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The effect of high frequency excitation upon the intensities of spectral lines

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UMI®
THE EFFECT OF HIGH FREQUENCY EXCITATION UPON THE
INTENSITIES OF SPECTRAL LINES

by
Charles H. Bachman

A Thesis Submitted to the Graduate Faculty
for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject Physics

Approved:

Signature was redacted for privacy.

In charge of Major Work

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Head of Major Department

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Dean of Graduate College

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1935
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# TABLE OF CONTENTS

## I. INTRODUCTION

| A. Electrical Discharge in Gases | 4 |
| B. Direct Current Excitation | 4 |
| C. High Frequency Excitation | 5 |
|   1. Ring discharge | 5 |
|   2. Glow discharge | 6 |
|   3. Purity of gas | 7 |
| D. Statement of Problem | 8 |

## II. THEORETICAL CONSIDERATIONS

| A. Theory of Electrostatic Discharge | 10 |
| B. Oscillator Theory | 16 |
|   1. Fields of different oscillators | 16 |
|   2. Measurement of potential | 17 |
| C. Photometric Theory | 18 |
|   1. Review of intensity measuring methods | 18 |
|   2. Theory of logarithmic sector disc | 20 |

## III. EXPERIMENTAL

<p>| A. Apparatus | 23 |
|   1. Gas system | 23 |
|   2. Photometric apparatus | 30 |
| B. Method of Procedure | 31 |
| C. Results | 32 |</p>
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.</td>
<td>DISCUSSION OF RESULTS</td>
<td>40</td>
</tr>
<tr>
<td>V.</td>
<td>CONCLUSIONS</td>
<td>47</td>
</tr>
<tr>
<td>VI.</td>
<td>SUMMARY</td>
<td>49</td>
</tr>
<tr>
<td>VII.</td>
<td>ACKNOWLEDGEMENTS</td>
<td>51</td>
</tr>
<tr>
<td>VIII.</td>
<td>BIBLIOGRAPHY</td>
<td>52</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

A. Electrical Discharge in Gases

The conduction of electricity through gases has been the object of a great many investigations during the past seventy-five years. The great majority of the investigations were, however, of a more or less descriptive nature until Townsend (68) proposed a theory of ionization by collision. His theory states, in brief, that a self-maintained glow discharge will occur when each electron traveling from cathode to anode creates, by collision with molecules, enough positive ions so that they in turn will give rise to another free electron by further collisions on their way to the cathode.

This simple theory has been modified and extended to include various imposed conditions such as non-uniform fields and higher pressures. J. J. Thomson has introduced the effect of positive ion bombardment of the cathode with its subsequent release of electrons under certain conditions. The simple theory as stated above, however, contains the fundamentals essential for a self-maintained discharge.

B. Direct Current Excitation

A typical direct current discharge tube is of glass. It contains some sort of gas usually under reduced pressure. Elec-
trodes are sealed into each end and to these are applied the exciting potential.

There are several features to the normal glow discharge. Most of the light originates in the positive column which extends through most of the tube, from the anode to a relatively dark space called the Faraday dark space. Next come the negative glow where a high ion density exists, the Crookes dark space and the first cathode layer which is just next to the cathode. The greater part of the voltage drop across the tube occurs in the cathode dark space so that this is a region of high field intensity while the long positive column is a region of comparatively low field intensity.

The voltage necessary for a self-maintained discharge in a particular gas depends upon the tube dimensions and the pressure, following a relation known as Townsend's law of similitude. In its simple form for plane parallel electrodes this relation reduces to Paschen's law: the sparking potential is directly proportional to the product of the gas pressure and electrode separation.

C. High Frequency Excitation

1. Ring discharge.

Hittorf(29) in 1884 was the first to observe that alternating voltages of practically any frequency could be
used to excite discharge phenomena. The earliest sources of potential difference used spark discharges from charged Leyden jar condensers. Damped oscillations of high frequency and high voltage but short duration were produced by this method. It was found that with this type of excitation the electrodes did not have to be inside the tube; in fact a discharge could be obtained by merely placing the tube in a region of sufficiently high field strength.

Because of the difficulty in measuring and of controlling these damped oscillations it is not surprising that conflicting opinions arose as to the mechanism of the high frequency discharge.

In the earlier studies of the electrodeless discharge using undamped oscillations and with the tube usually inside the oscillator coil, J. J. Thomson(61) and others(11), (39), (40), (54), (75), (76), (77) obtained predominantly what has been termed the "ring discharge" in which the glow forms rings centered around the axis of the tube. J. J. Thomson(61) and Davis(11) have developed theories of this type of discharge in which the electromagnetic field about the coil is the major contributing factor to the excitation.

2. Glow discharge.

By applying the potential developed across the oscillating
circuit to the discharge tube through the use of external sleeve electrodes, Townsend and Donaldson(66) among others, concluded that the electrostatic field of the oscillator was responsible for the discharge.

The controversy as to the origin of the excitation continued even after the advent of the electron tube which made possible undamped continuous oscillations and thereby allowed a more completely controlled study of the question. MacKinnon (43) and Knipp(38) among others, however, have pointed out that both views are right, the electromagnetic field producing the ring discharge under certain conditions and the electrostatic field producing the more common glow discharge under a wider range of conditions.


A high percentage of the work done on discharges in gases of both the a.c. and d.c. excited types is of questionable value. Indeed much of it is entirely worthless due to the effects of small amounts of impurities. Even minute traces of impurities in a gas, as has been pointed out by J. Thomson(64) and others(66), (32), (67) have a marked influence on the striking and maintenance voltages. Headrick and Duffendack(23) have shown the effects of impurities on spectroscopic work as well as on the voltage characteristics of the discharge. Considering the comparatively small spectral range of the visible region it is
doubtful if a gas can be considered pure simply because no impurities are noticed when the discharge is viewed through a direct vision spectroscope as has been assumed by some.

