobzerlegung ", the field strength was calculated, and the distribution of the electric field in front of the cathode was determined.

4). The proportionality of the amount of separation to the intensity of the electric field was found to hold good for the inner p- and s-components of H_γ.

5). The influence of the electric field on certain lines belonging to the secondary spectrum of hydrogen was also investigated and many interesting modes of separation were found.

In conclusion, the authors wish to express their hearty thanks to Prof. Mizuno for placing the resources of the Institute at their disposal, and also for the deep interest he has taken in the present investigation.

The authors' thanks are also due to Prof. Chikashige of the Chemical Institute for his kind advices.