STARK INTENSITIES
IN
HYDROGEN AND HELIUM

THE STARK EFFECT FOR KRYPTON

STARK INTENSITIES IN HYDROGEN AND HELIUM

A thesis submitted to the Faculty of Graduate Studies and Research at McGill University, in part fulfilment of the requirements for the degree of Doctor of Philosophy.

by

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FOREWORD AND ACKNOWLEDGEMENTS

Since this thesis represents contributions to two distinct fields of Stark effect research, it is presented in two independent sections.

In the first of these a detailed report is given of the Stark effect for krypton. This completes another in the series of investigations on the rare gases which are being carried out in this Laboratory under high dispersion.

This problem was initially investigated by the writer in 1930-31, at which time a general survey of the spectrum was made. A Hilger E_1 quartz spectrograph was used which was focussed to cover the visible spectrum. The Stark effect was found to be small; a few displacements in the red and green regions were however observed at high fields. The low dispersion of the spectrograph in this region precluded the detailed observation of patterns and the very accurate measurements of displacements. These observations served however to confirm experimentally the prediction that observable effects were only to be expected in the region from 4800 to 7000 A. A report of these experiments was presented at the Toronto meeting of the Royal Society of Canada in May, 1931.

In view of the interesting patterns observed by Dr. Heard in the xenon spectrum, it appeared desirable to investigate this region of the krypton spectrum in the hope that, under high dispersion, some of these small displacements might be resolved. Since the abnormal patterns observed in xenon are due to the wide spacing of the xenon terms, the even wider separation of those in krypton was expected to lead to further unusual types.

These experiments were carried out, and the observations, and their discussion and interpretation, form the subject matter of Section I.

The second part of this thesis comprises a report on a new investigation of the Stark intensities in hydrogen and helium by the canal ray method. The explanation of the divergent intensity measurements found for hydrogen from canal ray tubes, and their coordination with those obtained with the Lo Surdo method, constitutes an important outstanding problem in Stark effect research.

A new type of canal ray tube has been designed which permits operation at a far higher pressure than is usually the case. The results obtained with this source show a definite qualitative departure from those previously obtained and this departure is in the direction of a better agreement both with theory and with the Lo Surdo results.

Section II deals with the description of the experimental methods used, and a detailed discussion of the observations in connection with previous work in this field.

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The writer wishes to express his deep indebtedness to Dr. J. S. Foster, not only for his suggestion of these problems, but also for his continued guidance and advice during the progress of the work. He also wishes to thank Dean A. S. Eve, Director of the Department, for his friendly interest. Dr. H. G. I. Watson has assisted from time to time in the construction of apparatus.

Thanks are due to Messrs. Pye, Taylor, Tweeddale and Amesse of the Laboratory Staff for assistance of a technical nature.

In conclusion, grateful acknowledgement must be made to the National Research Council of Canada for the awards of a Bursary and a Studentship during the course of the work.

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SECTION I

THE STARK EFFECT FOR KRYPTON

SUMMARY

(1) The stark effect for Krypton has been observed in the region from 4800 to 6700 Å in electric fields up to 86 KV/cm. The spectrum was analysed by means of a 28 foot concave grating in a stigmatic mounting.

(2) A total of 45 lines belonging to the first spectrum of Krypton have been indentified on the plates. The great majority of these are affected by the electric field.

(3) No combination lines were found. The absence of such lines is, however, to be expected from the wide separation of the spectral terms. In this respect Krypton is similar to argon.

(4) The displacements, as first observed in xenon, are found to bear no relation to the hydrogen difference. This was originally thought to be the basis on which Stark displacements rested. In general the displacements are clearly dependent upon the relative spacing of terms in the manner first described by Pauli. Some marked limitations upon a complete application of Pauli's theory are set by our present incomplete knowledge of the normal spectrum.

(5) The patterns observed in almost all cases are definitely of the "abnormal" type. A definite pattern has been observed

for lines associated with the initial sharp series term $4s_5$.

(6) In no case does the full number of components predicted by theory appear. This is even true for strong lines in which the existence and resolution of the sub-levels is known from observations on other lines with the same initial term. The components expected may fail to appear in either polarisation, but in certain cases are associated with a particular initial sub-level. Possible explanations are discussed.

INTRODUCTION

Immediately after the discovery by Stark[1] of the effects of a strong electric field on spectral lines, attention was drawn to the apparent wide variety in the patterns and displacements caused by the field in hydrogen and helium lines. In striking contrast to the Zeeman effect, the magnitude of the Stark effect varies greatly from atom to atom, and even from line to line in the same series. While for the normal Zeeman effect, calculations made on a classical basis proved satisfactory, in the case of an electric field classical atomic dynamics was shown at once to be inadequate. Thus began the important role of the Stark effect in the testing of atomic theory.

The calculation on the basis of the Bohr theory of the Stark displacements in the hydrogen Balmer lines by Epstein[2] and Schwarzchild[3] is well known. This theory is adequate in the discussion of the number of components to be expected in each member of the Balmer series and also gives the correct numerical values for the displacements. Due to the neglect of the fine structure, however, it is not satisfactory as a basis for the explanation of the Stark patterns in general.

The clue to the discussion of Stark patterns in complex spectra was provided in an important paper by Kramers[4] in 1920. In this work the gradual transition from the complicated fine structure assumed to exist at very low fields to the observed Stark effect for hydrogen is described. Electron spin was, of course, neglected. From this paper one may conclude that the Stark pattern contributed by a given fine structure line varies with the type of line.

In the definition of the states of the hydrogen atom in low fields, Kramers uses three quantum numbers, n, n_1, and n_2. n and n_1 are the total and azimuthal quantum numbers respectively, while n_2 determines the component of angular momentum about an axis parallel to the field. These quantum numbers are subject to the restriction $n \geq n_1 \geq n_2 \geq 1$. An application of the correspondence principle yields the selection rule $\Delta n_2 = 0$ for components polarised parallel to the field and $\Delta n_2 = \pm 1$ for the perpendicular components. As the electric field increases, these quantum numbers become identifiable with those of Epstein through the relation

$$(n_1, n_2, n_3)\ \text{Epstein} \equiv \left[(n_1-n_2),\ (n-n_1), n_2\right]\text{Kramers}$$

The Stark patterns for the fine structure lines are dependent upon the azimuthal quantum numbers of the initial and final states and are thus constant within a given fine structure series. An application of the selection rule for n_2 then leads to the following patterns to be expected in hydrogen.

$\dfrac{\text{parallel components}}{\text{perpendicular components}}$	$\frac{2}{3}$ in the series	2_2-n_K	$K = 3,4,5\ldots$
	$\frac{2}{2}$ " " "	2_2-n_2	only
	$\frac{1}{1}$ " " "	2_2-n_1	and
		2_2-n_K	$K = 2,3,4\ldots$
	$\frac{1}{0}$ " " "	2_1-n_1	only

Fig. 1 shows the origin of the observed Stark pattern for H_β according to this theory. With the scale chosen, all the theoretically possible fine structure components at very weak fields cannot be shown. The theoretical fine structure triplets are shown at zero field. The Stark components appear in two groups corresponding to the two fine structure groups in which they originate. The narrow lines represent components contributed by fine structure lines emitted in a transition to a final 2_1 orbit; the heavier lines those produced by transitions to a final 2_2 orbit. Straight lines are used to show the connections with the fine structure. The Stark components are labelled with the azimuthal quantum numbers of the level in which they originate and at the base is given the Epstein notation for the components. The figure is not drawn to scale and serves merely to illustrate the origin of the Stark-Epstein components in the fine structure.

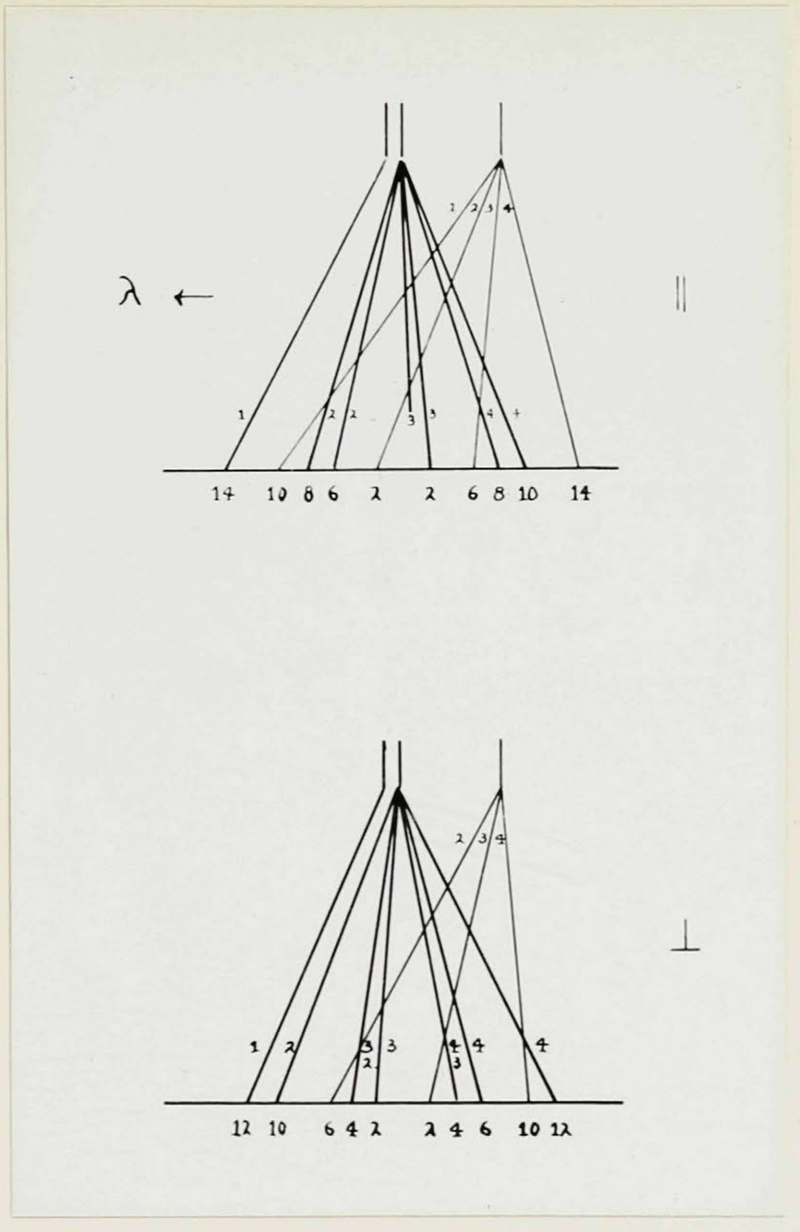
Figure 1.

Origin of the Stark Components of H_β in the Fine Structure.

Figure 2;

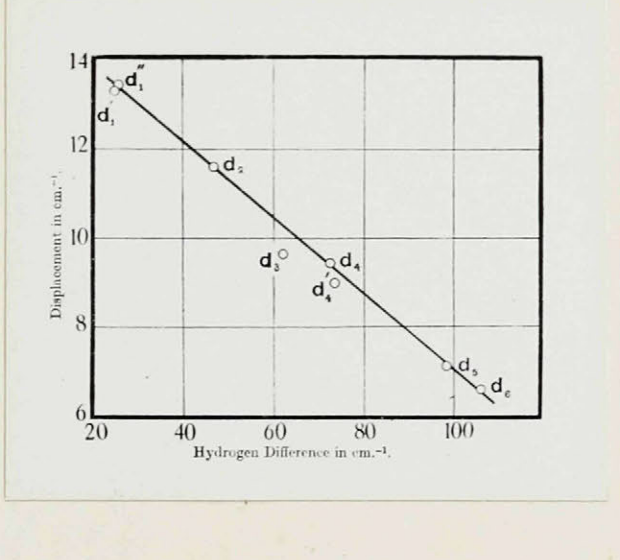
(a) Hydrogen Difference Relation for Neon 4d Levels.

(b) Hydrogen Difference Relation for Argon 5d Levels.



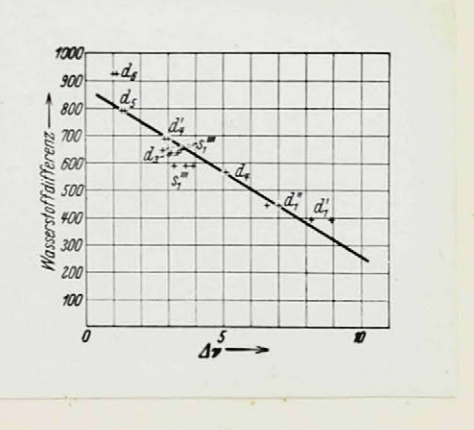
λ ←
||
⊥
14 10 8 6 2 2 6 8 10 14
12 10 6 4 2 2 4 6 10 12

FIG. 1



Displacement in cm.⁻¹.
Hydrogen Difference in cm.⁻¹.

(a)



Wasserstoffdifferenz →
Δν →

(b)

FIG. 2

With the introduction of wave mechanics, the problem has been reconsidered by Schrödinger[5], by Schlapp[6], and by Rojansky[7]. Using the wave equations of Darwin and Dirac, Schlapp has investigated the fine structure, taking into account the effects of electron spin. Results are worked out in detail for H_α , and lead to an asymmetry in the displacements at low fields which should persist into fields susceptible to observation. This effect has been verified by McRae[8].

After an exhaustive study of helium, Foster[9] was able to draw the important conclusion that the patterns discussed above for the Balmer lines of hydrogen could be carried over into the parhelium and orthohelium spectra if it be assumed that the final levels are unresolved.

In the case of parhelium this is to be expected by analogy with the normal Zeeman effect, since electron spin does not enter into this spectrum. The m values of the perturbed levels are given by the resolved parts of the vector ℓ (in this case equal to j) in the direction of the field. The restriction to be imposed on the m values is $\ell \geq m \geq 0$. This is precisely analogous to the normal Zeeman effect since the electric field does not distinguish between positive and negative m values. The selection rule is $\Delta m = 0, \pm 1$ for parallel and perpendicular components respectively. On this basis a complete explanation of the observed patterns was obtained. In view of the close analogy with the Zeeman effect these have been termed by Foster "normal" patterns.

For orthohelium, however, one might expect complications arising from the electron spin. This was found not to be the case. The explanation of this is given by assuming that the perturbed levels are specified by m_ℓ and m_s values corresponding to the resolved parts of the vectors ℓ and s along the field. Δ m = 0, $\pm$ 1 as is the case in parhelium, while $\Delta m_s = 0$ in all transitions. This is analogous to high field conditions in the Zeeman effect.

If we pass from helium to other complex spectra, we find that in most cases the patterns obtained may be discussed in the same way. Complete data are only available in the rare gases which, for obvious experimental reasons, a re particularly suited for Stark effect observations. A complete analysis of neon has been carried out by Foster and Rowles(10). With few exceptions it was found that electron spin did not enter into the specification of the patterns, but that they were determined by m_ℓ values in the manner described. This may be interpreted as meaning that the ℓ s coupling was broken down by the field. A few exceptions were noted, however, in diffuse terms with j = 1. In these cases, the absence of a component arising from the transition m = 2 to m = 1 suggested that in these cases the ℓ s coupling was retained and that the m values were specified by the resolved part of j along the field. These may be termed "abnormal" patterns.

Conclusive evidence of the existence of these abnormal patterns has recently been furnished by the work of Harkness and Heard on xenon[11]. The wide separation of the multiplet terms might lead one to expect the appearance of patterns of this kind. Under the high dispersion employed, a large number of patterns were completely resolved; the majority of these proved to be of the abnormal type. The importance of this spectrum lies in the fact that both types of pattern were definitely observed. Thus the xenon spectrum affords a decisive test for any theory regarding the origin of Stark patterns.

Investigations in the spectra of the alkali metals had earlier afforded evidence of the existence of abnormal patterns for certain lines. The sodium D lines, for example, were investigated in absorption (inverse Stark effect) by Ladenburg[12]. The results indicated that abnormal patterns were present. Investigations by Grotrian and Ramsauer[13] upon certain principal series lines of potassium yield further examples of abnormal patterns.

Other complex spectra which have been fairly completely examined are argon[14] and mercury[15]. In neither case was definite evidence as to patterns obtained.