J. Thomson(64) finds that with any mercury attached to the system it is impossible to keep mercury trapped out for any length of time. The author has had the same experience and also found that glass which had previously been exposed to supposedly trapped mercury gave rise to a very strong 2536Å mercury line when placed in a mercury free system and had to be replaced with new glass. The use of McLeod gauges and mercury pumps then is to be questioned except for studies of mercury.

To insure the utmost of gas purity it is necessary that the vacuum system be free from possible sources of contamination. High frequency excitation with external electrodes eliminates possible contamination from cathode effects and the presence of metal parts in the system.

D. Statement of Problem

Much work has been done on discharge characteristics of gases, such as striking and maintenance potentials, and gas conductivity for different frequencies and pressures using high frequency excitation, but the study of intensities of spectral lines, excited by this method, is practically un-
untouched. The purpose of this investigation is to determine the effect of varying the frequency of excitation on relative intensities of some of the lines of the Balmer series of hydrogen. To the author's knowledge the only contribution to this problem has been published by Stuhlman and McCay (53) whose results and work will be discussed later in this paper.
II. THEORETICAL CONSIDERATIONS

A. Theory of Electrostatic Discharge

It has been stated that the high frequency discharge may be caused by either the electromagnetic field, the electrostatic field, or both. Probably the theory for the case of the electromagnetic discharge has been best set forth by J. J. Thomson(61) while the most acceptable theory for the electrostatic or glow discharge, has been presented by J. Thomson(64), (65). In the present investigation the alternating potential was applied to the tube by means of external "sleeve" electrodes which insured a discharge of the electrostatic type. The following theory of the high frequency glow discharge and conditions for ionization follow the presentation of J. Thomson(65) very closely and the reader is referred to the original articles for a more complete discussion.

Consider an electron of mass m, and charge e, free to move in an alternating electric field E, of frequency f, applied in direction x.

The equation of motion is

\[ m \frac{d^2x}{dt^2} = Ee \cos 2\pi ft; \]  

and if \( x = 0 = \frac{dx}{dt} \) at \( t = 0 \)
\[
\frac{dx}{dt} = \frac{Ee}{2\pi f_m} \sin 2\pi ft, \quad (2)
\]
and \(x = (1 - \cos \omega t) \frac{Ee}{(2\pi f_m)^2} \quad (3)

It will be noticed that relativity corrections have been neglected and the approximation \(dx = 0\) is justified since the velocity of agitation of electrons at room temperatures is of the order \(10^5\) cm./sec. while ionizing velocities are of the order \(10^6\) cm./sec.

For the electron to have sufficient energy to ionize a molecule colliding with it at time \(t\), the first condition for ionization must be obtained:

\[
\frac{1}{2}m \left( \frac{Ee}{2\pi f_m} \sin 2\pi ft \right)^2 > Ve, \quad (4)
\]

where \(V\) is related to the ionizing potential of the gas. Now for a given \(t\), \(x\) is given by (3). If the electron is slowing down it must collide before \(x\) becomes less than \(L\), a distance proportional to the mean free path of the electron, and if it is speeding up it must not collide before \(x\) becomes greater than \(L\). From (2) we see that \(\frac{dx}{dt}\) varies sinusoidally with \(t\) so that for a given small increment of time the distance traveled would depend upon the value of \(t\), or the position on the sine curve.

For the case of the electrons speeding up we can write from (3)
\[
\frac{Ee}{(2\pi f)^2 m} \left[ 2n + 1 + (-1)^{n+1} \cos k\pi \right] < L \quad \text{if } k < \frac{1}{2} \quad (5)
\]

and for the case of the electrons slowing down
\[
\frac{Ee}{(2\pi f)^2 m} \left[ 2n + 1 + (-1)^{n+1} \cos k\pi \right] > L \quad \text{if } k > \frac{1}{2} \quad (6)
\]

where \(2\pi ft = (n + k)\pi\), \(n\) is an integer, \(k\) is a fraction, and \(2n\) is to take into account the number of complete vibrations the electron might pass through, that is, the total distance.

When \(k = \frac{1}{2}\), (5) and (6) reduce to
\[
\frac{Ee}{(2\pi f)^2 m} (2n + 1) = L \quad (7)
\]

If the electron is not to be absorbed by the glass at very low pressures a fourth condition must obtain. That is:
\[
x = \frac{Ee}{(2\pi f)^2 m} < d \quad (8)
\]

where \(d = \) tube length.

The four conditions (4), (5), (6), and (8) vary in importance with varying pressures. Unless the pressure is very low or the frequency is very high \((>10^7 \text{ per sec.})\) it can be shown that the fourth condition, (8), is of no importance and the second and third conditions, (5) and (6), may be simplified to
\[
\frac{Ee}{(2\pi f)^2 m} (1 - \cos 2\pi ft) < L \quad (9)
\]

Elimination of \((2\pi ft)\) from (4) and (9) yields
\[
E > \frac{V}{L} + \frac{L(2\pi f)^2}{2 e/m} \quad (10)
\]

and writing \(L = \frac{k}{p}\) where \(p = \) gas pressure
This represents the mode of variation of the ionizing field, \( E \), with pressure for a given frequency and gas.

Writing (10) as

\[
E = A + B f^2
\]  

(13)

we obtain the mode of variation of the ionizing field, \( E \), with frequency for a given gas and pressure.

