

The Conditions Necessary for the Absorption
of Ultra-Short Waves in Hydrogen

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ABSTRACT

A review is given of the work published to date on the absorption of ultra-short radio waves in excited hydrogen. A fairly detailed quantum mechanical analysis is given of the whole problem of intensity ratios for the Balmer line components. Theoretical intensity ratios are calculated; and the application of these results to the experimental problem is pointed out, together with the necessity for making preliminary investigations of the experiment values of these ratios.

The experiment described measured the values of the intensity ratios for H_{α} and H_{β} at five different pressures, by means of an analysis with a spectrograph crossed with a Fabry-Perot interferometer.

A discussion is given of the significance of the measured values, and from them predictions have been made concerning the probable success of an experiment to measure the absorption of ultra-short waves in hydrogen.

I. INTRODUCTION

The general experimental problem of observing the absorption of ultra-short radio waves in excited hydrogen is one whose results are of considerable theoretical importance. The overwhelming successes of the present quantum theory in explaining the features of emission and absorption spectra in various known wave-length regions lead one to suppose that its predictions must also be valid even when the radiation involved falls in the less familiar region of ultra-short radio waves. Nevertheless, such a supposition involves no little extrapolation, and it must be submitted to rigorous experimental verification if we are to rely on it.

Fortunately, an opportunity for experimental verification presents itself in the simplest of all spectra: namely, the Balmer series of atomic hydrogen. This was pointed out by Grotrian¹⁾, and may be seen quite easily upon examining the well known term scheme of hydrogen. Figure 1 shows part of this term scheme, in which (for convenience) the levels having the same total quantum number are drawn with wider separations than a true scale would permit. The selection rules by no means forbid transitions between levels of different energies and in adjacent columns, even though they are of the same total quantum number. But such transitions correspond to wave-lengths far out of the

1) W. Grotrian. Graphische Darstellung der Spektren von Atomen, v. 1, p. 37, Berlin 1928.

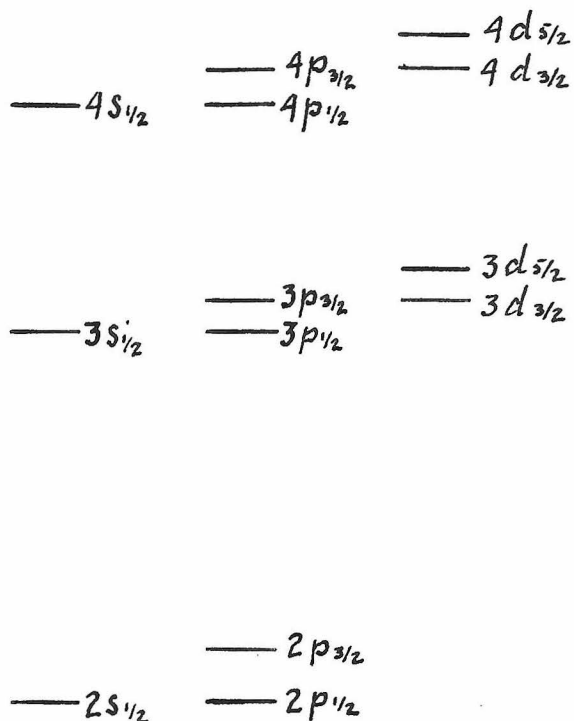


Figure 1

optical regions, for the energy differences between the levels involved are in every case exceedingly small. Table 1 lists the permitted transitions of this kind between s, p, d, and f levels for total quantum numbers between 2 and 6, together with the corresponding calculated wave-lengths. These wave-lengths may be calculated from elementary theory. (See, for example, H. E. White, Introduction to Atomic Spectra. McGraw-Hill, 1934) Thus there arises quite naturally out of

Table 1

| Levels | Wave-length(cms) | Levels | Wave-length(cms) |
|-----------------------|------------------|-----------------------|------------------|
| $2p_{3/2} - 2s_{1/2}$ | 2.74 | $5p_{3/2} - 5s_{1/2}$ | 42.83 |
| $3p_{3/2} - 3s_{1/2}$ | 9.25 | $5d_{5/2} - 5p_{3/2}$ | 128.5 |
| $3d_{5/2} - 3p_{3/2}$ | 27.75 | $5f_{7/2} - 5d_{5/2}$ | 257.0 |
| $4p_{3/2} - 4s_{1/2}$ | 21.93 | $6p_{3/2} - 6s_{1/2}$ | 74.0 |
| $4d_{5/2} - 4p_{3/2}$ | 65.78 | $6d_{5/2} - 6p_{3/2}$ | 222.0 |
| $4f_{7/2} - 4d_{5/2}$ | 131.6 | $6f_{7/2} - 6d_{5/2}$ | 444.0 |

the well-established and complete knowledge of the optical spectrum predictions of characteristic radiations which must be identified with ultra short radio waves. It is of great importance, therefore, to check experimentally the existence of transitions like those listed in Table 1.