An attempt has been made by Ladenburg[16] to explain the appearance of these two pattern types by means of a quite complete analogy with the Zeeman effect. Defining "weak" and "strong" fields precisely as in the case for magnetic fields, he suggests that for weak fields m values are determined by j values, while for strong fields they are determined by ℓ values. Thus we have an electrical analogue of the Paschen-Back effect. No such transition from abnormal to normal patterns has as yet been obtained.

Passing from a consideration of Stark patterns to the problem of the magnitude of the displacements, we find two main theories holding the field - a formula derived by Pauli[17] from the dispersion theory of Kramers-Heisenberg, and the hydrogen difference rule first proposed by Bohr[18]. We will discuss first the Bohr theory which, however, is strongly contradicted by recent experimental evidence. To be explicit, helium may be considered as a typical complex spectrum and compared with the simple Bohr hydrogen atom.

It is well known that to each simple hydrogen term there corresponds a group of helium sub-levels. These sub-levels are, on the Bohr theory, associated with orbits of the series electron which are almost Keplerian in character save for a small portion which lies close to the nucleus. Moreoever this nuclear distance is least for the orbits of greatest eccentricity and these orbits are those of least angular momentum. The change in the central field which causes the helium orbits to depart from those of hydrogen produces the greatest effect on those orbits which approach closest to the nucleus. This effect consists in the superposition of a rotation of the whole orbit in its plane upon the electron motion. Since the hydrogen difference, the difference in value between the term in question and the hydrogen term of the same principal quantum number, is a measure of the nearest approach of the electron orbit to the nucleus, we see that in the hydrogen difference we have a measure of the speed of rotation of the orbit in its plane. These hydrogen differences are greatest for the sharp terms ($\ell = 0$) and decrease as we pass to the principal, diffuse, ---- terms with ℓ values, 1,2-----.

Considering the position of an electron in an elliptical orbit, we readily see that under the influence of an external electric field the time mean position will be displaced an amount proportional to the applied field. Moreover, the faster the rotation of the orbit, the less will be this displacement. The potential energy of the electron with reference to the external field is given by the product of field into displacement. Thus we see from the Bohr frequency relation that the effect of the electric field is to produce, in the case of a rotating orbit, a displacement proportional to the square of the field. If, however, the orbit revolves slowly, or not at all,as is the case in the simple hydrogen orbit, then the electric centre may be displaced an amount which may increase over many revolutions of the electron in its orbit, and a large displacement may result which will be limited not by the field strength, but by other considerations. Thus Stark displacements in hydrogen are proportional to the field, while those in helium depend on the square of the field, in accordance with experiment at low fields.

Summing up the results of the previous discussion, we should expect that in the case of a complex spectrum, Stark displacements should be proportional to the square of the field, and that there should exist some connection between the displacement of a group of terms and their hydrogen differences.

The Pauli formula takes its departure from the dispersion theory developed by Kramers and Heisenberg immediately before the advent of quantum mechanics. The results of this theory are in agreement with those obtainable from matrix mechanics[(19)]. The dispersion theory considers the frequencies and intensities of the lines emitted from atoms when perturbed by the alternating electromagnetic field of an incident light wave. Allowing the frequency of the light to decrease to zero, Pauli developed a formula which should describe the energy changes due to a weak electrostatic field. The analysis shows that the displacement of an energy level in an electric field depends upon its separation from certain other levels, and upon the transition probabilities between these levels and the given level. To a first approximation it is only necessary to consider levels related to the given level (n, ℓ, j, m) by $\Delta \ell = \pm 1$, $\Delta j = 0, \pm 1$ and $\Delta m = 0$. In this case the Pauli formula runs:

$$\Delta E_{n,m,\ell,j} = \Delta E^{(1)}_{n,m,\ell,j} + \Delta E^{(2)}_{n,m,\ell,j}$$

where

$$\Delta E^{(1)}_{n,m,\ell,j} = -\frac{1}{2} F^2 \frac{1}{2h} \left[\frac{|\alpha_{n,m,\ell+1,j \to n,m,\ell,j}|^2}{\nu_{n,m,\ell+1,j \to n,m,\ell,j}} - \frac{|\alpha_{n,m,\ell,j \to n,m,\ell-1,j}|^2}{\nu_{n,m,\ell,j \to n,m,\ell-1,j}} \right]$$

and

$$\Delta E^{(2)}_{n,m,\ell,j} =$$

$$-\frac{1}{2} F^2 \frac{1}{2h} \left[\sum_{n'>n,\ \ell'=\ell\pm 1,\ j'=j,j\pm 1} \frac{|\alpha_{n',m,\ell',j' \to n,m,\ell,j}|^2}{\nu_{n',m,\ell',j' \to n,m,\ell,j}} - \sum_{n'<n,\ \ell'=\ell\pm 1,\ j'=j,j\pm 1} \frac{|\alpha_{n,m,\ell,j \to n',m,\ell',j'}|^2}{\nu_{n,m,\ell,j \to n',m,\ell',j'}} \right]$$

Until very recently the Bohr hydrogen difference rule has been accepted as the criterion for the magnitude of Stark displacements. The data in its support has been well organised by Stark[20]. The strongest evidence in its favour is provided by the experiments in neon and argon. In Fig. 2 are shown plots of the displacements of the d levels against hydrogen differences for these gases. In the case of neon the 4d levels are plotted, for argon the 5d levels. As is readily seen the points lie reasonably well along a straight line. These curves are taken from the papers of Foster and Rowles, and of Ryde.

The more recent work on xenon, however, has shown this to be definitely incorrect. For this spectrum no direct connection between displacements and hydrogen differences is to be observed. The agreement in the other cases must be assigned to a fortuitous grouping of the term values about the hydrogen terms.

While a detailed discussion of the experimental results obtained for Krypton will be given later, a brief summary showing their bearing on the foregoing would not seem out of place.

In general it may be said that for Krypton the effect follows the trend expected in view of its spectral position among the rare gases. Thus while neon, with its very close term grouping, is characterised by normal patterns, large displacements and numerous combination lines, argon, which has the most random term distribution among the rare gases, shows small displacements, no combination lines and no patterns. (The absence of observed patterns is probably due to the low dispersion employed by Ryde). In the intermediate positions we find xenon and Krypton, of which xenon the more nearly resembles neon. As a result of the wider spacing of the term values, xenon shows both normal and abnormal patterns, the latter being greatly in the majority. Displacements are still large, but combination lines are not numerous. Krypton, which is intermediate in position between xenon and argon, shows abnormal patterns, small displacements and no combination lines appear. The remaining gas, radon, might be expected from its spectrum to return to the neon type. Since the Stark effect for helium is completely known theoretically, it is not discussed here.

While the Krypton Stark effect is generally of the type expected, yet some interesting features are found. As a result of the small displacements, clearly resolved patterns are few; when they appear, however, they are of the abnormal type. The full number of components expected from the selection rule for m never appear, even when it is known from other lines with the same initial level that the sub-levels are present and resolved. Whether this is due to a very unusual intensity distribution among the components, or to the operation of an unknown selection principle remains uncertain.

With regard to the magnitude of the displacements, Krypton furnishes another example of the failure of the hydrogen difference rule. This is to be expected in consequence of the observations in xenon. Their explanation on the basis of the Pauli principle seems satisfactory, but due to our incomplete knowledge of the normal spectrum a complete application is impossible. It is difficult to reconcile this observation with Ryde's results for argon in which an excellent agreement with the hydrogen difference rule was found (cf Fig.2)

The First Spectrum of Krypton

The first spectrum of Krypton has been analysed by Meggers, de Bruin and Humphreys and in a later paper revised and extended by the same authors[21].

In the unexcited state the atomic configuration of neutral Krypton has a closed shell with two 4s and six 4p electrons ($4s^2\ 4p^6$). According to Humd's theory[22] the normal state is a singlet $^1S_0$. The terms which represent the excited states of the atom result from the interaction of the series electron with the electron group s^2p^5 which is characteristk of the unexcited state of the ion Kr^+. The term arising from this configuration is an inverted $^2P_{2,1}$.* These levels have a separation of 5371 cm.$^{-1}$ We may therefore derive the terms representing the excited states of the neutral atom by finding the resultant obtained by adding in turn the electrons ns, np, nd, etc. to the term ^2P.

The notation introduced by Paschen in his analysis of neon and retained by other workers in the rare gases will be used in this discussion. A translation into the quantum notation is included.

The Krypton terms, with their coordination to the limits $^2P_{2,1}$, together with their quantum notation, are presented in Table I.

In addition we have the three f terms observed, X (1), Y (2), Z (2) with the innter quantum numbers indicated. The addition of an f electron to the (s^2p^5) configuration of Krypton gives rise to the term group.

$$^1D_2,\ ^1F_3,\ ^1G_4,\ ^3D_{1,2,3},\ ^3F_{2,3,4},\ ^3G_{3,4,5}.$$

Thus nine f terms have not been identified as yet.

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* In the following, inner quantum numbers of terms of even multiplicity are increased by one-half.

TABLE I

Limits	$^2P_2$				$^2P_1$	
s terms	$^3P_2$	$^3P_1$			^3P_o	$^1P_1$
	s_5	s_4			s_3	s_2
p terms	$^3D_1$	$^3D_3$	$^3D_2$		$^3S_1$	$^1P_1$
	p_{10}	p_9	p_8		p_4	p_3
	$^3P_1$	$^3P_2$	^3P_o		$^1D_2$	^1S_o
	p_7	p_6	p_5		p_2	p_1
d terms	^3P_o	$^3P_1$	$^3F_4$	$^3F_3$	$^3P_2$	$^1D_2$
	d_6	d_5	d_4'	d_4	s_1''	s_1''''
	$^3F_2$	$^3D_2$	$^3D_3$	$^3D_1$	$^1F_3$	$^1P_1$
	d_3	d_1''	d_1'	d_2	s_1'''	s_1'

An examination of the list of observed terms shows that many of the terms converging to the $^2P_1$ limit have not been discovered. In cases where they are known, it is usually only for a very few values of the running number. This is true, for example, of p[illegible] - p_4, the $s_1' - s_1''''$, and all the f terms converging to this limit. The absence of these terms renders a detailed application of the Pauli principle unsatisfactory in this spectrum.

If the list of the KrI lines published by Meggers and his co-workers is considered with a view to possible Stark displacements, it is noticed that the number of lines of a reasonable intensity likely to be characterised by observable displacements is very limited. This is in strong contrast to neon and xenon where the diffuse and fundamental series are strong. In Krypton the diffuse series lines, though numerous, are in general faint for satisfactory observation. The lines having the 4d levels as initial states lie in the infra red in the region 7700-8700 A. Experiments carried out by Dr. Heard on xenon showed the very great difficulty of working with a Lo Surdo source in this region even with the greatly improved plates recently developed at the Eastman Kodak Laboratories. Moreover, the displacements might be expected to be very small. The latter point is borne out by the present investigation in which even the 5d levels, for which the displacements should be comparatively large, are little affected.

The only region which appears reasonably suitable for investigation lies between 4800-6600 A. In this wavelength range lie all the diffuse series lines which appear accessible to observation. These lines have their origin in the 5,6 and 7d levels.

EXPERIMENTAL

The Vacuum System

The Krypton used in these experiments was obtained from the Airco Company of New York. The gas was very pure. It was supplied in a flask containing approximately 250 cc. and was subdivided into glass capsules containing about 10 cc. at 15 cm. pressure. One of these containers was sealed on to the vacuum system, and the gas admitted to the storage vessel by breaking a fragile tip on the container with a magnetic hammer.

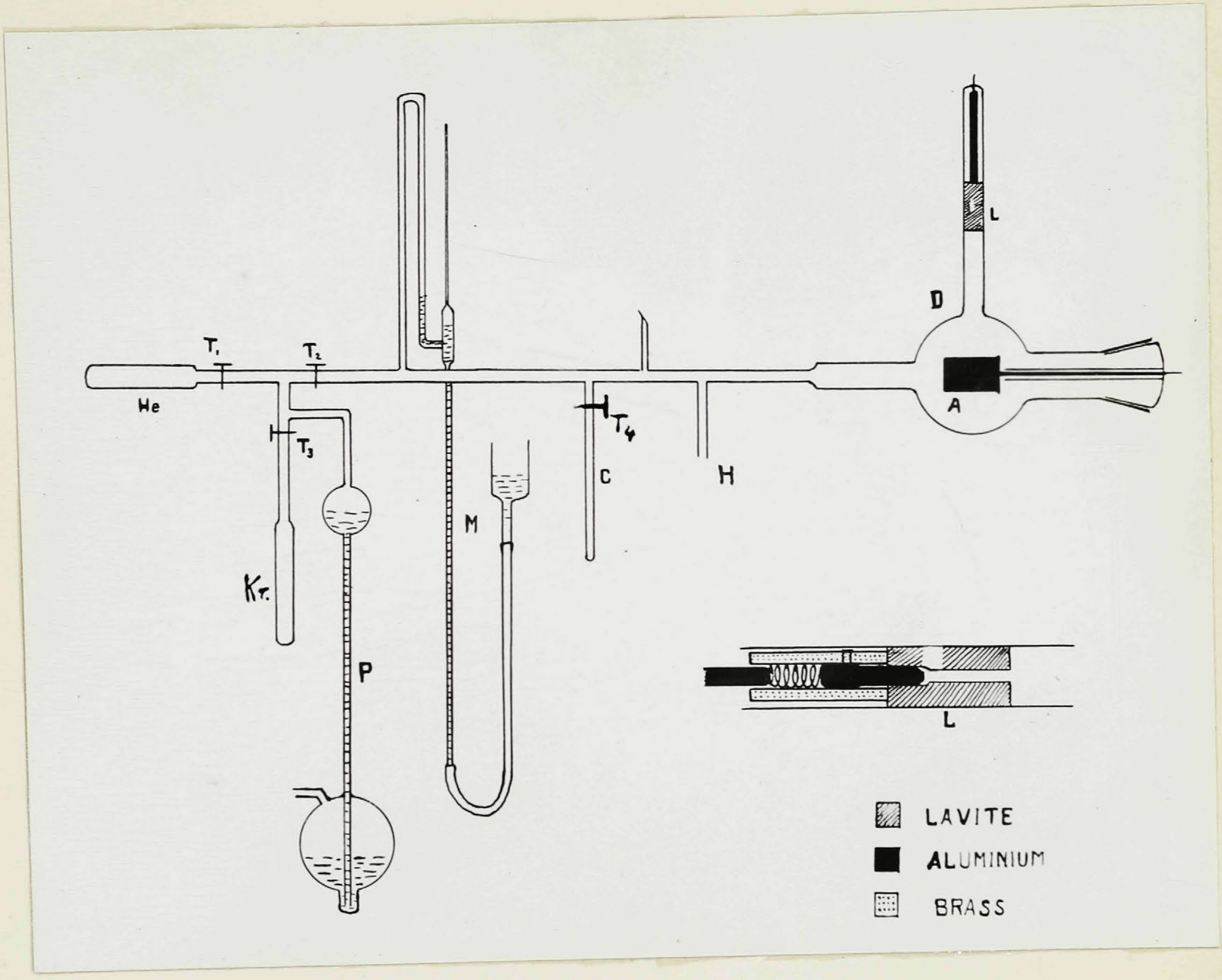
The vacuum system is shown diagrammatically in Fig. 3 (a). It was built by Dr. J. F. Heard in connection with his work in xenon and was adopted to its present purpose by the writer. The Krypton was stored in the reservoir Kr, and was admitted to the discharge tube section through the taps T_3 and T_2. The quantity admitted was controlled by means of the combined manometer and transfer pump P. A helium reservoir, He, also connected to this manometer through a tap T_1. Pressures were measured with the McLeod gauge M, and the system was evacuated through H by means of a "Hy-Vac" pump. A charcoal bulb C was used to purify the helium and to clean up any residual gas left by the pump. A tap T_4 served to disconnect this charcoal bulb when desired. The discharge tube D was connected to the vacuum system by means of two ground glass joints in order to facilitate the adjustment of the light on

Figure 3.

(a) The Vacuum System.

(b) The Discharge Tube.

FIG. 3



(a)   (b)

FIG. 3

the slit of the spectrograph. Pyrex glass was used throughout.

The Discharge Tube

The discharge tube is shown at D in Fig. 3 (a), and an enlarged cathode section in Fig. 3 (b). It was of the general Lo Surdo type as modified by Foster(9) and commonly used in this Laboratory. Essentially it consisted of 250 cc. Pyrex bulb into which a heavy cylindrical aluminium anode was fitted through a large ground joint. The anode could thus be easily removed for cleaning. From opposite sides of the bulb tubes led to the cathode section and the vacuum system.