The four conditions given denote the necessary conditions for ionization and if it were not for recombination and diffusion to the walls they would also be the conditions for a discharge. Consider the rate of destruction of the ions due to diffusion to be given by \( \beta n \) and that due to recombination given by \( \gamma n \) while formation is at the rate \( \alpha n \) where \( n \) is the ion concentration. Then

\[
\frac{dn}{dt} = (\alpha - \beta) n - \gamma n^2
\]  

(14)

and

\[
n = \frac{\alpha - \beta}{\gamma + (\alpha - \beta - \gamma)} e^{-(\alpha - \beta)t}
\]  

(15)

When \( t = \infty \)

\[
n = \frac{\alpha - \beta}{\gamma}
\]  

(16)

For self-maintained discharge \( \alpha - \beta \) must be great compared to \( \gamma \). Since neither \( \beta \) nor \( \gamma \) depend upon gas
pressure (12) will represent the mode of variation of the field with varying pressure necessary to maintain discharge, but the actual value of \( E \) will not be given by the equation unless \( \beta \) and \( \gamma \) are small. Townsend (71) has found that there is no appreciable recombination in a high frequency discharge.

Data obtained by Kirchner (35) for air and oxygen are in good agreement with the general formula (12).

In a discharge using sleeve electrodes the field will not be uniform (65) but to a first approximation we may take \( E = P/d \) where \( P \) is the peak potential difference between the electrodes and \( d \) their distance apart. Writing (11) as

\[
P = \frac{V_p d}{K} + \frac{2\pi f^2 K d}{p e/m}
\]  
(17)

we find for minimum \( P \)

\[
P_m = \frac{dP}{dp} = \frac{V_d}{K} - \frac{2\pi f^2 K d}{p^2 e/m} = 0
\]  
(18)

from which

\[
\frac{V_d p}{K} = \frac{2\pi f^2 K d}{p^2 e/m}
\]  
(19)

so

\[
P_m = \frac{V_d p}{K} + \frac{V_d p}{K} = 2V_d p
\]  
(20)

Also from (19)

\[
P_m = \frac{2\pi f^2 K^2}{V e/m}
\]  
(21)

Equation (17) indicates that the potential should increase with the frequency. However, at high pressures the additive term is rather small unless the frequency is very high. Since
the amplitude of the free oscillations of the electrons varies inversely as the square of the frequency it might be expected that the diffusion losses become smaller for increasing frequencies. A complete expression for the maintenance potential might be of the form

\[ P = \phi(f) \left[ \frac{V}{k} + \frac{2 \pi^2 K d}{p \ v^2} \right] \]  

(22)

where \( \phi(f) \) is a function such that it decreases as \( f \) increases.

To summarize it can be seen that whereas the life of a gas ion is relatively short for d.c. discharges due to the sweeping out effect of the field it is possible, in a high frequency discharge, to arrange the dimensions, pressure, frequency, and field so that the ion life will be comparatively long. The ions will oscillate back and forth about an approximately fixed center, recombination and diffusion will be at a minimum and the conditions for ionization will be approximately the conditions for maintenance of the discharge. That is, equation (11) becomes the necessary and sufficient condition for the initiation and maintenance of a glow discharge. This presupposes that the condition, equation (8), be satisfied and it can be seen therefore that for this theory of a "typical" discharge to apply, the distance between electrodes must be considerably greater than the amplitude of oscillation of a free electron in the field.

It has been shown (64), (56), (50), that if the gas pressure is above the critical pressure Paschen's law may
be extended to the case of the high frequency discharge. J. Thomson(64), in some work attempting to verify inequality (11), finds that the frequencies of the order of 10 which he used were not high enough. He concludes that obtaining sufficiently high frequencies is a rather difficult problem particularly if external electrodes are to be excluded due to charges taken up by the glass.

**B. Oscillator Theory**

1. Fields of different oscillators.

The choice of oscillator to be used for producing the high frequency alternating potential used in electrodeless discharges reduces actually to a single tube oscillator or one of the push-pull type. Both kinds have been used in the study of high frequency discharge. Obviously what is desired is a uniformly directed magnetic field and if the discharge tube is to be inside the coil, the coil should be designed either for maximum electric or magnetic field according to its desired use.

The general opinion has been that a magnetic field under radio-frequency excitation is analogous to the field obtained in the same coil with direct current. Stuhlman and Githens (59) have found that whereas this is true for a well designed, dynamically balanced, tuned plate, tuned grid, push-pull oscillator, the field around the coil of a tuned plate, tuned grid,
single tube oscillator is far from symmetrical. Although the absolute necessity of a push-pull oscillator for the case of the discharge situated away from the coil and using sleeve electrodes is doubtful, its use seems desirable if merely to keep the discharge tube under more symmetrical conditions as well as to insure greater stability in the oscillator itself.

When the potential is applied by means of external sleeve electrodes it was assumed in equation (17) that the field is approximated by taking $E = \frac{P}{\alpha}$. J. Thomson(65) and Banerji and Genguli(2), (3) have shown the potential distribution in electrodeless discharges and it is seen that although the assumption is justified for a first approximation there is considerable variation in the field with different forms of the discharge.


One of the most difficult things to measure in the high frequency discharge is the potential applied to the electrodes. This is especially so at very high frequencies. The method most generally used is that in which the current in the tank circuit of the oscillator, the frequency of oscillation, and the capacity in the tank circuit are determined. Then the relation $V = \frac{I}{2\pi f C}$ gives the R.M.S. value of the potential across the condenser. Several variations of this method have been used by different investigators. It can be seen that the voltage determinations are only as accurate as the values of current,
frequency, and capacity used in their calculation. Peak values will of course depend upon the wave form. Most of the investigations so far have made use of frequencies of the order of $10^7$ per sec. or below. For higher frequencies considerable difficulty is encountered in making the desired measurements accurately, particularly in the case of the current, because skin effect makes ordinary meter calibrations useless.