It must be recognized at the outset, however, that any attempt to observe as emitted radiation any of the transitions listed in Table 1 is almost certain to fail. It will be shown later in this paper (under the section entitled "Theory") that the probability of the spontaneous emission of such radio waves from excited atoms is so negligibly small that one could not hope to detect it, even with far more sensitive apparatus than any now available.

The experimental approaches, therefore, to this problem have been of two sorts: (1) to observe directly the absorption of radio

waves in a body of excited hydrogen gas; and (2) to observe in the finestructure of the Balmer lines modifications in the relative intensities of the components as an indirect result of absorption of radio waves by the excited hydrogen.

The first approach has been that of most experimenters in this field. The first published work to appear was that of Betz²⁾, who used for a source of ultra short waves a simple Hertzian oscillator excited by a high frequency Tesla coil. This gave radiation sufficiently intense, but strongly damped, and hence of questionable wavelength. These waves were then caused to fall upon a sizeable metal mirror which focussed them on a vacuum thermocouple, the thermocouple being situated at the center of a glass bulb containing the absorbing gas. Reasonable precautions were taken to assure the purity of the absorbing gas and to keep experimental conditions constant by making the gas stream continuously through the apparatus. The thermocouple was connected to a galvanometer whose readings gave a measure of the amount of absorption which had occurred in the gas. The hydrogen (in a long discharge tube) was excited by low frequency current.

Betz tried 14 different wave-lengths between 3 cm and 30 cm in nitrogen, in oxygen, and in hydrogen. His published results showed fairly constant absorption in oxygen and nitrogen, apparently independent of the wave-length; but in excited hydrogen, strongly marked and

2) O. Betz. Ann. d. Phys. 5 15, p. 321, 1932.

selective maxima of absorption at wave-lengths 3 cm, 9 cm, and 28 cm. Furthermore, the location of these maxima on the wave-length scale appeared to be independent of the exciting current for the hydrogen, and hence could not be explained away as occurring at plasma-frequencies.

Concerning these apparently conclusive results of Betz, however, there seems still to be some disagreement. Even Klumb, at whose suggestion Betz attempted the problem wrote³⁾ in commenting on the results: "The truth of such an assumption cannot be positively established by a single research, particularly in a wave-length region which is experimentally so difficult. A large number of questions, for example the unexpected magnitude of the absorption, need to have light thrown upon them by further researches."

Two years later there appeared a thesis by E. E. Schneider⁴⁾ in which he reported a similar experiment, undertaken at the suggestion of Klumb. Schneider's apparatus and technique were much like those of Betz, except that he evaluated the absorption in arbitrary units by finding positions of resonance for the bridge in a Lecher-wire system. Schneider worked with wave-lengths between 22 cm and 33 cm, and hence (as may be seen from Table 1) was searching for evidence only of the transition $3p_{3/2} - 3d_{5/2}$. His absorption curve shows 2 maxima, one at wave-length 26.7 cm and the other at about 28.3 cm. This double peak instead of a single one at 27.75 cm might conceivably have been due

3) H. Klumb. Phys. Ztschr. 33, p. 445, 1932.

4) E. E. Schneider. Freiburger Dissertation, 1933.

(he suggests) to a Stark effect in his discharge tube.

In the year after the publication of Schneider's thesis there appeared a long paper by Haase⁵⁾ which reported an apparently thorough investigation of the entire experimental method of measuring absorption in hydrogen directly. With considerable elaborate apparatus, he repeated the previous work (in his words) "more carefully". Haase did take particular care to eliminate from his absorption curves the discontinuities which he found to be due to the comparability of some of the wave-lengths used with certain physical dimensions of his apparatus. In the end he concluded that he had observed no absorption whatever which could not be adequately explained as due to the absorption by the free electrons in the excited hydrogen. Furthermore, he concluded after an estimate of the number of excited hydrogen atoms (made by observing the total amount of emitted H_{α} light) that the greatest energy which could be absorbed by these excited atoms in the most favorable case corresponded to a galvanometer deflection much too small to be observed.