The details of the cathode section are shown in Fig. 3 (b). The cathode was contained within a lavite cylinder on to which the glass tube was tightly drawn. The aluminium cathode was of 2 mm. diameter and fitted snugly into a hole in the lavite. Immediately above the cathode surface a hole of 1 mm. diameter continued through the lavite to the side toward the anode. The cathode was backed a fraction of a mm. away from the shoulder in the lavite formed at the junction of the two holes. A narrow slit of about 3 mm. length was cut through the lavite wall immediately in front of the cathode. The light from the Crooke's dark space emerged through this slit.

The cathode was clamped into a brass collar by means of a set screw, and the latter was held firmly in place against the base of the lavite with a steel spring and an aluminium rod. The cathode connection was made with a heavy tungsten wire sealed into the Pyrex tube. The cathode surface was polished as carefully as possible and cleaned with alcohol before assembly.

The discharge tube was cooled by means of a blast of compressed air.

The Optical System

The spectrum was analysed with a 28 foot concave grating in a stigmatic mounting. The grating contains approximately 15,000 lines to the inch and is exceptionally fast in the first order, a factor of the greatest importance for Stark effect work. The dispersion in the region considered is 3.8 A/mm.

The light from the discharge tube was focussed on the slit by means of an F 2.7 Zeiss Tessar lens of 5 cm. focus. A quartz Wollaston prism was used to separate the components polarised parallel and perpendicular to the field. The magnification on the slit was about two.

The photographic plates used in the region 6600-5800 A were Wratten Hypersensitive Panchromatic Plates, while for the region 5800-4800 A, Wratten Panchromatic Plates proved the most satisfactory. All plates were sensitised before use by bathing in a 4% ammonia solution for 45 seconds.

The High Potential Source

The high potential source used in these experiments was a split transformer Kenotron rectifier which has been described elsewhere(9). It is capable of delivering a maximum current of 100 m.a. at 10,000 volts.

A water resistance was connected in series with the discharge tube to steady the current. The potential across the tube was measured with an electrostatic voltmeter and was kept constant during an exposure by varying a resistance in series with the primary of the high voltage transformer.

Experimental Procedure.

During the evacuation of the vacuum system, the lavite cylinder containing the cathode was roasted thoroughly with an air-gas flame. This tended to drive out any adsorbed gases.

Helium was then admitted to a pressure of about 1.5 mm. and purified by means of the charcoal and liquid air. After about twenty minutes the high potential source was turned on. At this stage the tube would usually run fairly hard (about

2 m.a. at 8,000 volts), but it would rapidly soften due to the emission of gas from the electrodes and lavite as a result of the bombardment. After half an hour the tube would again harden up, and an hour's run would usually suffice to restore the original conditions. No attempt was made to force up the potential during this running in period. During this stage the light was focussed on the slit of the spectrograph and the Wollaston prism adjusted.

The vacuum system was then pumped out to a pressure of from 0.5 to 0.9 mm. The Krypton was never used pure, but always in admixture with helium. The charcoal bulb was then disconnected, and Krypton admitted until the pressure reached a value of from 1.2 to 1.5 mm. The actual pressure used varied from tube to tube and was adjusted until the operation proved satisfactory. Under these conditions the terminal voltage was commonly 10,000 volts and the current about 1 m.a.

The exposure was then started. The voltage across the tube was maintained at a constant value. During the course of a run, the tube would gradually soften until the current reached a maximum of about 2.5 m.a. When the current reached this value, the tube would usually break down, the current increasing to 10 m.a. or more and the voltage dropping to a few thousand volts. This occurred in general after from two to seven hours. This break down may be attributed to the heavy sputtering of the cathode under the bombardment of the heavy Krypton ions. After an average exposure a pit of from 2 to 3 mm. in depth was formed in the cathode.

In general it may be said that the operation of a Lo Surdo tube in a heavy gas such as Krypton is not so satisfactory as in a light gas such as hydrogen or helium. The discharge is usually somewhat unstable, and the life of the tube a great deal shorter. Since in Stark effect work, especially in Krypton, it is necessary to work with faint lines and instruments of high dispersion, satisfactory photographs are quite hard to obtain. It is, in fact, necessary to work with a fairly wide slit, with a corresponding loss in resolving power and accuracy of measurement.

EXPERIMENTAL RESULTS AND DISCUSSION

Description of Plates 1a, b, c, d.

In Plates 1a, b, c, d, are reproduced sections of photographs showing the Stark effect for Krypton in the region 6700-4800 A. The enlargement from the original plates is approximately 2.5:1.

The maximum field strength in Plates 1b,c,d is 84 KV/cm. The additional reproduction in 1d without double image prism analysis shows a maximum field of 86 KV/cm. These field strengths were calculated from the splitting measured in H_α.

In Plate 1a, the maximum field is 61 KV/cm. as determined from the helium group 2P - 4Q (λ 4922) which does not appear in the section reproduced. The other sections of this plate are not included since no Krypton lines appear.

In each case the parallel components are to the right, the perpendicular to the left. The additional photograph in 1d is introduced since it shows a number of lines in this region with somewhat greater intensity.

The neutral Krypton lines are identified with their wavelengths and combinations, while Krypton spark lines are shown with their wavelengths only. A number of foreign lines (mercury and helium) are identified with their wavelengths.

The exceptional strength of the mercury lines is very noticeable.

The measurements discussed in the following sections are based upon these plates, with reference to others to clear up doubtful points as to the number of components, patterns, etc.

Absence of Combination Lines

It was pointed out in the Introduction that the field strength at which a combination line first appears is dependent on the separation between its initial level and the neighbouring d level. In view of the wide spacing of the Krypton term values, combination lines are not expected to appear except at very high fields. A rough estimate of the field strength necessary may be made by assuming it to be proportional to the separation of the f and d levels. In neon it was found that a field of 60 KV/cm. was necessary to bring out a combination line whose initial level was separated approximately 50 $cm.^{-1}$ from the neighbouring d level. Since the separation in Krypton for all the lines observed is greater than 100 $cm.^{-1}$, considerably higher fields than those attained would be necessary to bring out the combination lines.

A complete lack of combination lines has also been reported by Ryde for argon[14]. Since the Krypton and argon spectra are very similar, this may be attributed to the same cause. In xenon, where the terms are somewhat less widely spaced than in argon and Krypton, an intermediate condition was found in which the number of combinations appearing was small compared with that in neon and other more compact spectra.

<u>Discussion of Observed Patterns</u>.

It has been noted that the wide spacing of the xenon terms had proved favourable for the production of abnormal patterns. For these the perturbed levels are specified by values which are derived from the j values of the term in question with the restriction $j \geq m \geq 0$. The far more open spacing of the Krypton spectrum might be expected to yield further examples of unusual patterns. This has proved to be the case.

It has not been found possible to describe the patterns observed in Krypton in an entirely satisfactory manner as either normal or abnormal. As a general conclusion, however, it may be said that the perturbed levels are specified by rather than by ℓ values.

Due to the small magnitude of the displacements (particularly among the 5d terms) examples of patterns for which the analysis appears complete are comparatively scarce. Nevertheless, the examples available show that complications of considerable interest are present. These difficulties may be best illustrated by the following examples.

The term $6d_3$ ($j = 2$) figures as initial level in two observed lines $2p_{10} - 6d_3$ and $2p_6 - 6d_3$. The j value of $2p_{10}$ is 1, and hence we should expect that the observed pattern, whether normal or abnormal, should be 2/3 (two parallel and three perpendicular components). The closest examination of the line (Plate 1 a) fails, however, to reveal a trace of one of the expected perpendicular components. Since the s component associated with the initial level with $m = 0$ is frequently weak in comparison with the others (compare parhelium), this is not very surprising, although its complete absence is striking on account of the strength of the other two components. Comparing this pattern with that of $2p_6 - 6d_3$ (Plate 1 c) we find, however, a more important departure from the pattern expected. Assuming the m values of the final state are specified by j (in this case equal to 2) we should expect a 3/3 pattern. The correct number of s components appear, but the initial sub-level corresponding to the missing s component of $2p_{10} - 6d_3$ now fails to contribute a p component. The provisional assignment of the value $m = 0$ to this level thus leads to difficulties, since the $0 \rightarrow 0$ transition usually yields a component of average intensity. The perturbed levels corresponding to these lines (not drawn to scale) are shown in Fig. 4 a; the missing components are shown by broken lines.

Figure 4.

(a) Transitions from $6d_3$ to $2p_6$ and $2p_{10}$.

(b) Transitions from $6d_4$ to $2p_9$.

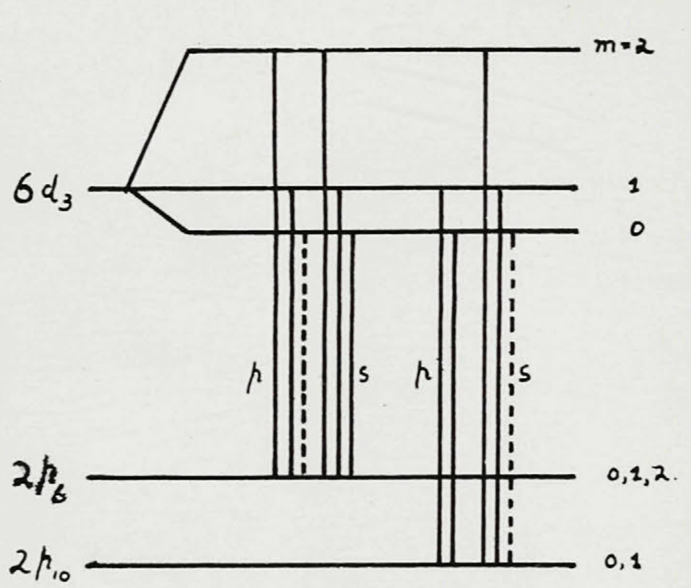


Fig. 4 a

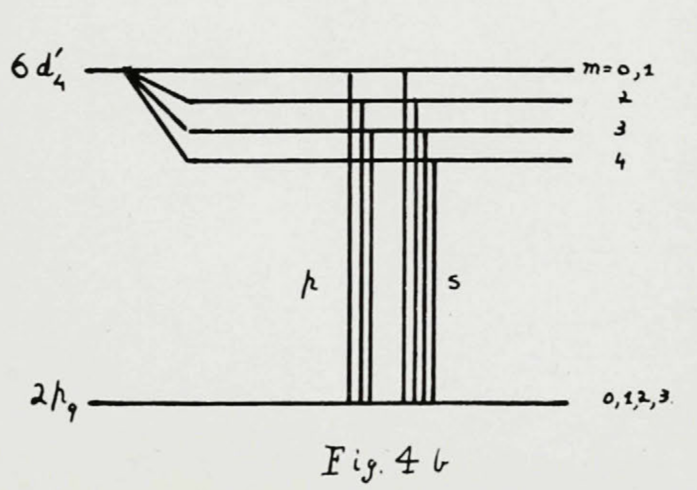


Fig. 4 b

Another incomplete pattern is found in $2p_6 - 6d_1'$ ($\Delta j : 3 \rightarrow 2$). In this case, in place of the expected 2/3 or 3/4 for a normal or abnormal pattern respectively, we find the pattern 2/1. (See Plate 1 c).

An interesting example of the same phenomenon occurs in connection with the sharp series lines associated with $4s_5$ ($j = 2$) as initial state. This level has been observed in combination with $2p_7$ (1), $2p_8$ (2), $2p_9$ (3) and $2p_{10}$ (1) with j values as indicated. A consideration of the displacements of these lines indicates the presence of three perturbed levels with separations $+4.0$, $+4.8$ and $+5.7$ cm^{-1} from the initial level in a field of 84 KV/cm. Thus for $4s_5$ the m values are 2,1,0 corresponding to an abnormal pattern. The expected abnormal patterns of $2p_i - 4s_5$ may be tabulated in comparison with those observed as follows:

	Expected	Observed	Reference
$2p_7$	2/3	2 components*	Plate 1 d
$2p_8$	3/3	1/1	" 1 c
$2p_9$	3/3	2/2	" 1 c
$2p_{10}$	2/3	1/1	" 1 b

observed without Wollaston prism

It should be pointed out that $2p_7 - 4s_5$ and $2p_8 - 4s_5$ are both faint, and the non-existence of other components is not certain.

The other two lines, however, are quite strong. The possibility of the double character of both polarisations of $2p_9 - 4s_5$ arising from unsteady fields or a foreign line is ruled out by a comparison with other plates.

The patterns afforded by the lines $2p_9 - 6d_4'$ and $2p_9 - 7d_4'$ (Δ j: 4 $\rightarrow$ 3) show the nearest approach to those expected. (See Plates 1 d and 1 b). The observed pattern, 3/4 in both cases, makes it certain that the patterns are abnormal. The pattern to be expected is thus 4/5. The observations can be explained by assuming that two of the levels (probably m = 0 and m = 1) are unresolved. On this basis, the origin of the observed pattern is as shown in Fig. 4 b.

A consideration of the observed patterns shows, then, that many of the components expected to appear have a very low, if not vanishing, intensity. The existence and resolution of the levels in which these components should originate moreover is definitely established in some cases. (This is clear, for example, in the $2p_{10} - 6d_3$ and $2p_6 - 6d_3$ lines discussed above).

A somewhat similar phenomenon has been observed for neon(10). A number of lines exhibited a simpler pattern than the 2/3 normal pattern which predominated. The 2 component in the s polarisation was missing, and this, in the standard case, was the strongest component in the pattern. An additional feature noticed was that the intensity of the perpendicular component was much greater than that of the parallel. This does not appear to hold in the present case. A typical example of such a neon line is $2p_9 - 5d_1'$ (Δ j: 3 -> 3).

In a consideration of possible explanations of these effects, the possibility of an addition to, or modification of, the existing selection rules must be considered. For example, it was noticed by Foster and Rowles that in the case of neon a normal pattern resulted when $\Delta \ell = \Delta j = \pm 1$. That such is not the case for Krypton is shown by the line $2p_6 - 6d_1'$. An empirical rule to cover the present observations must be of a definitely more complicated character. It does not seem possible to arrive at such a selection principle, if one exists, from the rather limited experimental data available. A detailed investigation of the argon spectrum, which shows many similarities with that of Krypton, should introduce fresh experimental evidence. The spectrograph used by Ryde in his recent investigations proved inadequate to resolve the patterns.

The absence of the parallel component (Δ m : 0 -> 0) in $2p_6 - 6d_3$ (Δ j : 2 -> 2) suggests the operation of the Zeeman effect selection rule which forbids this transition. In fact, the following considerations might lead one to expect that an estimate of the Stark intensities for Krypton might be made from the well-known Zeeman effect intensity formulae.

With the application of a very weak electric field, the Stark components are emitted with relative intensities which are given by the Zeeman intensity formulae. Since the electric field does not distinguish between positive and negative m values, it is necessary to multiply the Zeeman intensity factors by 2 except when $\Delta m = 0$. As the electric field increases, combination lines appear and the components of the original line share their intensities with these new lines and components. The mechanism of this modification is clearly illustrated in the calculation of the relative intensities in the helium Stark effect[23]. In these calculations the Zeeman effect formulae are multiplied by factors which are functions of the field strength and the displacement of the component considered. As the field approaches zero, these factors tend to unity. In the case of Krypton, it is found that the combination lines do not appear at field strength up to 80 KV/cm. Hence, we may suppose that the Zeeman intensities persist without radical alteration to these fields. Accordingly the intensities have been calculated for a number of typical lines from the formulae developed by Krönig and Goudsmit[24] with the modification indicated above. With the exception of the $2p_6 - 6d_3$ line, the values obtained do not explain the observations.

A direct observation of Zeeman intensities for neutral Krypton, however, to see whether these Stark effect intensity anomalies also occur in the Zeeman effect might prove interesting.

In addition to these intensity effects in completely resolved patterns, a number of diffuse series lines show a simple displacement of quite large magnitude. Among these are those with initial levels $6d_1'$, $6d_1''$ and $5d_2$ with j values 1, 3 and 2 respectively. It is uncertain whether in these cases the sub-levels are unresolved, or whether the components arising from some of them are not observed as is the case in the preceding examples. In this connection it may be significant that in many cases the p and s components do not have exactly the same displacement. Moreover, displacements of this magnitude without resolution of the sub-levels are unusual. The majority of the displacements reported by Ryde for argon appear to be of this character, as may also be the case for those neon displacements discussed previously. The peculiar polarisation effect, however, found in neon was not observed in Krypton.