C. Photometric Theory

1. Review of intensity measuring methods.

The methods most commonly used for measuring spectral light intensities have been discussed by Harrison(21). He has divided them into single exposure and multiple exposure methods and further classified these as to the source, requirements for use, and convenience and accuracy. As pointed out by Harrison the ideal method is one of the single exposure auto-calibration type where the illumination along each line is controlled by having sections of the line reduced in intensity by known amounts. This eliminates considerable time of operation, insures constant exposure time, and is at least as accurate as any other method when correctly used. Instruments for use in this method are the step-sector disc, logarithmic sector, step-weaker, wedge weaker, and some eight or ten others of similar nature.

The logarithmic sector used in this investigation has become more popular recently since faults previously suspected
of it have been studied by Webb(78), whose work indicates that the device is very accurate when correctly used. The suspected sources of error in the use of the sector have been the intermittency effect and the failure of the reciprocity law. The first is the difference in density due to a continuous exposure of energy \( I \) and that due to a second exposure of equal energy given intermittently. The reciprocity law states that for various exposure times and intensity values, equal densities will be obtained for all exposures having energy values \( I = \text{constant} \).

Webb(78) has shown that the intermittency effect is really only a manifestation of the reciprocity law failure, and that if the disc is operated so that the frequency of flash is above a certain critical value an intermittent exposure of average intensity \( I \), will yield the same photographic effect as a steady exposure of absolute intensity \( I \). That is, the intermittency effect becomes the reciprocity law failure at frequencies above the critical value.

The critical value of the frequency is that for which on the average there is only one quantum per flash striking the effective receptive area of the emulsion grain. It varies with the emulsion and varies directly with the average intensity of the intermittent exposure. From this it appears that the greater the sector wheel speed the more accurate the results. Speeds of several hundred r.p.m. or more are essential in
nearly all work, 1800 r.p.m. being suggested by Harrison(21).

Baly, Mortop, and Riding(1) and others have proved conclusively that the reciprocity law is valid for the sector photometer, that is, the Schwarzschild constant is unity for normal exposures on the straight line portion of the emulsion characteristic curve.

The procedure used by Twyman and Simeon(74) in obtaining relative intensities of a pair of lines necessitates determining the difference between the ends of the lines. These points are of course definitely under exposed and it has been shown by Twyman and Harvey(73) that under these conditions for some five different plates the Schwarzschild constant is of the order of 0.95 rather than unity. They also find that over a range of wavelengths from 2572Å to 3784Å the value of this constant does not vary appreciably.

2. Theory of logarithmic sector disc.

The sector disc used in this investigation, figures 1 and 2, is built to the same equation as that of Twyman and Simeon(74) but has two curves symmetrically placed whereas theirs has the curve on only half the disc. This arrangement makes possible shorter exposures and better balance of the wheel.

Let \( \phi \) be the circumferential aperture expressed as a fraction of a complete circle:

\[
\phi = \frac{x}{180} = \frac{2x}{360}
\]
The sector curve is obtained from the relation
\[
\log \theta_2 - \log \theta_1 = 2(\lambda_2 - \lambda_1) \quad (23)
\]
where \( \lambda \) is the distance in mm. measured inward radially from the outermost part of the curve. At the outer edge \( \theta = 1 \) and \( \lambda = 0 \) so that the curve of the sector becomes
\[
- \log \theta = 2\lambda \quad (24)
\]
Returning to (23) and assuming that the ratio of two exposure times \( t_1 \) and \( t_2 \) are proportional to the corresponding angular sector openings \( \theta_1 \) and \( \theta_2 \), this assumption being justified (74), we have
\[
\log t_1 - \log t_2 = 2(\lambda_2 - \lambda_1) \quad (25)
\]
From Schwarzschild's law,
\[
\left( \frac{t_1}{t_2} \right)^p = \frac{I_2}{I_1} \quad (26)
\]
we have
\[
p(\log t_1 - \log t_2) = \log I_2 - \log I_1 \quad , \quad (27)
\]
and combining (25) and (27)
\[
\log I_2 - \log I_1 = 2p(\lambda_2 - \lambda_1) \quad , \quad (28)
\]
From this it is seen that the intensity ratio of two lines depends upon the difference in their lengths and the value of \( p \), Schwarzschild's constant. However, in a study of the variation in intensity ratios it can be seen that the value of \( p \) is immaterial so long as its constancy is insured by using plates of the same emulsion batch and identical conditions of development.
III. EXPERIMENTAL

A. Apparatus

1. Gas system.

The general arrangement of the gas system is shown in figure 3 and the photographs, figures 2, 4, and 5. Hydrogen generated electrolytically was dried by passage through a $P_2O_5$ trap and applied to one side of the hollow palladium tube. Diffusion of the hydrogen through the palladium was controlled by heating the tube by passing an electric current through it, the gas then being led into one end of the discharge tube. The other end of the discharge tube led in turn to a ball valve, $CO_2$ trap, stopcock, and 2 oil diffusion pumps backed with a Genco Hyvac pump.

The hydrogen generator consisted of the typical electrolytic cell, using platinum electrodes and a dilute solution of phosorphoric acid, the hydrogen being retained and led into the $P_2O_5$ drying tube.