In summarizing the attempts of the experimenters who have sought by direct means to observe selective absorption of ultra-short radio waves in excited hydrogen, one can only say that considerable disagreement seems to exist. Certainly it is advisable to consider the second approach to the problem mentioned above: namely, to detect the characteristic long wave-length transitions in hydrogen indirectly

5) T. Haase. Ann. d. Phys. 23, p. 657, 1935.

through the examination of the Balmer line finestructure. As far as the writer is aware, there has been no publication to date of successful researches along this line, although Haase⁶⁾ mentioned that Reinecke⁷⁾ (in Germany) had attempted the method without success.

A close examination into the theory and practice of this indirect method of approach has shown that the conditions under which it may be expected to yield a satisfactory result are considerably more complicated than (apparently) has been generally recognized. In the following section of this paper it will be made clear that only under special conditions of excitation could such an experiment be expected to yield any result whatever. It was therefore essential to carry out a preliminary investigation of the conditions necessary for the absorption of the characteristic long wave-lengths in hydrogen. That has been the purpose of the research here reported. This paper will be concerned with (1) an application of quantum theory to the problem to predict more precisely than has been done what changes one may expect in the intensities of Balmer line fine structure, and (2) an experimental investigation of the availability of the conditions required by the theory.

II. THEORY

Speaking qualitatively, the idea of the method under discussion is very simple. Consider for example the transition $3p_{3/2} - 3d_{5/2}$.

6) T. Haase. loc. cit.

7) R. Reinecke. Berliner Dissertation, 1932.

In order to study it, we must resolve the two main components of the first Balmer line, H_{α} . Actually, H_{α} consists of seven permitted jumps which may be resolved into two components, as follows:

| | |
|-------------------------------|---------------------------------|
| | $3p_{3/2} \rightarrow 2s_{1/2}$ |
| shorter wave-length component | $3p_{1/2} \rightarrow 2s_{1/2}$ |
| | $3s_{1/2} \rightarrow 2p_{1/2}$ |
| | $3d_{3/2} \rightarrow 2p_{1/2}$ |
| | $3s_{1/2} \rightarrow 2p_{3/2}$ |
| longer wave-length component | $3d_{5/2} \rightarrow 2p_{3/2}$ |
| | $3d_{3/2} \rightarrow 2p_{3/2}$ |

Consequently, one might expect that a body of hydrogen which is emitting H_{α} , upon being irradiated with radio waves of exactly 27.75 cm, would show the absorption represented by $3p_{3/2} \rightarrow 3d_{5/2}$ as a strengthening of the longer wave-length component at the expense of the shorter.

Since, however, the present quantum theory permits the calculation of all of the features of the hydrogen spectrum, including the transition probabilities, a more quantitative analysis of the problem is at once suggested. The results of such an analysis prove to be considerably more illuminating than the simplified explanation just given, and they lead to at least one unanticipated conclusion. The methods and the notation in the following are mainly those of Condon

and Shortley⁸⁾. Also a long article by Bethe⁹⁾ concerning one- and two-electron spectra served as an excellent reference.

Einstein's probability of spontaneous emission¹⁰⁾, (denoted by A) on account of a transition from a level n^2L_j to a level $n'^2(L\pm 1)_{j'}$

may be expressed in terms of the electric moment matrix element (with spin) in accordance with the following equation:

$$A(n^2L_j \rightarrow n'^2(L\pm 1)_{j'}) = \frac{64\pi^4 e^3}{3h} \left| (n^2L_j \ddot{P} n'^2(L\pm 1)_{j'}) \right|^2 \Xi(j, j')$$

where $\Xi(j, j+1) = (j+1)(2j+3)$ σ = wave number corresponding to the transition