Tables of Displacements

In Table II is presented the displacements of the Krypton lines observed, together with remarks as to the type of pattern when this can be deduced.

Table III contains a few additional lines from the plate without double image prism analysis reproduced on Plate 1d.

Displacements of Individual Terms

A consideration of the data presented in Tables II and III shows no definite evidence of the displacements of final levels. This is in accordance with direct observation upon a number of principal series lines of the type $1s_i - 2p_j$, and with the results on the other rare gases.

Accordingly Table IV has been prepared on the assumption that the final state contributes nothing to the observed displacement of a line. The assignment of m values to the displacements is rather arbitrary except in the case of the odd perpendicular component to which must be assigned the highest m value. The hydrogen difference of each of the observed terms has also been tabulated.

TABLE II

STARK DISPLACEMENTS AND PATTERNS FOR KRYPTON

Field Strength 84 kV/cm.

Wavelength A.	Notation and j values	Displacements ($cm.^{-1}$) p	s	Type of pattern and remarks
6456.29	$\underset{3}{2p_9} - \underset{4}{5d_4'}$	+1.8	+1.3	Broadened to red
6421.03	$\underset{2}{2p_8} - \underset{3}{5d_4}$	+2.8	+2.3	
6413.65	$\underset{3}{2p_9} - \underset{3}{5d_4}$	+2.4	+1.8	
6373.58	$\underset{2}{2p_8} - \underset{2}{5d_4''}$	+3.0	+2.5	
6351.90	$\underset{2}{2p_8} - \underset{3}{5d_1'}$	+4.3	+3.9	Faint
6346.66	$\underset{3}{2p_9} - \underset{3}{5d_1'}$	+3.0	+3.3	
6241.39	$\underset{2}{2p_8} - \underset{2}{4s_5}$	+4.1	+4.6	
6236.34	$\underset{3}{2p_9} - \underset{2}{4s_5}$	+6.0 +4.1	+5.5 +5.8	Abnormal
6222.71	$\underset{2}{2p_8} - \underset{1}{4s_4}$	+5.7	+5.6	
6163.65	$\underset{2}{2p_6} - \underset{1}{6d_5}$	-4.8	-4.5	
6151.38	$\underset{2}{2p_6} - \underset{2}{6d_3}$	0 -7.6	+2.5 0 -7.3	Abnormal
6082.85	$\underset{1}{2p_{10}} - \underset{0}{5d_6}$	0	0	

TABLE II (continued)

STARK DISPLACEMENTS AND PATTERNS FOR KRYPTON

Field strength 84 KV/cm.

Wavelength A.	Notation and j values	Displacements (cm^{-1}) p	s	Type of pattern and remarks
6075.24	$\underset{2}{2p_6} - \underset{3}{6d_1'}$	+14.0 +16.6	+14.5	
6056.11	$\underset{1}{2p_{10}} - \underset{1}{5d_5}$	0	0	
6035.82	$\underset{1}{2p_7} - \underset{2}{6d_1''}$	+ 8.7	+10.2	
6012.11	$\underset{1}{2p_{10}} - \underset{2}{5d_3}$ $\underset{2}{2p_6} - \underset{2}{5s_5}$	+ 2.0	+ 1.4	Broadened to red
5993.85	$\underset{1}{1s_4} - \underset{1}{2p_4}$	0	0	
5879.[illegible]	$\underset{1}{1s_4} - \underset{1}{2p_3}$	0	0	
5870.92	$\underset{1}{1s_4} - \underset{2}{2p_2}$	0	0	
5866.74	$\underset{1}{1s_2} - \underset{1}{3p_{10}}$	Very small $+^{ve}$	Very small $+^{ve}$	
5832.85	$\underset{3}{2p_9} - \underset{4}{6d_4'}$	+ 4.5 + 2.2 0	+ 7.9 + 4.5 + 2.2 0	Abnormal
5827.07	$\underset{1}{2p_{10}} - \underset{2}{4s_5}$	+ 5.5	+ 4.1	Abnormal
5824.50	$\underset{2}{2p_8} - \underset{3}{6d_4}$	+ 4.8	+ 7.5 + 5.1 - 6.4	Abnormal p component double (r)

TABLE II (continued)

STARK DISPLACEMENTS AND PATTERNS FOR KRYPTON

Field Strength 84 KV/cm.

Wavelength A.	Notation and j values	Displacements (cm.$^{-1}$) p	s	Type of pattern and remarks
5820.10	$\underset{3}{2p_9} - \underset{3}{6d_4}$	+ 7.0	+ 4.8	Faint
5805.55	$\underset{2}{2p_8} - \underset{2}{6d_1''}$	+ 9.9	+ 8.0	
Field strength 61 KV/cm.				
5707.51	$\underset{1}{1s_2} - \underset{2}{3p_6}$	0	0	
5672.45	$\underset{2}{1s_5} - \underset{1}{2p_4}$	0	0	
5649.56	$\underset{0}{1s_3} - \underset{1}{3p_{10}}$	Very small +ve	Very small +ve	
5580.39	$\underset{1}{1s_2} - \underset{0}{3p_5}$	+ 1.3	+ 1.3	
5570.29	$\underset{2}{1s_5} - \underset{1}{2p_3}$	0	0	
5562.25	$\underset{2}{1s_5} - \underset{2}{2p_2}$	0	0	
5520.52	$\underset{3}{2p_9} - \underset{4}{7d_4'}$	+ 7.8 + 3.3 0	+14.2 + 7.8 + 3.3 0	Abnormal
5516.66	$\underset{0}{1s_3} - \underset{1}{3p_7}$	0	0	
5504.94	$\underset{1}{2p_{10}} - \underset{0}{6d_6}$	- 1.4	- 1.4	Abnormal

TABLE II (continued)

STARK DISPLACEMENTS AND PATTERNS FOR KRYPTON

Field Strength 61 KV/cm.

Wavelength A.	Notation and j values	Displacements (cm.$^{-1}$) p	s	Type of pattern and remarks
5504.02	$2p_8 - 7d_4$ 2 3	+19.3	+19.3	
5500.71	$2p_{10} - 6d_5$ 1 1	-2.4	- 3.3	
5490.94	$2p_{10} - 6d_3$ 1 2 $3p_7 - 7s_4$ 1 1	+ 1.1 0	0 - 5.4	Abnormal

TABLE III

STARK DISPLACEMENTS IN KRYPTON

Field Strength 84 KV/cm.

Wavelength A	Notation and j values	Displacements (cm.$^{-1}$)
6652.24	$\underset{1}{2p_7} - \underset{2}{5d_1''}$	+ 3.2
6576.42	$\underset{1}{2p_7} - \underset{2}{4s_5}$	+ 4.9 + 5.8
6556.55	$\underset{1}{2p_7} - \underset{1}{5d_2}$	+ 9.9
6488.07	$\underset{1}{2p_7} - \underset{1}{4s_4}$	+ 6.5
6448.78	$\underset{3}{2p_9} - \underset{2}{5d_3}$	+ 1.4

TABLE IV

DISPLACEMENTS OF INITIAL TERMS OF KRYPTON

Field Strength 84 KV/cm.

J	Term	Displacements ($cm.^{-1}$)						Hydrogen difference
		m = 0	1	2	3	4	Unknown	
2	$4s_5$	+5.7	+4.8	+4.0	..			-2265
1	$4s_4$						+5.6	-2313
1	$3p_{10}$						Small $+^{ve}$	-2159
1	$3p_7$						0	-2585
2	$3p_6$						0	-2634
0	$3p_5$						Small $+^{ve}$	-3033
1	$2p_4$						0	-12101
1	$2p_3$						0	-12424
2	$2p_2$						0	-12450
0	$5d_6$						0	+ 924
0	$6d_6$	-1.4						+ 537
1	$5d_5$						0	+ 852
1	$6d_5$						-4.5 -4.8	+ 525
4	$5d_4'$						+1.8*	+ 749
4	$6d_4'$	0	0	+2.2	+4.5	+7.9		- 434
4	$7d_4'$	0	0	+3.3	+7.8	+14.2	**	+ 273

*Lines broadened to red. Probably unresolved components

**Measured at a field strength of 61 KV/cm.

TABLE IV
(continued)

DISPLACEMENTS OF INITIAL TERMS OF KRYPTON

Field Strength 84 KV/cm.

j	Term	Displacements (cm^{-1})						Hydrogen difference
		m = 0	1	2	3	4	Unknown	
2	$5d_3$						2.0*	+ 731
2	$6d_3$	+2.5	0	-7.5				+ 493
3	$5d_4$						+2.8 +2.3 +1.8	+ 631
3	$6d_4$	+7.5	+5.0	-6.4				+ 396
3	$7d_4$						+19.3**	+ 206
2	$5d_1''$						+3.0 +2.3	- 535
2	$6d_1''$	+10.2	+8.7	+8.0				+ 340
3	$5d_1'$						+3.8 +3.0	+ 482
3	$6d_1'$						+16.6 +14.2	+ 289
1	$5d_2$						+ 9.9	+ 269

*Lines broadened to red. Probably unresolved components

**Measured at a field strength of 61 KV/cm.

Magnitudes of Term Displacements

A comparison of the measured displacements of Table IV with the hydrogen differences of the terms fails to show any systematic connection between the two. The comparison may best be made for the 6d levels. While it is true that the largest displacements are found in the terms of smallest hydrogen difference, yet, especially for large values of the differences, the displacements are most irregular. A far greater accord with this theory is, however, shown in Krypton than in xenon. In the latter case it was found that the displacements increased with the hydrogen differences. While the departure from the results of the hydrogen difference theory is greater for xenon than for Krypton, nevertheless it is not possible to fit the observed displacements on a smooth curve when plotted against the hydrogen difference.

A detailed application of the Pauli principle to the Krypton spectrum is impeded as a result of our incomplete knowledge of the normal spectrum. In particular, we have very little information about the terms arising from the configuration in which the case has a j value of 1/2. These are the terms which converge to the upper limit $^2P_1$. Moreover, only three of the twelve terms have been identified. These are believed to be among those which converge to $^2P_2$.

It is important to consider whether we can deduce anything about the probable position of these missing terms. With regard to the p terms, p_1, p_2, p_3 , p_4, it may be said with some confidence that they lie much higher in the energy diagram than the known terms. The missing $s_1' - s_1''''$ terms are certain to lie well away from the initial levels we are considering, since the $4s_1^{'-''''}$ terms are higher than the 6d levels. The f terms, on the other hand, are likely to be irregular in their order, but it may be assumed that the grouping among them will be closer than that among the d terms. The greatest uncertainty rests in the position of the three f terms converging to $^2P_1$. No probable location for them can be deduced and so they must remain an unknown factor. It is to be expected, however, that two of them will be quite close to one another, the other widely separated.

Despite this uncertainty in the normal spectrum, the application of the Pauli theory proves satisfactory. For the 5d terms no trouble whatever is found. All of these terms are displaced to the red, with the exception of the two lowest terms, which are undisplaced, and the higher the term lies in the energy diagram the greater the displacement. These observations are to be expected as a result of the position of the 5 X, Y, Z and $3p_2$, $3p_3$, $3p_4$ terms above the 5d levels.

In the case of the 6d levels similar arguments hold for most of the displacements. Small negative displacements for the lower terms may be ascribed to the presence of the 5p levels, while the greater positive displacements of the uppermost terms may be explained as due to the 6 X, Y, Z terms. Some uncertainty remains as to the large displacements of the $6d_4$ and $6d_4'$ terms which lie in the centre of the group. These displacements may be accounted for if we assume that an unknown f term with $j = 5$ lies between them. It must be admitted, however, that unless this term lies in the lower part of the group, this position implies a wider spacing between the 6 f terms than was expected.

Thus it appears that, while the hydrogen difference rule fails to indicate the magnitude of the observed displacements, this is possible on the Pauli theory with only one assumption as to the position of an unidentified term.

Lines of Ionised Krypton

A number of lines have been identified as belonging to the ion Kr^+. Some of these have been marked on Plate 1. These lines may usually be recognised due to their enhancement at high fields.

None of these lines show a displacement due to the field.

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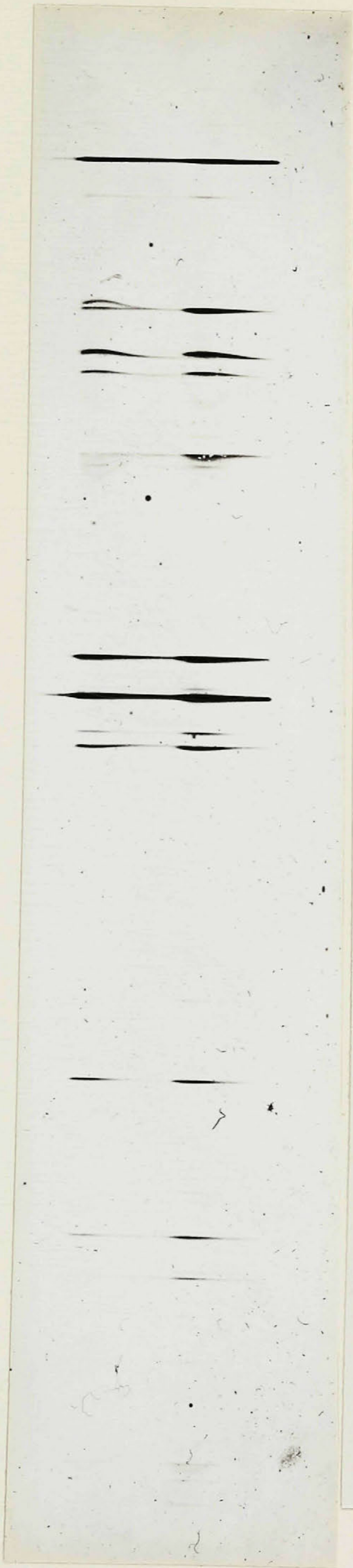
Plate 1 (a).

Field Strength 61 KV/cm.

Region 5450 - 5725 A.

PLATE 1a



5641	Hg.
5490.9	$2p_{10} - 6d_3, 2p_7 - 7s_4$
5500.7	$2p_{10} - 6d_5$
5504.0	$2p_8 - 7d_4$
5504.3	$2p_{10} - 6d_6$
5516.7	$1s_3 - 3p_7$
5520.5	$2p_9 - 7d'_4$
5562.2	$1s_5 - 2p_2$
5570.3	$1s_5 - 2p_3$
5580.4	$1s_2 - 3p_5$
5633.2	Kr^+
5649.6	$1s_3 - 3p_{10}$
5672.5	$1s_5 - 2p_4$
5682.6	Kr^+
5690.6	Kr^+
5707.5	$1s_2 - 3p_6$

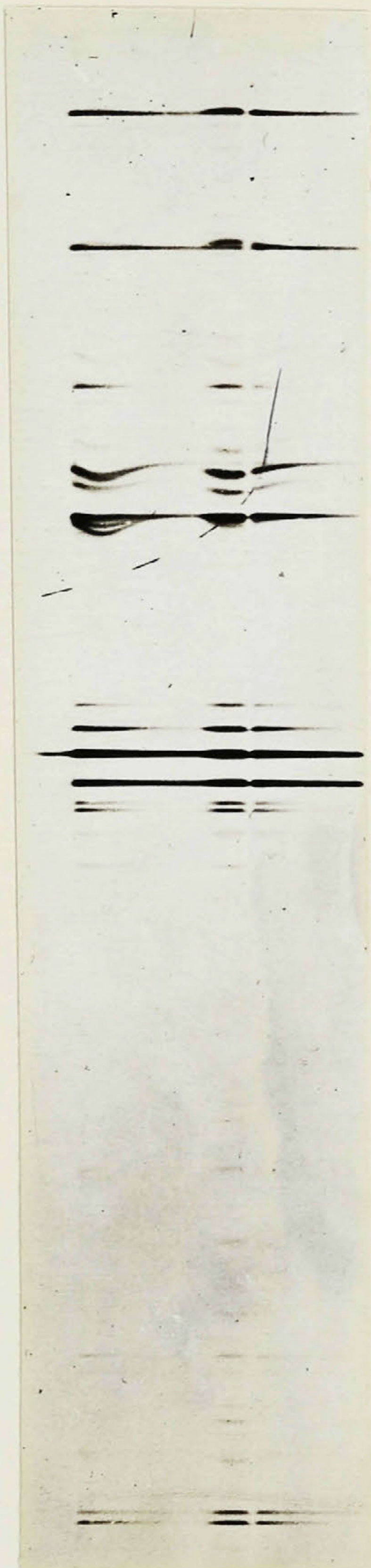
PLATE

Plate 1 (b).