The palladium tube was 20 cm. long, 0.008" in wall thickness, closed at one end and had a platinum collar attached to the open end for sealing through a graded seal to Pyrex.

Except for the window the system was entirely of Pyrex with all sealed glass joints. The only grease present was in the stopcock between the $CO_2$ trap and the pumps where the
Diagram of Gas System

Figure 3
Fig. 4 Photograph of Apparatus

Fig. 5 Photograph of Apparatus
natural gas flow together with the trap tended to prevent contamination due to grease vapor.

The discharge tube was 4.8 cm. in diameter and 75 cm. long, and drawn to 2.5 cm. at one end where a Corex window \( \frac{1}{2} \) mm. thick was sealed on. A side tube of 10 mm. diameter led from the center of the discharge tube to the Pirani and ionization gauges. The other end led to a ball valve which was merely a 7\( ^{\text{th}} \) ball bearing ground into a glass valve seat and \( \frac{1}{16} \) which, operated from the outside by a magnet, made a convenient constriction. The ball and seat were fine ground and worked some with jeweler's rouge and proved to be very efficient and useful when used in conjunction with the palladium tube for maintaining pressures. It also proved very worthwhile by preventing back flow into the discharge tube when the trap was heated from time to time to remove condensed impurities. The \( \text{CO}_2 \) trap was kept immersed in a vacuum bottle of solid \( \text{CO}_2 \) and acetone. The stopcocks were of large bore and lubricated with Apiezon grease L having a vapor pressure of about \( 10^{-7} \) mm. mercury according to the makers.

The diffusion pump on the high vacuum side was water-cooled and of the well known umbrella type while the other was aircooled and of the vertical stream type. Both pumps were electrically heated and were operated with Apiezon oil B having a vapor pressure at ordinary temperatures of less than \( 10^{-7} \) mm. of mercury according to the manufacturers.
The Pirani gauge consisted of an 8 ohm single wire tungsten filament centered in an 18 mm. diameter tube. It was connected in a bridge circuit in the usual way, this being balanced with the filament at about 100° C. In operation constant temperature of the surroundings was insured by keeping the gauge in an ice water bath. The gauge was calibrated for hydrogen before attaching to the gas system under consideration, the calibration being obtained for pressure against current to the bridge.

The range of pressures within which this investigation was to be kept, 1 mm. to $10^{-3}$ mm. of mercury, proved to be a very convenient range for this particular gauge and was checked accurately in the calibration by means of a carefully constructed McLeod gauge.

No attempt was made to use the ionization gauge for measuring the pressure changes during the experiment since these pressures were above its limit of usefulness. It was connected in the system merely to make certain the system was tight and to ascertain the degree of vacuum attainable with the pumping system used. Rough checks made with it indicated vacua of greater than $10^{-5}$ mm. of mercury. Extreme accuracy here would require considerable time and care particularly with the diffusion of hydrogen through the palladium tube at room temperatures to contend with. This was not thought to be worth while, particularly as subsequent spectroscopic evidence indicated that
sufficient vacuum was being obtained for cleaning out the discharge tube.

Since the gas system had all glass seals it was possible to bake out the entire tube at about 500°C including the ball valve and up to the CO₂ trap. The few inches of connecting tubing to the palladium tube and the pressure gauges and the trap could be thoroughly flamed, making possible thorough heating of all glass from the palladium tube to the stopcock at the pumps.

2. Oscillator.

The source of high frequency excitation was a tuned plate, tuned grid, push-pull, oscillator using 100 watt, type 852 tubes. The wiring diagram is shown in figure 6. The two condensers in the tank circuit were carefully calibrated by the substitution method with a General Radio type 224L Precision Condenser at a frequency of about 10⁷ per sec.

Radio-frequency current in the tank circuit was measured with a Weston thermocouple ammeter, 0-10 ampere range, with an isolantite base which was adjusted by the makers to read correctly at a frequency of 2 x 10⁷ per sec., to within 13% and not more than 18% error at 10⁸ and 10⁷ per sec. The ammeter was placed between the two condensers at the potential minimum and was separately shielded as were the two tank condensers, the shields being grounded to the negative high voltage lead.
From frequencies of about $9 \times 10^7$ per sec. down to $5 \times 10^7$ per sec., a General Radio type 458 absorption meter was used, while frequencies below $5 \times 10^7$ per sec. were measured with an absorption meter which had been carefully calibrated with a General Radio type 224L Precision Wavemeter up to about $2 \times 10^7$ per sec. Calibration between $2 \times 10^7$ and $5 \times 10^7$ per sec. was obtained using harmonics.

Since the frequency, capacity, and r.f. current are used in the calculation of the potential across the condensers, considerable care was taken in the calibration of the instruments for their measurement. Potential was applied to the discharge tube by means of two fine wires as shown in figure 3. These were used in place of large copper or lead bands which frequently have been used in this type of work because they would introduce less capacity into the circuit and seemed to have no objectionable features as far as this investigation was concerned. An electrode spacing of 30 cm. was used throughout the work.

3. Photometric.

The logarithmic sector discussed in the section on photometric theory was constructed with an accuracy of $\pm 0.05$ mm. in "1" for values from 0 to 11 mm. and was operated at a speed of 3200 r.p.m. The spectrograph was a Bausch and Lomb medium quartz instrument with a dispersion of 21Å per mm. at 3500Å and 117Å per mm. at 6500Å. W. and W. Panchromatic plates all
of the same emulsion batch were used and were developed in
developer formula D-19 for 4 minutes at 20°C.