$\Xi(j, j) = j(j+1)$

$\Xi(j, j-1) = j(2j-1)$ h = Planck's constant

The electric moment matrix element with spin may in every case be reduced to a corresponding matrix element which is really independent of the spin. This follows from the fact that the electric moment vector commutes with the vector electron spin. Elaborate general formulae for accomplishing this reduction may be found in Condon and Shortley's book (above mentioned) on page 69. A single example is given here:

$$(n s l_j \ddot{P} n' s l_{-1} j) = (\pm) (n l \ddot{P} n' l_{-1}) \frac{\sqrt{P(j) Q(j)}}{2j(j+1)}$$

- 8) E. U. Condon and G. H. Shortley. The Theory of Atomic Spectra. Macmillan 1935.
- 9) Bethe. Handbuck der Physik v. 24, part 1, 2nd ed. 1933.
- 10) Einstein, Phys. Ztschr. 18, p. 121, 1917.

where s = spin quantum number

l = angular momentum quantum number

$$j = l + s$$

$$P(j) = (j - s + 1)(j + l + s + 1)$$

$$Q(j) = (s + l - j)(j + s - l + 1)$$

A matrix element without spin may be, in turn, merely an integral of the radial eigenfunctions, as follows:

$$(nl; P; n'l-1) = \frac{e}{\sqrt{4l^2-1}} \int_0^\infty r R(nl) R(n'l-1) dr$$

where e = the charge on the electron, and where the R's are the radial eigenfunctions.

The evaluation of the radial integral which appears in the last equation is a rather difficult problem which has received the attention of several able theorists. Calculations of it have been made by Epstein¹¹⁾, Bateman¹²⁾, Gordon¹³⁾, and others. According to Gordon, the value of the radial integral (in atomic units) is given by

$$\int_0^\infty r R(nl) R(n'l-1) dr = \frac{(-1)^{n'-l}}{4(2l-1)!} \sqrt{\frac{(n+l)!(n'+l-1)!}{(n-l-1)!(n'-l)!}} \frac{(4nn')^{l+1} (n-n')^{n+n'-2l-2}}{(n+n')^{n+n'}}$$

$$\times \left[F\left(-n_r, -n_r', 2l, \frac{-4nn'}{(n-n')^2}\right) - \left(\frac{n-n'}{n+n'}\right)^2 F\left(-n_r-2, -n_r', 2l, \frac{-4nn'}{(n-n')^2}\right) \right]$$

11) Epstein, Proc. Nat. Acad. Sci. 12, p. 629, 1926.

12) Bateman, Partial Differential Equations, p. 453.

13) Gordon, Ann. d. Phys. 2, p. 1031, 1929.

where $n_r = n - l - 1$ and where the F's are hypergeometric functions.
 $n_{r'} = n' - l$

We are interested only in certain special cases of this general formula, in which it may be greatly reduced and simplified. These are as follows:

$$\int_0^{\infty} r R(np) R(2s) dr = 2^{17} n^7 (n^2 - 1) (n - 2)^{2n-6} (n+2)^{-2n-6}$$

$$\int_0^{\infty} r R(nd) R(2p) dr = 2^{19} 3^{-1} n^9 (n^2 - 1) (n - 2)^{2n-7} (n+2)^{-2n-7}$$

$$\int_0^{\infty} r R(nl) R(nl-1) dr = 2^{-2} 3^2 n^2 (n^2 - l^2)$$

Thus, in the fashion just outlined, one may calculate the probability A of spontaneous emission for any transition in which we are interested in this problem. Let us suppose that at a given instant there are N(II) electrons in the upper level II of a certain transition II \rightarrow I then

$$N(\text{II}) A(\text{II} \rightarrow \text{I}) \tag{5}$$

is the rate at which spontaneous transitions occur. This quantity is proportional to the actual observed intensity of the emitted radiation corresponding to the transition II \rightarrow I.

But in this problem we must be interested in the interaction of radiation of characteristic wave-length with the atom. Hence we must calculate Einstein's coefficients B(I \rightarrow II) and B(II \rightarrow I), which are respectively the probability of absorption and the probability of

induced emission. The B's are quantities such that the radiation produces transitions from I to II by absorption at the rate

$$N(I) B(I \rightarrow II) \rho(\sigma) \quad (6)$$

and such that the radiation stimulates the emission processes from II to I at the rate

$$N(II) B(II \rightarrow I) \rho(\sigma) \quad (7)$$

(We assume that the radiation field is isotropic and unpolarized and that it has spectral energy $\rho(\sigma) d\sigma$ in unit volume in the wave-number range $d\sigma$ at σ)

The relations between the A's and the B's may be simply calculated from purely statistical considerations. The following formulae may be easily derived:

$$B(II \rightarrow I) = \frac{1}{8\pi h c \sigma^3} [A(II \rightarrow I)] \quad (8)$$

$$B(I \rightarrow II) = \frac{g(II)}{g(I)} B(II \rightarrow I) \quad (9)$$

where g represents the statistical weight of a level = $(2j + 1)$.