Field Strength 84 KV/cm.

Region 5750 - 6000 A.

PLATE 16



5769.6	Hg
5790.7	Hg
5805.5	$2p_8 - 6d_1''$
5820.1	$2p_9 - 6d_4$
5824.5	$2p_8 - 6d_4$
5827.1	$2p_{10} - 4s_5$
5832.9	$2p_9 - 6d_4'$
5866.7	$1s_2 - 3p_{10}$
5870.9	$1s_4 - 2p_2$
5875.6	He
5879.9	$1s_4 - 2p_3$
5993.9	$1s_4 - 2p_4$

Plate 1 (c).

Field Strength 84 KV/cm.

Region 6000 - 6300 A.

PLATE 1

6012.1	$2p_{10} - 5d_3$, $2p_6 - 3s_5$
6035.8	$2p_7 - 6d_1''$
6056.1	$2p_{10} - 5d_5$
6075.2	$2p_6 - 6d_1'$
6082.9	$2p_{10} - 5d_6$
6151.4	$2p_6 - 6d_3$
6163.7	$2p_6 - 6d_5$
6222.7	$2p_8 - 4s_4$
6236.3	$2p_9 - 4s_5$
6241.4	$2p_8 - 4s_5$

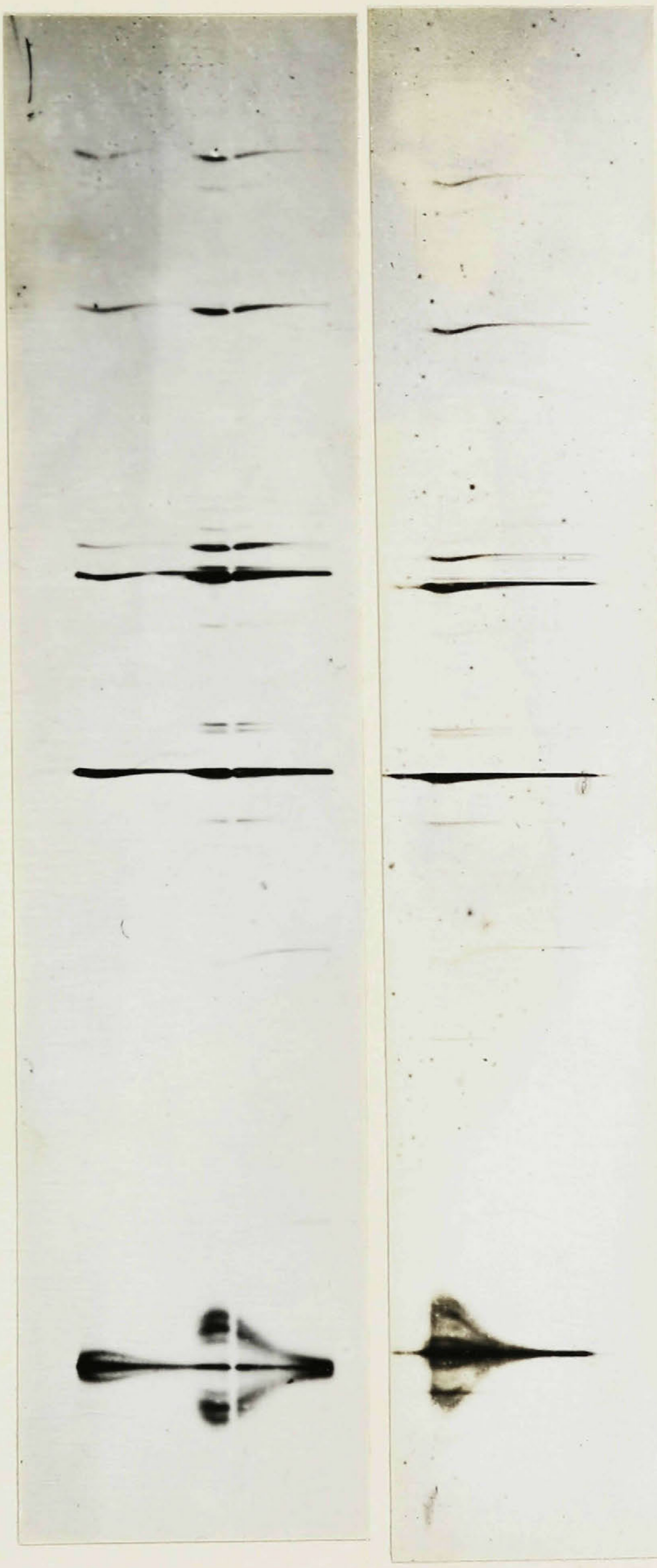
Plate 1 (d).

Field Strengths (1) 84 KV/cm.

(2) 86 KV/cm.

Region 6330 - 6600 A.

PLATE 1d



6346.7	$2p_9 - 5d_1'$
6351.9	$2p_8 - 5d_1'$
6373.6	$2p_8 - 5d_1''$
6415.7	$2p_9 - 5d_4$
6421.0	$2p_8 - 5d_4$
6448.8	$2p_9 - 5d_5$
6456.3	$2p_9 - 5d_4'$
6488.1	$2p_7 - 4s_4$
6536.6	$2p_7 - 5d_2$
6562.8	H_α
6576.4	$2p_7 - 4s_5$

SECTION II

STARK INTENSITIES IN HYDROGEN AND HELIUM

SUMMARY

1) A new type canal ray tube is described which may be operated at gas pressures as high as one-half mm. This tube is applied to the measurement of the relative intensities of the Stark components in hydrogen and helium. The electric fields obtained vary between 90 and 130 K.V. per cm.

2) Results obtained for H_β show qualitatively that agreement with theory is obtained for both polarisations. This is in contradiction to the findings of former workers at lower gas pressures.

3) A comparison of photographs of H_β taken from pure hydrogen and from a helium hydrogen mixture show no marked change in the intensity distribution.

4) In the case of helium, also, a general qualitative agreement with theory is obtained.

INTRODUCTION

Since the discovery by Stark[1] in 1913 of the effects of an intense electric field on the light emitted by atoms, the problem of the relative intensities of the components in the various Stark patterns has been one of considerable theoretical and experimental interest. Just as one of the major triumphs of the quantum theory of Bohr was the calculation of the Stark displacements in hydrogen by Epstein[2] and Schwarzchild[3], so a notable achievement of the new mechanics was the calculation of the relative intensities of Stark components in hydrogen by Schrödinger[4], and in helium by Foster[5]. The publication of these results greatly reduced the divergence which had previously existed between theory and observation. The relative intensities of Stark components, however, are known to depend upon experimental conditions which introduce factors not considered in the theory. This is especially true in the case of hydrogen. No full explanation has been offered for the many variations from the Schrödinger theory.

In the present investigation, fresh experimental evidence has been introduced through the use of a new canal ray tube which will operate at gas pressures as high as one-half mm. Thus the two main sources used in the study of the Stark effect have been made to overlap in the important matter of gas pressure. The resulting plates are clear and final, though results are only quoted qualitatively. The quantitative findings will be included in the published report after the completion of the calibration of the intensity marker.

The two principal methods which have been used in Stark effect research are the canal ray method of Stark, with which the German school have worked with great success, and that first employed by Lo Surdo(6) which up to the present has alone been used by Foster and his co-workers at McGill University. While the intensity measurements carried out in this Laboratory by the Lo Surdo method show on the whole an excellent agreement with theory, those obtained in Germany with the canal ray method show very definite divergencies under certain experimental conditions. One of the major differences between the two methods lies in the wide difference in the gas pressures employed. These are from one to five mm. of mercury in the Lo Surdo source, as contrasted with few hundredths of a mm. in a canal ray tube. In addition to this difference, in the canal ray method, we find superimposed upon the Stark intensities all the varied intensity and polarisation phenomena known to be associated with the properties of canal ray beams. Nevertheless, since canal ray intensities have been observed to vary radically with the pressure in the field space(7), and the general dependence of spectral intensities upon the pressure is notorious, it seemed to the writer important to investigate the persistence of the canal ray phenomena at considerably higher pressures.

In considering the theoretical intensities, it must be borne in mind that the quantities actually calculated are the transition probabilities between the levels concerned in a uniform electrostatic field. If we take these as proportional to the intensities of the Stark components, several important assumptions are implicitly made. For example, we assume that the number of atoms in each of the initial states is the same. This is a factor which is known to be variable with the experimental conditions (e.g. the work of Gaviola in mercury[8]), and indeed a concentration of atoms in the initial states concerned has been assumed by Langstroth[9] to explain the excessive strength of the P-P and p-p combination lines in the helium Stark effect. Another factor which might be considered is the presence, under actual experimental conditions, of other perturbing forces than the uniform field considered in the theory. In view of the close theoretical connection between intensities and displacements, however, these might be expected to manifest themselves in variations in the displacements as well as in the transition probabilities. No such variation has been reported. An attempt may be made to explain the observed anomalies in Stark intensities by a variation in the excitation function to the various initial levels. In this case the perturbations caused by a change in experimental conditions might be out-weighed by those due to neighbouring atoms as a result of an increase in the pressure. It must be admitted, however, that such an explanation does not appear entirely satisfactory.

In considering the experimental intensities in detail, it is perhaps more convenient to depart from the historical sequence and to deal first with those obtained with the Lo Surdo method.

The most complete investigation of intensities in hydrogen has been carried out by Foster and Chalk(10). With minor exceptions an excellent agreement with Schrödinger's theoretical results was obtained. It should be noted that in these investigations the hydrogen was never used pure, but always in admixture with neon or helium. The lines investigated were H_α, H_β, H_γ and a few components of H_δ.

In his experiments on the asymmetry in the displacements of H_α which arise in the fine structure, McRae(11) noticed certain interesting features regarding the intensities. If pure hydrogen was used a decided intensity asymmetry was observed; this decreased with a reduction of the gas pressure used in the discharge tube, and disappeared if the hydrogen was mixed with a rare gas. This asymmetry consisted essentially in the fact that the ratios $^{-1}/_{+1}$ and $^{+3}/_{-3}$ were both greater than one. Since +1 and +3 have a common initial level, as do -1 and -3, this cannot be explained by assuming a concentration of atoms in a favoured initial state. No satisfactory explanation for these results has been put forward.

Thus in hydrogen the theoretical intensities are obtained with the Lo Surdo method if the hydrogen is greatly diluted with a rare gas. A good approximation is also obtained if the pressure in a pure hydrogen discharge tube is reduced to about one mm.

A complete investigation of the relative intensities in typical helium line groups has been carried through by Langstroth(9) in this Laboratory. The groups chosen for investigation were the par helium groups 2P-4Q (λ 4922) and 2P-5Q (λ 4388), and the corresponding ortho helium groups 2p-4q (λ 4471) and 2p-5q (λ 4026). For the most part there is detailed agreement with theory, although definite departures appear in a few lines and components. The observed discrepancies fall into two general classes, those which appear to the same degree in all the components of a line (these may be connected with the azimuthal quantum number), and a small group with deviations of much smaller magnitude which appear only in certain components of a line (these may be connected with the magnetic quantum number). Of the first type it is found that the P-P and p-p combinations are decidedly too strong for the theory, as was earlier reported by Dewey[12]. These discrepancies, as was mentioned before, may be accounted for by assuming a concentration of atoms in the initial states concerned due to favouritism in the mechanism of excitation. This explanation is supported by experiments on the normal helium spectrum carried out at Utrecht[13]. No satisfactory explanation for the variations of the second class has been put forward.

Passing now from a consideration of the experimental intensities as measured with the Lo Surdo method to those obtained from canal ray tubes, we find a far greater variety in the measured intensities. As was mentioned in an earlier paragraph, we must expect to find superimposed upon the Stark intensities a wide range of independent effects arising from the peculiarities of the source. A great mass of experimental data is available on this subject, only a small portion of which can be mentioned here.

A number of investigators[14] have considered the state of polarisation of the light emitted from a canal ray beam. If the atom emitting the light experiences the polarising impacts of surrounding atoms (Umladeleuchten), then the ratio I_p / I_s is greater than one. I_p (I_s) refers to the intensity of the light with its electric vector parallel (perpendicular) to the canal ray direction. If, however, the canal rays run into a high vacuum (Abklingleuchten), then this ratio is equal to one. A similar phenomenon occurs in considering the sum of the p to that of the s components in the Stark effect.[15]

Another point, of interest later in connection with Stark intensities, lies in the observations carried out on spectral intensities at different angles to the canal ray beam. Typical of this is the work of v. Hirsch and Schön[16], who discuss the relative intensities of hydrogen and helium lines when viewed in two directions inclined at equal angles to the direction of the canal ray beam, one being towards the source, the other in their direction of motion. Experiments were made on hydrogen canal rays running into helium, and on helium canal rays running into hydrogen. For H_α, H_β and He $\lambda 4472$ emitted from moving atoms, a positive axial effect was observed. For H_α, H_β, $\lambda 4472$ from stationary atoms, and for He $\lambda 3889$ from both moving and stationary atoms the effect lies within the experimental error. This subject has been discussed by Stark in very great detail.[17]

Considering the experimental results on Stark intensities obtained with the canal ray method, we find that these are only complete in the case of hydrogen. It was early observed by Stark and Kirschbaum[18], and independently by Wilsar[19] that in the parallel field arrangement (field direction parallel to that of the canal rays) an asymmetry resulted which was reversible with the field direction. In the case of an accelerating field this asymmetry consisted in the strengthening of the long wave length components as compared with the short. The magnitude of this effect was found by Lunelund[20] to increase with increasing canal ray velocity. A summary and discussion of these early results has been given by Stark in his two books on the subject.[21]

By far the most complete investigation of canal ray intensities in hydrogen has been carried out more recently by Mark and Wierl[22]. The results may be summarised in comparison with the theoretical calculations of Schrödinger as follows. In the parallel field arrangement, the intensity asymmetry mentioned in the preceding paragraph was confirmed. In addition it was found that the relative intensities of the components differed from those predicted by Schrödinger. This holds both for hydrogen canal rays running into nitrogen between the field plates, and for hydrogen excited with nitrogen canal rays, i.e. both for moving and stationary hydrogen atoms.

If, however, the perpendicular field direction is used, then different results are obtained for different conditions in the observation space, and for different directions of observation. For a direction of observation perpendicular to the field and with hydrogen canal rays running into hydrogen gas between the field plates, an agreement with the theoretical values was obtained for the p components, but not for the s components. If the direction of observation is changed to one along the lines of electric force (from the positive to the negative electrode), then the distribution among the long wave length components agrees with theory, while that among the short wave components does not. In this arrangement, of course, only the s components emerge and these are observable at all azimuths about the field direction, in contradistinction to the transverse effect for which only those oscillations contribute to the s components whose electric vectors lie parallel or anti-parallel to the canal ray direction. For hydrogen canal rays running into a high vacuum, and for hydrogen excited by nitrogen canal rays, no agreement was found, and the results in the two cases were similar.

As a result of their experiments Mark and Wierl conclude that:

(1) Agreement with Schrödinger is never reached in the case of fields parallel to the canal ray direction.

(2) In the case of perpendicular fields, agreement is only obtained if hydrogen canal rays run into a residual gas between the field plates, and then only for the p components. (The above hold for a direction of observation perpendicular to the field).

(3) Agreement is found for the long wave length s components when viewed along the field.

Some interesting observations on the Balmer lines, which have however no connection with those previously discussed, have been made by v. Traubenberg, Gebauer and Lewin[23] Using the perpendicular field arrangement electric fields up to 1.4×10^6 volts per cm. were obtained. It was found that the Stark components of a given Balmer line disappear entirely when a certain definite field strength is reached. This critical field strength is lower for the higher members of the series, and for a given line is lower for the long wave length components than for the short. In fields over 10^6 volts per cm. only H_α and H_β remain and these are unaffected by fields up to the maximum attained. The problem, which is essentially one of ionisation, has been considered theoretically by Lanczos[24], and excellent agreement with experiment obtained.