B. Method of Procedure.

To insure repeatable results the following procedure was
followed in obtaining the data from which intensity ratios
were calculated. The discharge tube was first baked out for
several days at about 500°C. During this time it was con-
tinually on the pumps and was flushed with hydrogen several
times a day. Spectrograms were taken from time to time with
the quartz spectrograph to determine the effect of the baking
upon the gas purity. Several hours before making a run hydrogen
was admitted to the palladium tube chamber and the tube heated
by passing current through it. The stopcock between pumps and
discharge tube was then closed causing the gas pressure to
rise to probably several cm. of mercury. The stopcock between
the palladium tube chamber and the hydrogen generator was closed,
current to the palladium tube shut off, and the gas system opened
to the pumps again. The gas system could be pumped down rapidly
but when closed off the pressure rose gradually due to the
diffusion of hydrogen from the palladium tube chamber. For
this reason the system was pumped out for a length of time
sufficient to give the desired pressure when the pumps were
closed off and pressure equilibrium attained through the
palladium tube.

When the desired pressure was thus obtained the oscillator
Intensity ratios are obtained at each wavelength and the number of measurements were made of each, and the number of averages was determined by the other end, which were clearly defined. The estimated wavelength point of the time and then read the ten times. The best procedure seemed to be to place the scale at the 0.1 mm scale in the focus plane. In making these measure-

* The time lenses were measured with an eyepiece having a 0.1 mm scale in the same stock solution.

* All plates were developed under the same conditions used to develop the same stock solution.

* The discharge mechanism, because the plate was attached to the discharge tube, was turned off. This was a few minutes after the discharge was checked again at the end of the run but always stopped and the oscilloscope set for the next frequency. The sector wheel was then started, the exposure made, the sector wheel ed by applying the plate voltage to the oscilloscope. The oscilloscope set for the third frequency, and the discharge strength with these values known, the exposure was checked, the same. The electrode specifications were recorded for each frequency, the electrode separation and the plate voltage at the electrode. The constant necessary to give constant k, the plate voltage at the electrode was adjusted to determine the condenser settings and k.
varying from 5 to 32.5 meters are plotted in figures 7 to 12 inclusive. Each set of curves represents variations in intensity for the pressure given on the figure and the six sets include a pressure range from about 0.3 to 0.004 mm. of mercury. The data included in each figure was obtained from a single plate. An applied potential of 1600 volts was maintained at the electrodes during all runs.

It was impossible to obtain a complete series of data at pressures higher than about 0.4 mm. of mercury and maintain constant potential and electrode spacing. At this pressure, with 5 meter excitation, the discharge could be made to glow faintly around the electrodes when an extra source of ionization such as a high frequency test coil was brought up to the tube but vanished as soon as the external source was removed. At 10 meters the result was similar except that the glow was a little stronger. A direct vision spectroscope showed the fiery purple discharge to be mostly molecular hydrogen. At 15 meters the discharge struck at approximately 5000 volts, three times the voltage used in the tests. The minimum maintenance voltage was about 2500 volts. The discharge consisted of a narrow brick-red column with fiery purple rings at the electrodes. At 19.6 meters the discharge struck at about 4000 volts with the same maintenance potential and had the same appearance except that the center column was a little thicker.
With 25.4 meter excitation the striking voltage was twice the test potential and the maintenance voltage equal to it, that is, 1600 volts. Here the discharge again had the same structure but a heavier central column. In addition, a bright blue-violet ring appeared just under the electrodes at the glass. At 32.5 meters the striking voltage was 3200 volts and the maintenance voltage about 2400 volts. The purple rings at the electrodes had vanished and the discharge was merely a heavy brick-red central column with the blue-violet rings under the electrodes.

As the pressure was decreased the discharge became more diffuse but remained brick-red in color. The glows at the electrodes rapidly spread out for shorter wavelengths and finally became a single diffuse column. Between 0.2 and 0.08 mm. of mercury the discharge assumed a constriction under the electrodes at 32.5 meters. This became less pronounced with decreased wavelengths until at 5 meters the glow was diffuse again. As the pressure was decreased the constriction became more pronounced but always decreased to a diffuse glow at 5 meters. The critical pressure at which the discharge snapped into three parts was just under 0.01 mm. of mercury.

At 0.001 mm. of mercury the discharge viewed through a direct vision spectroscope appeared to be mostly molecular. Spectrograms at this pressure showed \( H_\alpha \) weakened to about the same intensity as the fifth or sixth term and \( H_\gamma \) to be the
strongest line of the series. When the discharge was first started at this pressure it consisted of a long constricted glow with plasmoids buried in the constrictions as described by Wood(81). After about 20 seconds of operation the glow snapped into three parts and the plasmoids disappeared.

In the region of pressures around 0.005 mm. of mercury some difficulty was encountered due to an abrupt change in the type of discharge. At this point there seemed to be a critical set of conditions which determined whether the discharge was to be dim or very bright. With 5 meter excitation the discharge was definitely of the dim type for the test potential of 1600 volts.

Upon slowly increasing the voltage it suddenly changed to a very bright glow and the r.f. current, and thus the potential, rose to approximately double its former value. With care the voltage could be lowered perhaps half way to the original value before the discharge became suddenly dim again. This effect could not be noticed at 0.001 mm. of mercury. It was impossible to obtain the 1600 volts at the electrodes with the bright glow at 5 meter excitation. At 10 meters the effect was most troublesome as the desired 1600 volts seemed to be just above the maximum for the dim glow and very near the minimum voltage for the bright glow. With extreme care the data were obtained here for the bright glow. At 15 meters the effect was still in evidence but no difficulty was experienced in obtaining the desired voltage.
On the whole the effect seemed to be that the dim glow appeared suddenly as the frequency of excitation was increased or the voltage decreased. These may be the same phenomena found by J. Thomson(65) although he describes striations in two of his stages of discharge and no striations were obtained at the pressures of this investigation. Tube dimensions and field could easily account for this, however. With the exception of the 5 meter data at 0.004 mm. of mercury all data are representative of the bright glow.
IV. DISCUSSION OF RESULTS

The curves of excitation wavelength vs. intensity ratios show that there is at least one wavelength in the range chosen which is especially favorable for the excitation of H_α as compared with the rest of the Balmer series. Figure 7 shows this effect for an average pressure of 0.3 mm. of mercury. It will be noticed that 15 meter excitation increases the ratio H_α/H_β by nearly 100% while a similar percentage increase is noted for H_α/H_γ in the neighborhood of 10 meters and for H_α/H_β at 8 meters.

The same effect is noted in figure 8 at a pressure of 0.08 mm. of mercury, the only difference being a decided decrease in H_α resulting in a lowering of all the curves and bringing in the curve for the fifth term of the series and an indication of the sixth.

At 0.03 mm. of mercury, figure 9, the curves take a very different form. In addition to a further lowering of all term ratio curves each curve has a very decided minimum, one clearly defined maximum, and at the shorter wavelengths the curves seem headed for an even greater maximum.

The curves of figure 10 for 0.01 mm. of mercury show the same effect and in addition the whole series of curves is still lower indicating that the higher terms are more intense compared with H_α.
Figures 11 and 12 indicate that as the pressure is lowered through 0.004 mm. of mercury the terms above the fourth become less intense thus raising the whole series. However, Hγ has become equal to or greater in intensity than Hα. Also Hγ has become more intense than either Hα or Hβ, except at the critical wavelength of excitation where the intensities of the three lines assume their series order with Hα strongest.

From all the series of curves it is seen that as the pressure decreases to around 0.01 mm. of mercury the higher terms of the Balmer series become more and more intense. Below this pressure down to 0.004 mm. of mercury the first few terms tend to become even more intense than Hα while the terms from the fourth and greater appear to grow weaker compared with Hα. As has been stated spectrograms at still lower pressures show Hα and Hβ to be even less intense.

In attempting to explain conflicting data for some intensity ratios of the Balmer series obtained by several workers under widely different experimental conditions Herzberg (24) concluded that the ratios are affected by tube dimensions, pressure, and portion of the discharge viewed. The pressure variation is well illustrated in this experiment and it is also seen that to the above list should be added the factor, frequency of excitation.

If we assume that excitation of the higher terms of the series is most probable when we have maximum ionizing efficiency
of the discharge, the six sets of curves indicate that the most favorable pressure is between 0.03 and 0.005 mm. of mercury. Brasefield(4) has found maximum conductivity for 20 meter excitation to be between 0.01 and 0.02 mm. of mercury. He also shows that for pressures in the region 0.03 to 0.01 mm. of mercury the discharge efficiency decreases as the high frequency excitation changes from 30 to 25 meters. It then increases to a maximum at 20 meters and again decreases rapidly to 15 meters, the shortest wavelength he used.

If the relative heights of the curves are used as criteria for discharge efficiencies curves 9 and 10 show the efficiency decreasing from 32.5 meters to between 20 and 25 meters. It then reaches a maximum at 10 to 15 meters and a very inefficient discharge is indicated at 5 meters and shorter wavelengths. At pressures above and below the range 0.01 to 0.03 mm. of mercury this extreme inefficiency at the very short wavelengths does not seem indicated.

If we assume as before that high ionization efficiency of the discharge is favorable to excitation of the higher terms of the Balmer series it would seem that equation (22) should yield information in a general way as to the efficiency of the discharge for different pressures and excitation frequencies when subjected to a constant field as was done in this investigation.

Curves of the field necessary for initiation of the discharge vs. excitation wavelength for various pressures are
shown in figure 13. These curves were calculated by means of equation (22) for the conditions of the investigation. As has been suggested by J. Thomson the function \( \phi(f) \) in this equation is to account for a decrease in electron loss by diffusion. This loss should vary inversely with the amplitude of vibration of a free electron and as this varies inversely with the square of the frequency \( \phi(f) \) should be some inverse square function of \( f \). The function was assumed to be \( e^{-\left(\frac{f}{f_0}\right)^2} \) and the curves of figure 13 result.

It is seen that relative heights and shapes of the curves for different pressures are in general agreement with the experimental curves. With experimental data over a wider range of frequencies and pressures it should be possible to determine a much more accurate and probably more complicated value of \( \phi(f) \). It must be kept in mind that the calculated curves represent values of field at minimum striking potential whereas the experimental data are for a discharge already started. This should result in some difference in the curves due to cumulative ionization in the discharge already in operation. This might be the explanation of the double maxima of figures 9 and 10. In this pressure region for very high frequencies of excitation some of the higher terms of the series may be diminished due to collisions of the second kind in which the excited atoms would aid ionization rather than their respective intensities. This effect might be greater than that of the diminished diffusion
loss of $\phi(f)$ and in this case would result in the upward trend of the curves as shown in figures 9 and 10. In this case, of course, the general height of the curves would no longer indicate ionization efficiency in the same way as has been assumed.

The variation in maxima of different term ratios for a given pressure may also be due to the effect of cumulative ionization. Another factor which could affect the shape of the curves is the charge taken up by the glass walls. This probably varies with both pressure and frequency of excitation.