The investigation of helium intensities by the canal ray method is by no means complete. In addition to his early work[21], the problem has been recently considered by Stark[25]. In these experiments, however, the problem under investigation was the axiality of light emission as disclosed by the relative intensities for different directions of observation. Using the perpendicular field arrangement, the direction of observation lay in the plane containing the lines of force and the canal ray direction, and at different angles to the former. The results obtained indicate that if a line is displaced by the electric field to the red, then its intensity in the direction of the electric field is smaller than in the opposite direction. The reverse is true if the line is displaced to the blue. So far as the writer is aware, no detailed examination of the fine analysis of helium groups in connection with theory has yet been made by the canal ray method.

Reverting to the hydrogen intensities, the explanation put forward for the experimental results must be considered. At the time of the discovery of the reversible asymmetry in the parallel field case, Stark suggested the following explanation. The hydrogen atom is to be considered as being polarised by the action of the field. Moreoever, the atom is assumed to possess a large number of electrons and those lying close to the nucleus are supposed by their vibrations to produce the long wave components, those further away the short. Thus if the electrons on the forward side of the atom (with respect to its motion) are excited the more strongly, the experimental parts are explained. This hypothesis is, of course, untenable in this form on the Bohr theory. The conception of the observed anomalies arising in some manner from a polarisation of the emitting atoms, either due to the field or to the directed impacts of the canal rays, has been retained by Mark and Wierl. An attempt to treat the problem as one of polarisation on a wave mechanical basis has been made by Slack[26], but his treatment does not seem to explain the phenomena.

By means which will be discussed later, it has been found possible to operate canal ray tubes at far higher pressures than have been previously used. Satisfactory operation in the case of hydrogen is obtained between 0.4 to 0.5 mm. as compared with the 0.01 to 0.03 mm. used by Mark and Wierl in their investigations. It is perfectly feasible to operate Lo Surdo sources in this pressure range, so that a much more direct comparison between the two methods is now possible.

The perpendicular field arrangement is used, the direction of observation being perpendicular to the field and to the canal ray beam. The gas, hydrogen or helium, fills both field space and discharge tube at the same pressure. Since in the case of hydrogen it is desirable to stream the gas slowly through the system to remove any foreign gases, the pressure in the observation space may be slightly lower than that indicated by the gauge. With the rates of streaming used, this drop must be very small.

Reproductions of photographs obtained are given, together with the accompanying photometer traces. These comprise H_β both in pure hydrogen and from a helium mixture, and the 2P -4Q and 2p-5q helium groups. The field strengths range between 90 and 130 K.V. per cm.

A careful comparison of the photometer traces for H_β with those published by Mark and Wierl under similar experimental arrangements (with the exception of the pressure) indicates a different intensity distribution among the s components. While Mark and Wierl have reported an agreement with Schrödinger's theoretical results for the p components, a definite difference for the s components had been found. The new curves for the s components show a definite qualitative departure from those previously obtained, and this departure is in the direction of agreement with theory. In the case of the curves for the p components no new features are apparent.

In view of the rapid change of the relative intensities in helium with the field strength, it is not possible to discuss these results in any detail until the necessary calculations have been completed. In general, however, these intensities show a distribution which appears to approximate very closely to that expected theoretically.

EXPERIMENTAL

The Discharge Tube

A point of the greatest importance in the design of canal ray tubes consists in securing as great a light intensity as possible. In their later work in hydrogen, Mark and Wierl obtained satisfactory results by the use of very high currents in the main discharge (up to 120 m.a. at 20,000 volts). This, however, necessitates the use of a quartz discharge tube to withstand the severe heating arising from such a large power dissipation. Moreover, great care is required in the handling of such a large current in order to prevent violent fluctuations in the current, with consequent variation in the field plate potential. Since the only suitable high potential source available delivered a maximum current of 40 m.a. at 25,000 volts, it was thought desirable to consider means of focussing the discharge on to a small region of the cathode in the immediate vicinity of the canal. Thus the current density in the canal ray beam might be greatly increased for a given current in the main discharge. After considerable experimentation, it was found possible to do this by means of a lavite cylinder sealed into the glass immediately above the cathode surface. A conical hole, tapering toward the cathode, restricted the discharge to an area about four times that of the canal. A decided increase in the light intensity was obtained in this manner, it being possible to record the Stark components of the strong helium line 4472 in about ten minutes.

The most important result of this type of construction lies in the radically increased gas pressures at which the tubes can be satisfactorily operated. This point has been sufficiently stressed in the Introduction. Complications in the field plate arrangements arise, however, due to the increased tendency to sparking and general discharge at the higher pressures. These, however, are not serious if great care is taken in polishing the electrodes. It may be remarked that the increase in pressure by itself leads to an increase in the light intensity.(27)

The general design of the discharge tube is clear from Fig. 1. The total length is nearly one metre in order to provide a large cooling area. The glass in the immediate vicinity of the cathode, where the heating is most severe, is cooled by means of a blast of compressed air. The anode is a nickle disc of 3 cm. diameter by 3 mm. thick. The tube was constructed of Pyrex glass which, in general, proved adequate to withstand the heating. At high currents, however, the tube has occasionally cracked in the neighbourhood of the cathode. This is doubtless due to strains set up in the glass during

Figure 1.

The Vacuum System.

Figure 2.

Cathode Section of the Discharge Tube.

the process of sealing in the lavite cylinder. Careful annealing of these parts has almost entirely removed this trouble.

The important part of the tube, the cathode and field plate assembly, is shown in detail in Fig. 2. The tube leading to the anode, at this point of 2 cm. diameter, is waxed into a brass bushing (1), which in turn is waxed into the water cooled cathode (2). The brass bushing may be readily altered or replaced to take care of small variations in the size of the glass tube. Within the latter is sealed the lavite cylinder (3) in which is cut a tapered hole as shown. The smallest diameter of this hole is 4 mm. The actual cathode surface is a carefully polished aluminium disc of 2 mm. thickness which is screwed to the brass cathode. The canal rays pass through a circular canal of 2 mm. diameter into the field chamber. An adjustable slit cuts the width of the canal ray beam down to 0.5 mm.

The field plates, which are of polished alumunium, are mounted within a hollow brass cylinder (6) to which the earthed field electrode (7) is connected. The field plates are half cylindrical in shape. The earthed electrode is mounted on a brass sleeve (9) which fits snugly within the outer casing. As may be seen in the diagram, this sleeve is turned out at top and bottom to a radius equal to that of the electrodes.

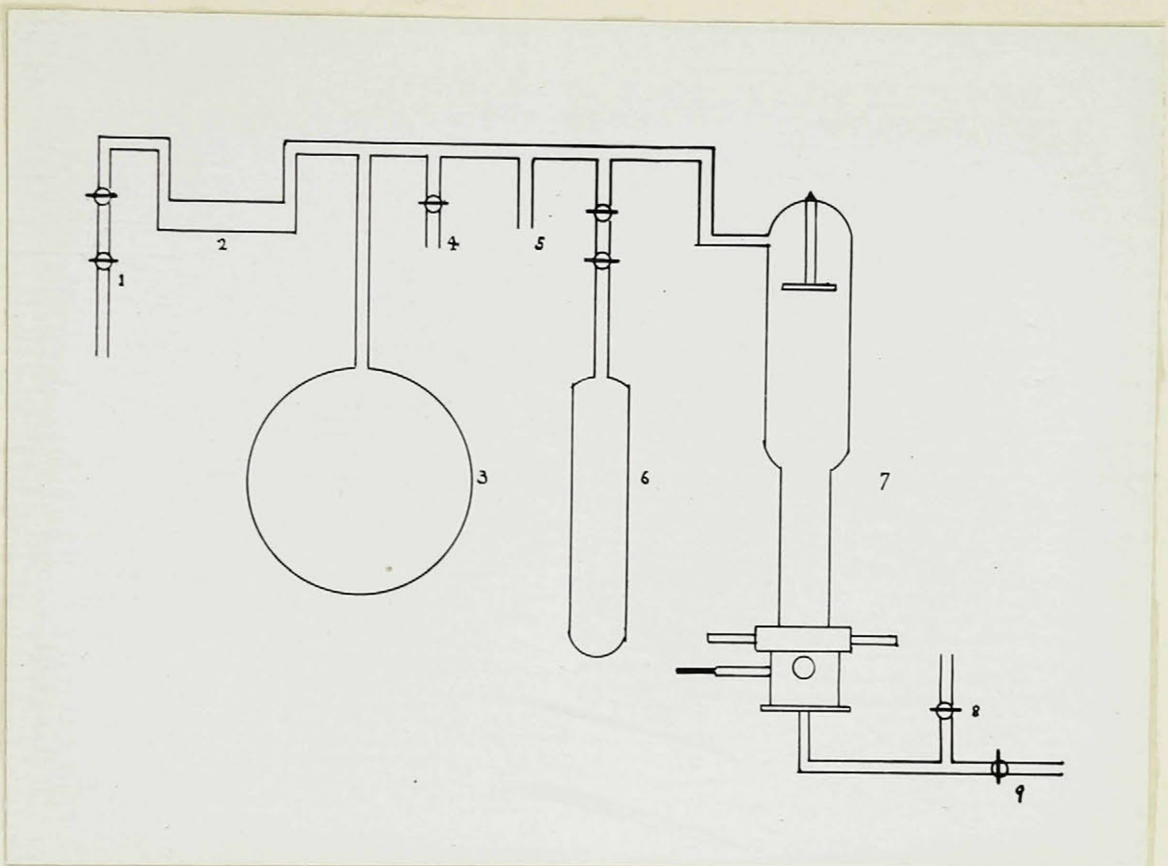


FIG. 1

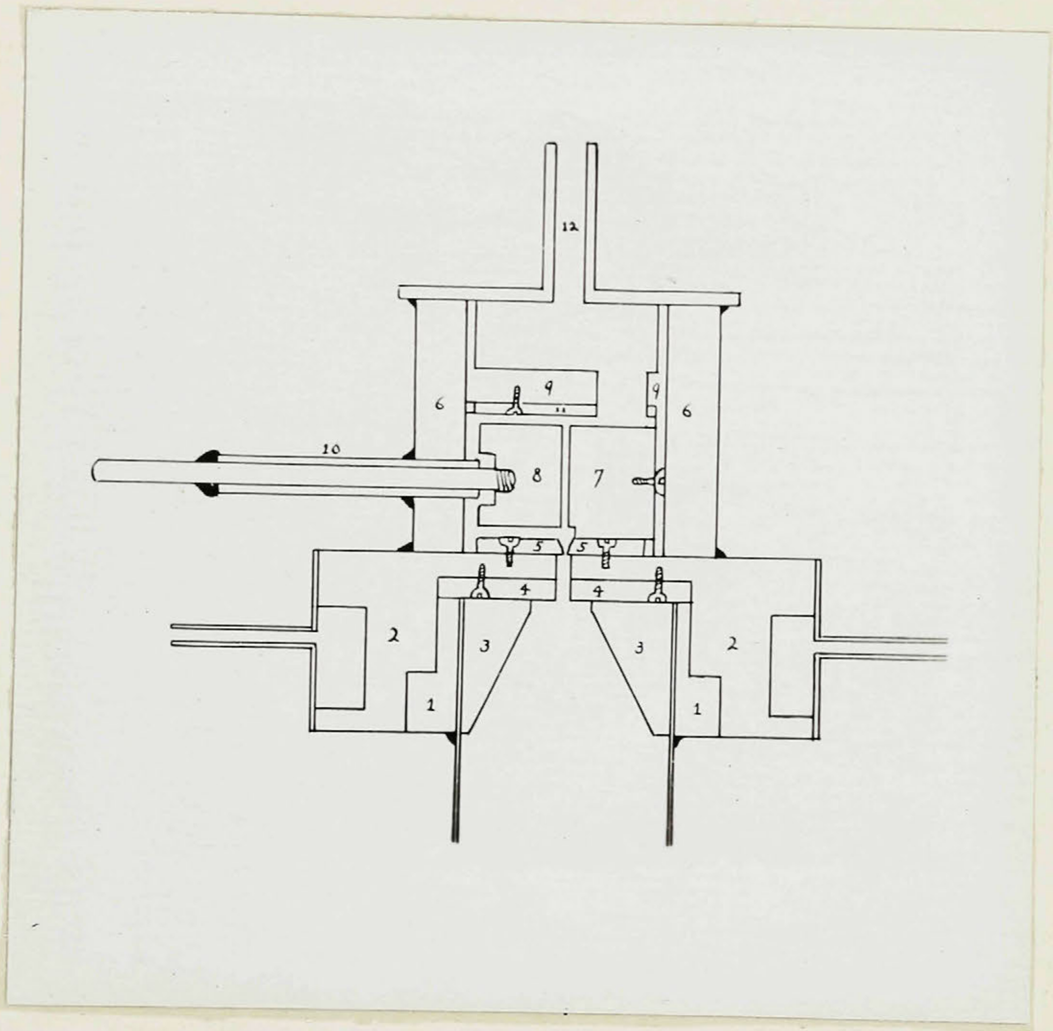


FIG. 2

Half the bottom part was then cut away leaving a half cylindrical shell into which the earthed electrode fits firmly. A passage around the top of this electrode permits evacuation of the discharge tube through the passage (12). The high potential electrode is supported and insulated from the casing by the glass tube (10) into which the brass supporting rod is waxed. The distance between the electrodes is usually about 0.7 mm. The canal ray beam, after traversing the field space, hits a stop (11) of polished aluminium which is screwed to the brass sleeve (9). The space between the high potential electrode and the earthed walls is kept down to approximately 1 mm. in order to reduce the discharge between the electrode and the walls as much as possible. The light from between the field plates escapes in a direction perpendicular to the plane of the drawing through two glass windows which are waxed over holes in (6). All waxed joints are made with deKhotinsky cement.

The Vacuum System

The vacuum system is shown diagrammatically in Fig. I. Two taps (1), one with a scratch cut part of the way round the barrel to act as a slow leak, lead to an electrolytic hydrogen generator. The hydrogen is dried by means of a liquid air trap which replaces the phosphorus pentoxide tube (2) originally used. A large ballast volume (3) serves to stabilize the pressure. A tap (4) may be used as an auxiliary pump connection and admits air to the system when necessary. The McLeod gauge is connected at (5), while (6) is a helium reservoir, the gas being admitted to the system as required by means of the two taps shown. The discharge tube (7) is mounted vertically and may be turned about a vertical axis by means of two ground glass joints not shown in the diagram. Taps (7) and (8) connect the vacuum system to a large charcoal bulb, and to the pumps respectively. Two glass diffusion pumps connected in parallel and backed by a 'Hy-Vac' pump served to evacuate the system. Pyrex tubing was used throughout.

The High Potential Sources

The source of high potential for the main discharge is a 'Proton' apparatus of Kipp and Zonen. This outfit, a full-wave rectifier, is capable of delivering a maximum current of 40 m.a. at 25,000 volts. The current and voltage are regulated by means of a primary resistance. The output of the rectifier is smoothed by two large condensers of 0.26 m.f.d. capacity supplied by the General Electric Company. Further smoothing is secured by the use of a large inductance and a water resistance in series with the discharge tube. The water resistance forms part of the water cooling system of the discharge tube.

The field potential is supplied by the 10,000 volt General Electric rectifier described in Part I of this thesis.

The potential across the field plates is measured with an electrostatic voltmeter and is kept constant by varying the primary resistance of the high voltage transformer.

The cathode is maintained at ground potential.

The Optical System

The light from the discharge tube is focussed on the slit of the spectrograph through a Wollaston prism by means of a condensing lens.

The spectrograph is the large glass instrument used in this Laboratory[28]. Three prisms are used in this instance. The lenses are doublets 3 inches in diameter and have a focal length of 45 inches. The temperature of the prism chamber is kept constant by means of a thermostat and electric heating coils. With the present arrangement the dispersion at H_β is 11.2A/mm.

Eastman 40' photographic plates are used and are developed in metol-hydroquinone.

Intensity Measurements

The method finally adopted for the intensity measurements is essentially that described by Ornstein[29]. A "step-reducer" is placed before the slit of the spectrograph and evenly illuminated with a continuous source of light. The densities on the steps are so adjusted that a series of marks is produced on the photographic plate varying uniformly from zero to maximum density.