The steady increase in intensities of $H_\beta, H_\gamma, H_\delta$ with respect to $H_\alpha$ at lowered pressures indicates that the population of these higher states becomes greater with decreased pressure. That the pressure is not the only factor here is indicated by the curves of figures 11 and 12 in which $H_\alpha, H_\beta,$ and $H_\gamma$ assume a different order as to intensity depending upon the frequency. This frequency variation is noticeable, however, only at low pressures. Stuhlman and McCoy (59) have shown that the relative intensities of $H_\alpha$ and $H_\beta$ vary with the power input to the tube, low power inducing $H_\beta$ stronger than $H_\alpha$.

It has been stated that purity of gas is essential to a study of the discharge. This investigation shows that spectroscopic purity is difficult if not impossible to obtain with this type of discharge. Little difficulty was experienced in obtaining a clean spectrum of molecular and atomic hydrogen in the visible region. However, spectrograms taken with a
quartz instrument showed that the gas might appear to be pure at higher pressures and yet show a number of impurities in the ultraviolet at lower pressures. The most persistent impurities were the 3035Å water-vapor band, the CO₂ bands at 2395Å and 2381Å which were in evidence only at pressures of a few microns and less, and a set of bands which it is believed are due to N₂ and which seem to appear only in an atmosphere of hydrogen. This latter set of bands is being investigated further. The water vapor band is believed due to the association of H₂ with the O₂ which is driven from the glass when the Si O₂ is dissociated by electronic bombardment. This evolution of O₂ has been studied by Wood(32) who found the same phenomena for several kinds of glass and quartz.

It is believed that the CO₂ which appears at the lower pressures is also released from the glass by electron impact. Both the ruby-red and the yellow-green fluorescence attributed by Wood to bombardment of the glass with low and high velocity electrons were noticed at pressures below the range of this investigation. It must be emphasized that although in this investigation the gas would have been taken as pure as evidenced by a glass spectrograph, it in reality contained impurities as shown by the quartz instrument. With the experimental set-up used it is doubtful if greater purity could have been obtained. Since most of the impurities seem to have originated in the glass walls it appears that a larger tube with internal elec-
trodes so placed that electronic bombardment of the walls would be a minimum would make possible greater purity.
V. CONCLUSIONS

The results of this investigation show a decided variation of intensity ratios of the Balmer series with frequency of the excitation voltage. In general there is a narrow region of excitation wavelengths varying from about 8 to 22 meters, depending upon the pressure and series term, in which excitation of the term is a minimum compared to $H_\alpha$.

The assumption that maximum ionizing efficiency of a discharge is synonymous with greater intensities of the higher terms seems to be justified although proof of a sufficiently great loss of excited atoms due to collisions of the second kind would nullify this assumption in proportion to the degree of occurrence of these collisions.

The relative intensities of the series terms compared with $H_\alpha$ increases with diminishing pressure to a maximum in the pressure range between 0.03 and 0.005 mm. of mercury below which $H_\beta$ and $H_\gamma$ continue to increase but the higher terms decrease in intensity.

Populations of the states giving $H_\beta$ and $H_\gamma$ are seen to increase with diminished pressure but also vary relatively with the frequency of the excitation voltage.

Based on the assumption that ionizing efficiency of the discharge and excitation of the higher terms vary directly with each other a value $\phi(f) = e^{-\frac{(f^2)}{(f^2)}}$ is chosen for J. Thomson's
equation for minimum striking potential. Curves calculated from this formula agree fairly well as to pressure and excitation frequency variations with the experimental curves. Better agreement might be obtained with a more complicated function $\phi(f)$ and more knowledge of the processes of cumulative ionization and space charge at the tube walls.

With this type of excitation and size of tube it is practically impossible to obtain spectroscopically pure hydrogen because of the release of gas due to bombardment of the glass walls by high velocity electrons. These impurities appear in the ultra-violet rather than the visible which probably accounts for their being overlooked in many investigations.
VI. SUMMARY

This thesis is the report of an investigation of the effect of high frequency excitation on the relative intensities of some of the terms of the Balmer series of hydrogen. A push-pull oscillator was used to insure a steady and uniform source of potential. External electrodes were used in applying the high frequency voltage to the discharge tube. The gas system was designed for maximum purity and the discharge tube was built considerably longer than the theoretical minimum length for the pressures and frequencies to be used. Intensity ratios were calculated from measurements of spectrograms which had been taken in conjunction with a logarithmic sector disc.

The experimental work consisted of obtaining spectrograms of the discharge under wavelengths of excitation voltage varying from 5.1 to 32.5 meters, the pressure and field remaining constant. Data for six pressures of from 0.005 to 0.03 mm. of mercury were obtained.

The results of the investigation show that:

1. There is a distinct variation in intensity ratios with excitation frequency.

2. There is a region of excitation frequencies which gives a minimum excitation of each term with respect to H_\alpha and that this region of frequencies depends upon pressure and the term under consideration.
3. Ionization efficiency and intensities of the higher terms of the series vary more or less directly with each other if cumulative ionization is negligible.

4. Intensities of the higher terms of the Balmer series increase as the pressure decreases to about 0.01 mm. of mercury. For further diminishing of pressure H_β and H_γ continue to increase in intensity while the higher terms decrease.

5. Populations of the energy states giving H_β and H_γ increase with decreasing pressure but vary relatively with the frequency of excitation voltage.

6. A value, \( e^{-\left(\frac{f}{f_0}\right)^2} \), can be chosen for \( \phi(f) \) of J. Thomson's equation for the striking voltage for this type of discharge. With this function the equation yields curves in good general agreement with the experimental results.

7. Some gas impurities appearing in the ultra-violet and not apparent in the visible region are inherent in this type of discharge due to electronic bombardment of the glass.
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