The step reducer in use was made in the following manner. A process plate was fastened to the carriage of a comparator facing a distant source of light. A fixed sheet of stiff paper pressed against the plate, the edge in contact with the plate having a clean cut, straight edge. The portion of the plate not covered by the paper was then exposed for a short time, the plate advanced .5 mm. and exposed again, and so on. In this manner a series of twelve steps was produced which, by a suitable choice of the exposure times, varied uniformly from zero to maximum density. A small piece of this plate was carefully varnished and mounted on a slide which fits the slit of the spectrograph.

Uniform illumination of the reducer is essential. This is secured by the use of a ribbon filament tungsten lamp in conjunction with a cylindrical lens. The lamp is operated from a low voltage transformer. The brightness of the lamp can be regulated within certain limits by means of a primary resistance. The voltage across the lamp is measured with a voltmeter and may be kept constant if desired.

The method of calibration has been fully described by Ornstein(29). A number of photographs are taken through the reducer with constant exposure time and lamp voltage but with varying slit width. Within wide limits the intensity for a continuous source of light may be considered as proportional to the slit width. A lower limit is set however, by the condition that at least the first diffraction maximum on each side of the central image must fall on the collimator.

These plates are then photometered, and the deflections, measured from total darkness on the thermopile slit, to the steps (Ui), and to the unaffected part of the plate (U_o), tabulated. The ratio $^{Ui}/_{U_o}$ for each step is then calculated and plotted against the logarithm of the intensity. We thus obtain a family of parallel curves, each corresponding to one of the steps on the reducer. If a straight line be drawn parallel to the intensity axis through the parallel portion of these curves, we may readily calculate from the intercepts of the curves on this line the relative absorptions of the several steps. This procedure must be repeated at each wavelength at which it is desired to use the reducer.

The photometer employed is the standard Moll instrument[30].

A comparison photograph taken through the reducer is placed on each Stark photograph. From the known intensity distribution among the calibration marks, the relative intensities of the Stark components may be obtained.

A typical set of intensity marks is seen in Plate 6.

In the procedure followed up to the present, the calibration marks and the Stark photographs are not the results of equal exposure times. Considerable uncertainty has been expressed as to the propriety of this procedure, which is, however, followed at Utrecht after an exhaustive study of the subject.[31] It is felt that experiments to justify this assumption must be carried out with the plates and method of development used in this Laboratory.

The routine work of calibrating the reducer has not been completed in time to incorporate numerical results in this discussion.

Experimental Procedure

As a result of the large mass of metal and lavite in the cathode assembly, it is necessary to operate the tube for about an hour at a high current to outgas these parts as much as possible. During this process, hydrogen is streamed rapidly through the discharge tube.

A rough alignment of the discharge tube with the slit may be effected by means of an iron arc mounted behind the discharge tube. The light from the arc passes between the field plates and through the lens - Wollaston prism system. Final adjustment is made by direct observation of the light on the slit of the spectrograph.

The first application of the field potential at these pressures (0.4 to 0.6 mm.) is frequently accompanied by discharge and unsteadiness. This quiets down after a few minutes operation, and the field potential may then be raised to its usual operating value of 10,000 volts. Due to the high current density in the canal ray beam, the current between the field plates is intimately connected with that in the main discharge. Since with the present cooling arrangements the former cannot with safety be increased beyond 10 m.a., a limit is placed upon the current in the main discharge. It is found that this limit is about 8 m.a. This influence on the field potential necessitates exceedingly stable conditions in the canal rays during an exposure. If care is taken, these can be obtained, and the field potential held constant within 1%. Exceedingly sharp lines are thus obtained.

An exposure in hydrogen is usually taken with the gas streaming slowly through the discharge tube. The water vapour is removed with a liquid air trap. Under these conditions the secondary spectrum is fairly strong and many displaced lines have been observed.

The gas is not streamed, however, during a run in helium; the pressure in this case is between 0.4 and 0.5 mm. The charcoal bulb is kept in constant communication with the vacuum system when helium is used to remove any foreign gases which may be liberated from the metal or wax. Hydrogen is present as an impurity in the helium and H_β is always found faintly on the plates. Other foreign lines frequently observed are due to aluminium and, occasionally, mercury.

The canal ray current is usually in the neighbourhood of 6 m.a. at about 15,000 volts. It was always adjusted to the value at which the particular tube appeared to run most steadily. Slight variations occur during a run in helium due to the hardening of the tube due to sputtering.

The exposure times vary from one to four hours depending on the light intensity obtained and the line to be investigated.

The slit width used is 0.05 mm.

Due to the wide range in the intensities to be compared, great care is necessary to avoid over-exposure of the stronger components, or under-exposure of weaker ones. This makes plates satisfactory for measurement rather difficult to obtain. Due to the variation of the Stark intensities in helium with the field strength, a further complication is introduced inasmuch as it is exceedingly difficult to obtain a number of plates at exactly the same field strength. Hence it is not possible in general to average the experimental values over a number of plates.

At the close of a Stark exposure, the condensing lens and Wollaston prism are removed and the tungsten lamp, cylindrical lens and step-reducers set up in position. A comparison spectrum is then placed upon the same plate, the exposure time for the latter usually being in the neighbourhood of ten minutes.

The life of a discharge tube is usually about twenty hours. The failure is due to the sputtering of the cathode surface, the canal ray beam becoming very unsteady. After the operation has become unsatisfactory, the cathode section must be taken apart, cleaned, polished, and re-assembled. In time an accumulation of sputtered metal on the lavite cylinder necessitates its removal, cleaning in hot sulphuric acid, and re-baking in an electric furnace. Its original condition can thus be restored.

Field Strengths

The field strengths are determined from the splitting observed in H_{β} which has appeared on all the plates obtained up to the present. If necessary, however, the fields may be obtained from the helium groups after the theory of Foster(5).

Description of Plates

Plate 1.

This a typical photograph of H_{β} taken in pure hydrogen. The upper are the s components, the lower the p. The accompanying photometer traces show a magnification of 9 from the original plate.

The components are numbered in the usual Epstein notation.

The conditions in the discharge, etc., are given in the Table at the end of this section.

Plate 2.

A photograph of H_β taken from a helium mixture. Only a trace of hydrogen was present.

The arrangement is the same as in Plate 7.

Plate 3.

(a) These are reproductions of photometer traces taken from a paper by Mark and Wierl (Zeit.f.Phys.53,526, Figs. 9 and 11, 1929). They show the s and p components of H_β taken in a field of 200KV/cm. perpendicualar to the direction of motion of the canal rays. In this case hydrogen canal rays were used and these ran into hydrogen at a pressure of 0.02 mm. between the field plates. The canal ray current and voltage were approximately 60 m.a. and 25,000 volts. The numerical quantities quoted above must be considered as only approximate, the actual values for this photograph not being given.

(b) The heights of the vertical lines represent the relative intensities of H_β as calculated by Schrödinger(4).

Plate 4.

This plate shows the parhelium group 2P-4Q (λ 4922). As before the upper are the s components, the lower the p.

The various components are labelled under the corresponding points in the photometer trace, together with the m values of the initial states. Two m values bracketed together indicate the presence of two unresolved components. This notation was introduced by Foster[5].

Plate 5.

This shows the parhelium 2p-5q (λ 4026). The foreign line may be identified with the strong mercury line 4046.

This is a reproduction of a plate taken during the initial stages of the experiments with high pressures (Jan. 27, 1933). At this time the spectrograph was arranged to show a number of lines in fair focus. The more recent plates (Plates 1, 2, 4) were taken with the spectrograph focussed critically in the region of H_β and He 4922. Accordingly the later plates, which are of considerably higher quality, only show He 4026 badly out of focus.

Plate 6.

This is a contact print of a typical plate showing the intensity marks. The H_β reproduced in Plate 2 was enlarged from this plate.

Experimental Conditions

Plate	1	2 & 6	4	5
Pressure (mm.)	0.50	0.47	0.50	0.45
Canal Ray current (M.A)	5	4	7	2
voltage (KV)	12	10.4	13	9.6
Field strength (KV/cm.)	99	92	120	132
Exposure time (hours)	2	3	2	2

DISCUSSION

A discussion of spectral intensities based only on the appearance of the plate and the photometer trace is of necessity of a qualitative nature. Provided, however, that the plate is not seriously over or under-exposed, a considerable amount of information is obtainable.

An inspection of the H_β plates (Plates 1 and 2) shows an apparent asymmetry between the long and short wave components. This, however, is almost certainly illusory, since a photometer trace across the intensity marks at the wavelengths concerned shows that the plate sensitivity has changed considerably in the interval. This is a factor requiring particular care in considering Stark effect intensities, especially in the case of H_α and H_β and neighbouring lines. The apparent difference in the ratios $p^{+8}/_{+10}$ and $p^{-8}/_{-10}$ and the corresponding $s^{+4}/_{+6}$ and $s^{-4}/_{-6}$ is probably due to the same cause (a similar phenomenon was observed by Mark and Wierl and traced to this effect). When the necessary corrections are applied, it is expected that these anomalies will disappear.

A comparison of the plates obtained from pure hydrogen and from the helium-hydrogen mixture shows that no effect of the type noted for McRae[11] is to be found in canal ray tubes under the conditions of the experiment. Within the limits imposed by the variation in plate sensitivity, no asymmetry is to be noted in either case. This would be in accordance with McRae's observation that the asymmetry tended to decrease with the pressure. A possible slight difference may exist in the relative intensities of the components, but, if so, it would not appear to be large. Examination of a number of plates tends to confirm the view that the relative intensities in the two cases are the same.

The most interesting point in connection with these hydrogen plates lies in the comparison of Plates 1 and 3 with the curves obtained by Mark and Wierl and shown in Plate 3(a). For the p components there appears to be no change of any significance. For these components Mark and Wierl report detailed agreement with Schrödinger. In the case of the s components, however, these workers found the value $\frac{4}{6} = 1.27$ as compared with the theoretical 1.55. A comparison of the curve for the s components of Plates 1 and 3 as against that of Plate 3 indicates that this ratio is substantially increased in the present investigation. This is particularly noticeable in the case of Plate 3.

While the hydrogen plates can be discussed in a reasonably complete qualitative way, this is not true in so large a measure for the helium groups shown in Plates 4 and 5. In helium the intensities vary quite rapidly with the field strength, and the intensities have not been calculated for fields exceeding 100 KV/cm. Since the numerical calculations are quite laborious, and only hold for a single field strength, it has not been thought desirable to carry them through until the actual experimental values had been determined. The observations do not show, however, any marked deviations from those expected from an extrapolation of the theoretical curves beyond the 100 KV/cm. limit.

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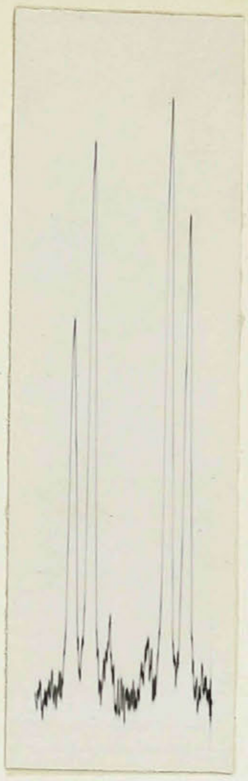
Plate 1.

H_β Photographed from Pure Hydrogen.

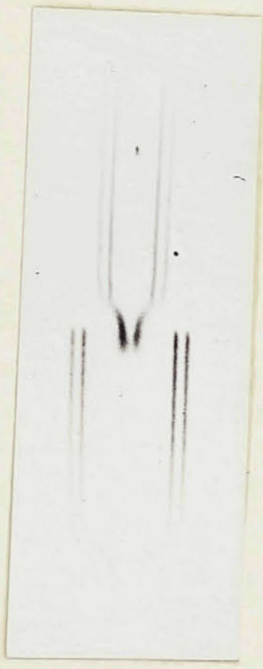
Field Strength 99 KV/cm.

PLATE

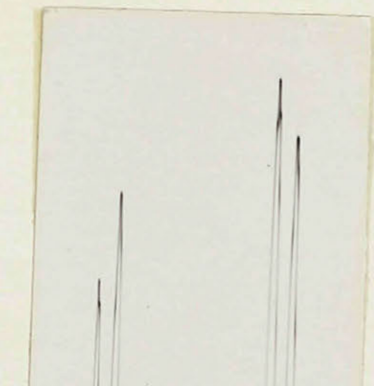


$\perp$

642 246



$\longleftarrow \lambda$



$\parallel$

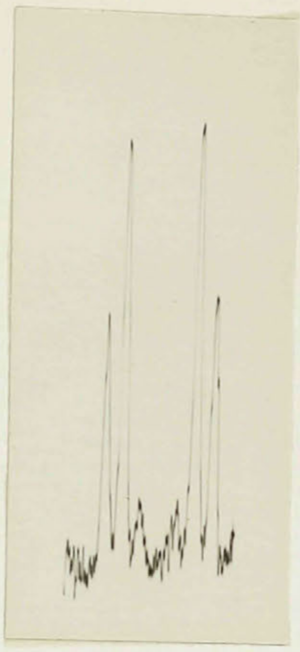
1086 6810

Plate 2.

H_β Photographed from a Helium-Hydrogen Mixture.

Field Strength 92 KV/cm.

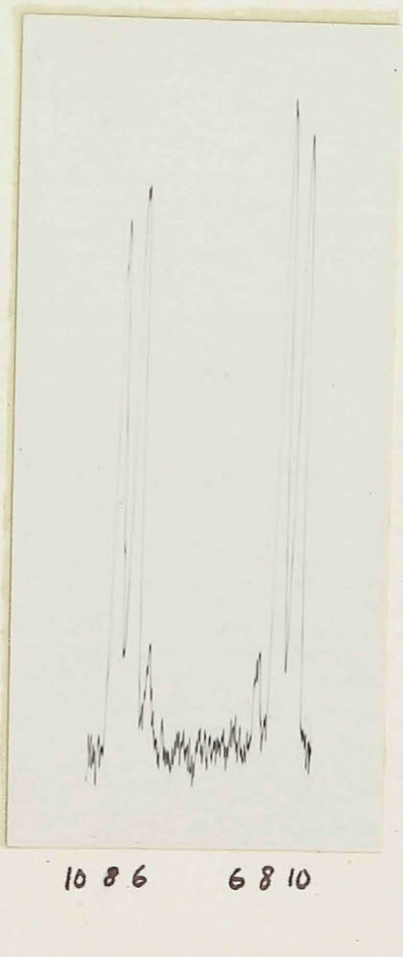
PLATE 2



$\perp$

6 4 2 2 4 6

$\longleftarrow \lambda$



$\parallel$

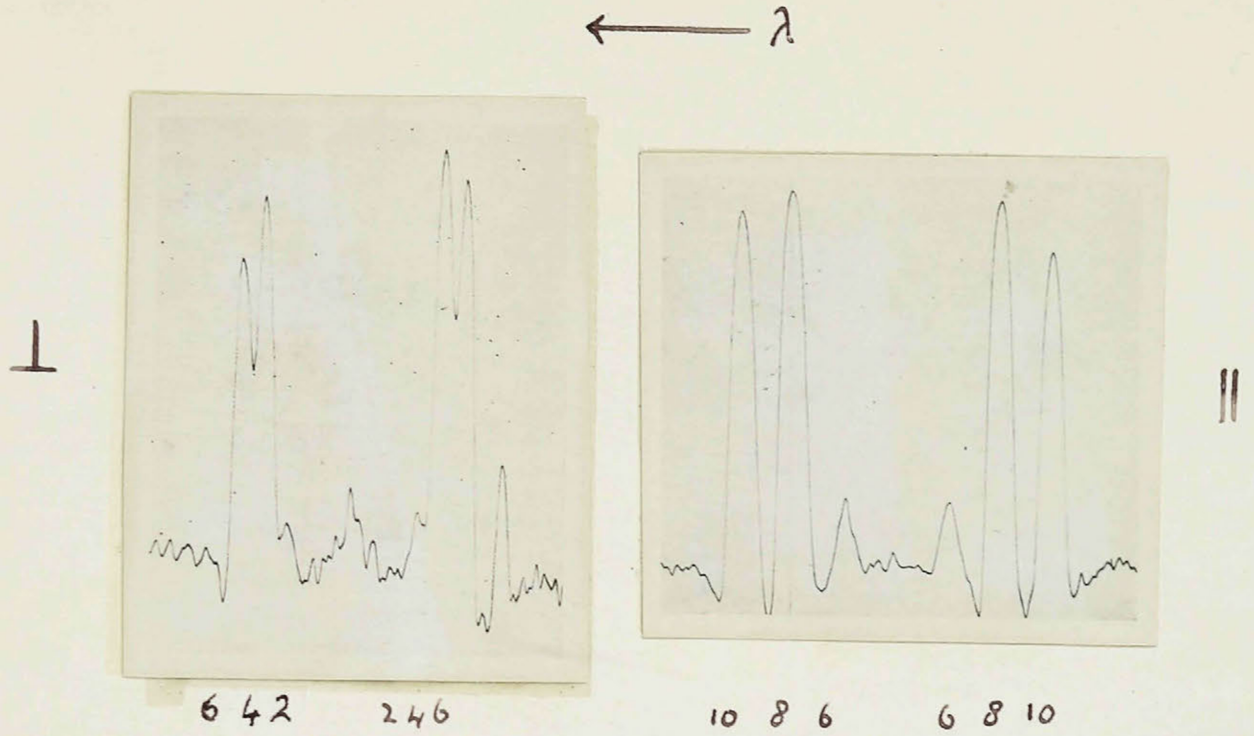
10 8 6   6 8 10

Plate 3.

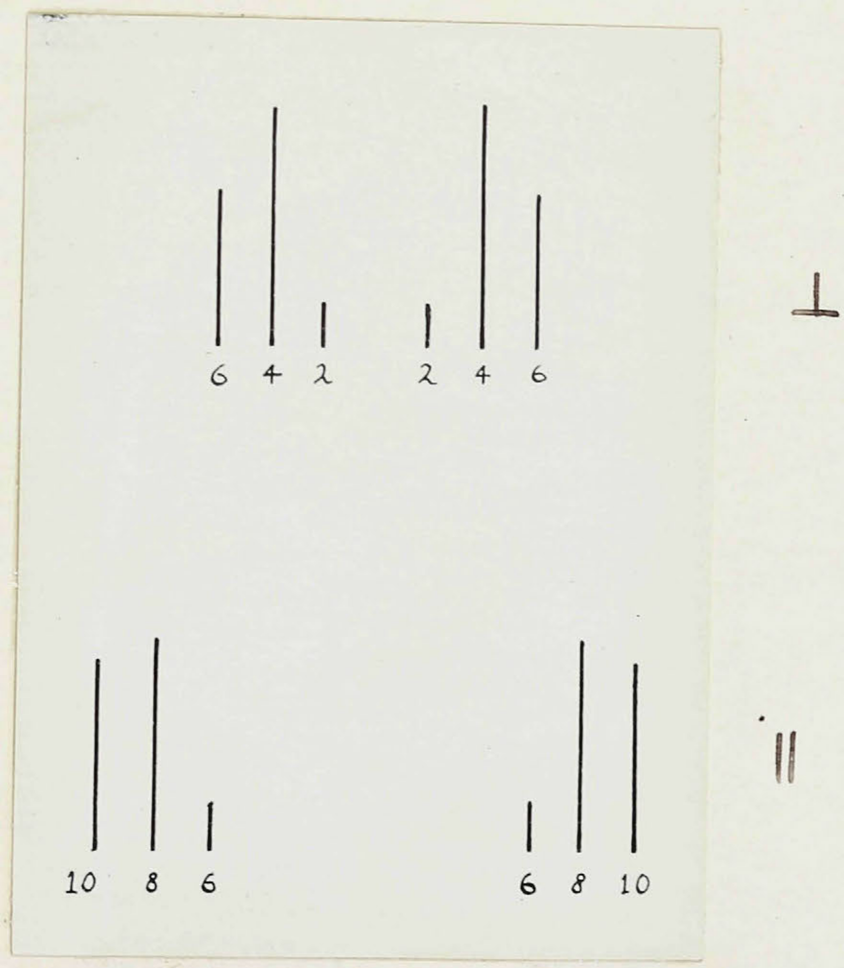
(a) Photometer Traces of H_β Published by Mark and Wierl.

(Zeit. f. Phys. 53, 526, Figs. 9 &11, 1929)

(b) Theoretical Intensities for H_β after Schrodinger.



(a)



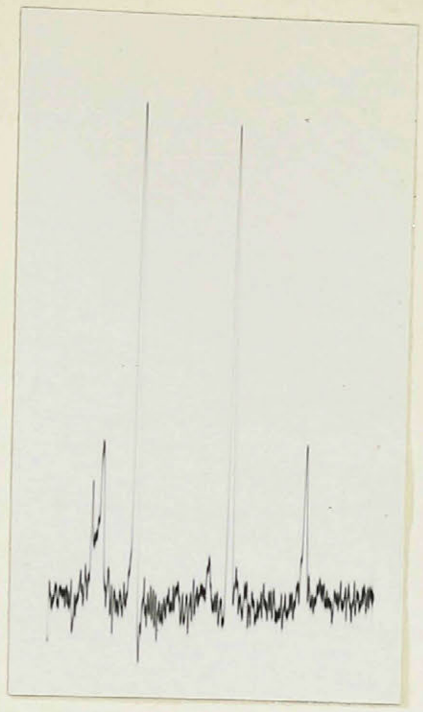
(b)

Plate 4.

2P - 4Q Group of Parhelium.

Field Strength 120 KV/cm.

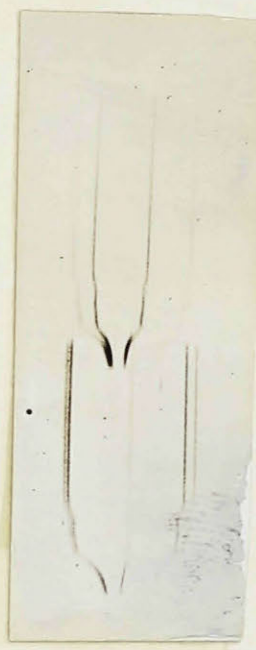
PLATE 4



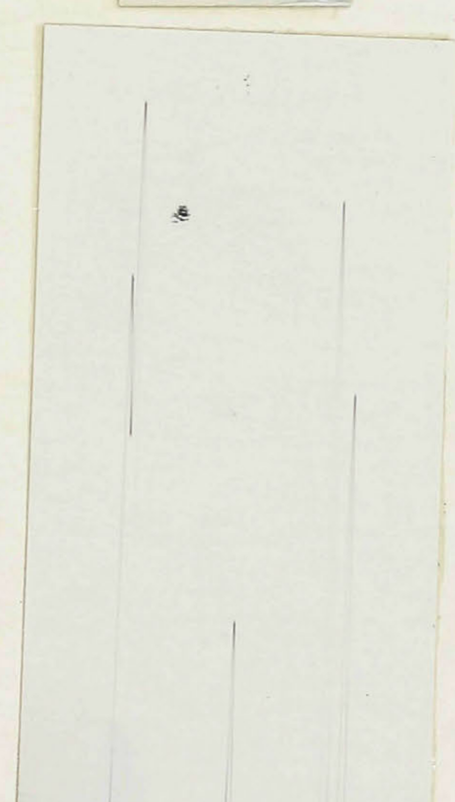
$\perp$

01 2 (1,0) 2 1

D F P



$\longleftarrow \lambda$



$\parallel$

01 (0,1) 10

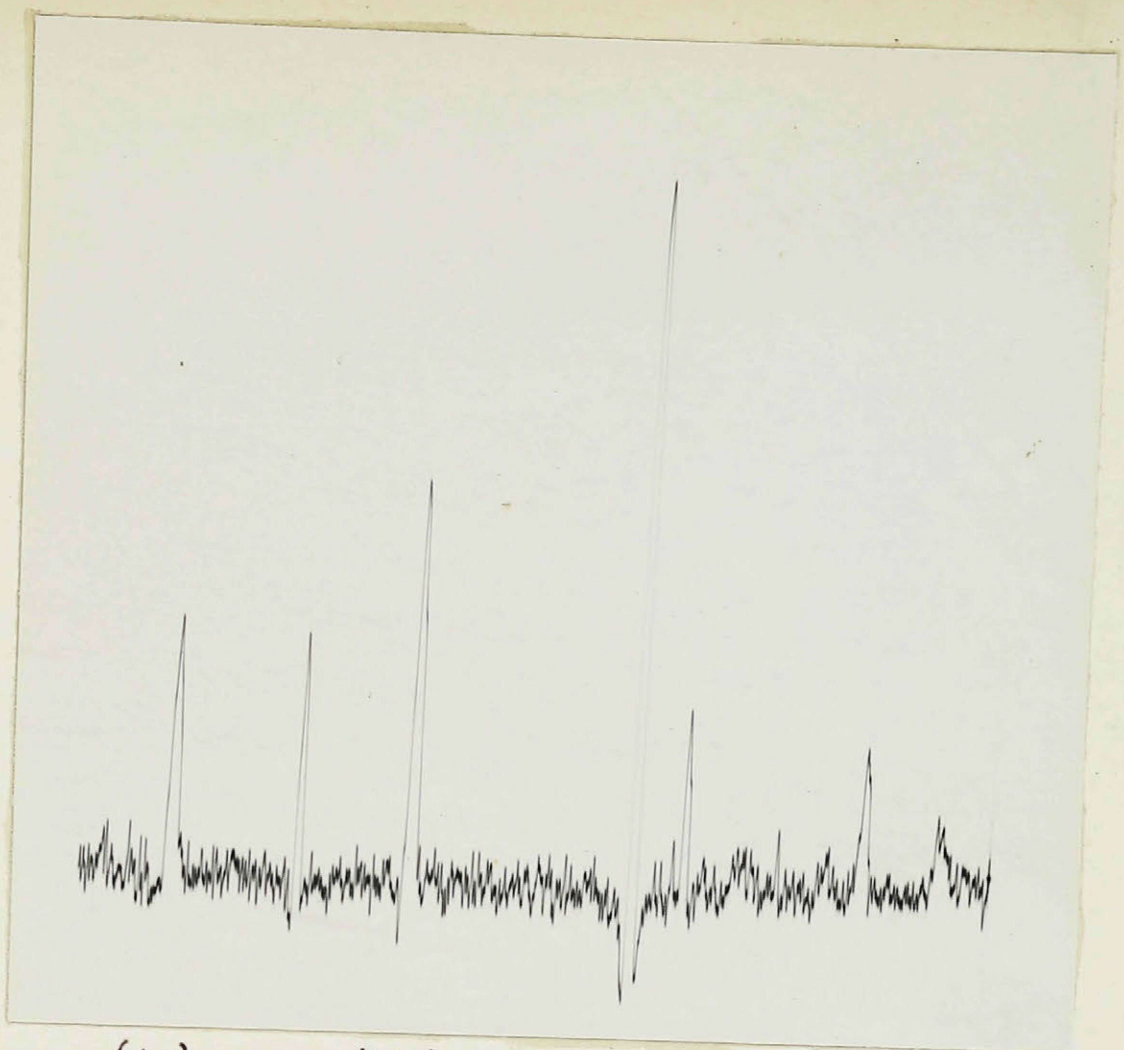
D F P

Plate 5.

2p - 5q Group of Orthohelium.

Field Strength 132 KV/cm.

PLAT

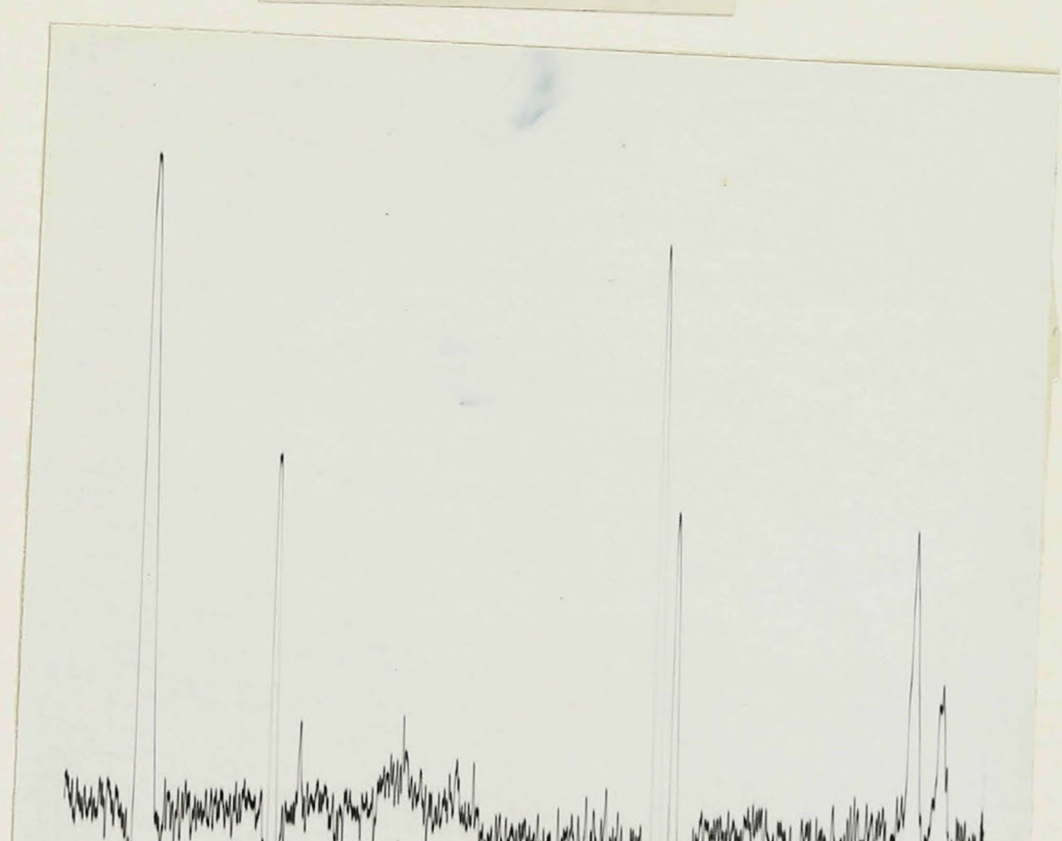


⊥

(1,0) (2,1,0) 2 1 0 2 (1,0)

p d f g

← λ



∥

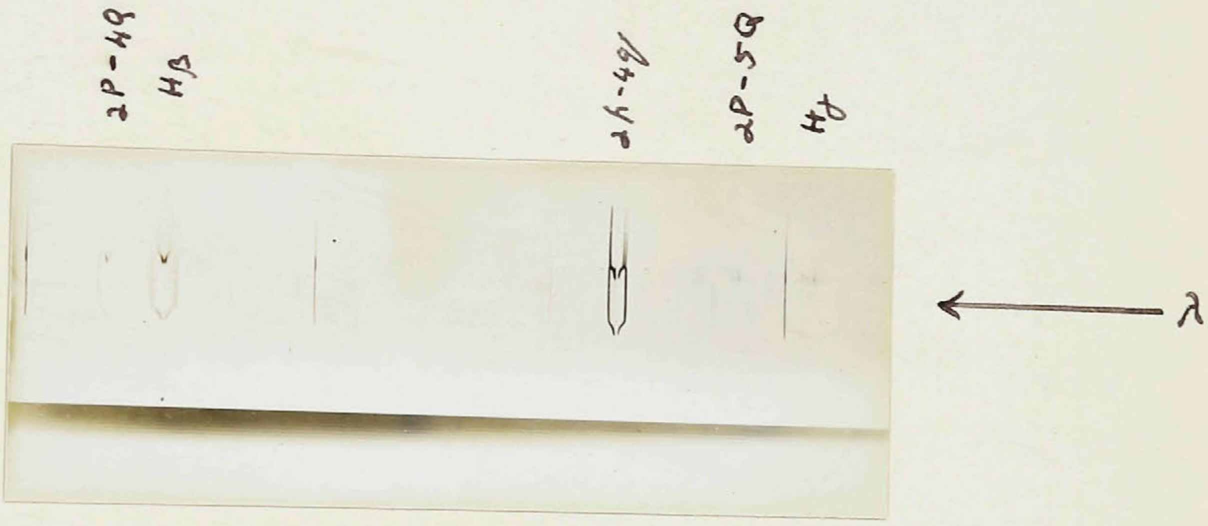
(1,0) (1,0) 1 0 1 0

p d f g

Plate 6.

Contact Print of a Typical Plate showing Intensity Marks.

Field Strength 92 KV/cm.


2P-4Q
Hβ
2P-4P
2P-5Q
Hγ
λ