As an example of the results of such calculations, Table 2 is given herewith. It shows the calculated values of the A's and B's for all permitted transitions among the eight levels involved in producing the H_{α} line.

Table 2

| Transition | A(II I) Spontaneous Emission Probability | B(II I) Induced Emission Probability | B(I II) Absorption Probability |
|---------------------------------|---|---|--------------------------------------|
| $3d_{5/2} \rightarrow 2p_{3/2}$ | $6.41 \times 10^7 \text{ sec}$ | 3.66×10^9 | 5.44×10^9 |
| $3d_{5/2} \rightarrow 3p_{3/2}$ | 3.44×10^{-9} | 14.9×10^9 | 22.4×10^9 |
| $3d_{3/2} \rightarrow 2p_{3/2}$ | 1.07×10^7 | 0.61×10^9 | 0.61×10^9 |
| $3d_{3/2} \rightarrow 2p_{1/2}$ | 5.35×10^7 | 3.05×10^9 | 6.10×10^9 |
| $3d_{3/2} \rightarrow 3p_{1/2}$ | 8.94×10^{-8} | 14.5×10^9 | 29.0×10^9 |
| $3p_{3/2} \rightarrow 2s_{1/2}$ | 2.23×10^7 | 1.27×10^9 | 2.54×10^9 |
| $3p_{3/2} \rightarrow 3s_{1/2}$ | 1.43×10^{-7} | 23.2×10^9 | 46.4×10^9 |
| $3p_{1/2} \rightarrow 2s_{1/2}$ | 2.23×10^7 | 1.27×10^9 | 1.27×10^9 |
| $3s_{1/2} \rightarrow 2p_{3/2}$ | 0.42×10^7 | 0.24×10^9 | 0.12×10^9 |
| $3s_{1/2} \rightarrow 2p_{1/2}$ | 0.21×10^7 | 0.12×10^9 | 0.12×10^9 |
| $2p_{3/2} \rightarrow 2s_{1/2}$ | 1.17×10^{-6} | 4.88×10^9 | 9.76×10^9 |

In Table 2, one may at once note two facts which are generally true for all the Balmer lines: (1) the spontaneous emission probabilities for the long-wave transitions are many orders of magnitude smaller than for optical range transitions; (2) the absorption probabilities and induced emission probabilities are of approximately the same order of magnitude for all transitions. This is on account of the factor σ^3 which appears in equation (8); and this explains why from an experimental point of view one must be concerned with absorption and induced emission, rather than with spontaneous emission, if one hopes to study the long-wave transitions in hydrogen.

It is the purpose of this discussion to make some experimentally verifiable prediction; hence one must investigate the relative populations of the upper and lower levels in a long-wave transition; i.e., one must inquire what are the relative values of $N(\text{II})$ and $N(\text{I})$ in the expressions (6) and (7).

If it be assumed that the emitting hydrogen source is in "natural excitation" (i.e. that the conditions of excitation are sufficiently isotropic to assure that the number of atoms in the $2j + 1$ states of the same level are equal), then the relative numbers of atoms in different levels is given by the Maxwell-Boltzmann law:

$$N(c) = g(c) e^{-\frac{E_c}{kT}} \quad (10)$$

where $g(c)$ is the statistical weight of a level C , provided that thermal equilibrium between the different levels obtains. This last proviso

requires further examination, but if we accept it for the moment, then the expression (6) becomes

$$g(I) B(I \rightarrow II) \rho(\sigma) e^{-\frac{E_I}{kT}}$$

and (7) becomes

$$g(II) B(II \rightarrow I) \rho(\sigma) e^{-\frac{E_{II}}{kT}}$$

Whence, in consequence of (9), the ratio of these last two quantities is simply

$$e^{\frac{E_{II} - E_I}{kT}} = e^{\frac{hc}{\lambda kT}}$$

where λ is the wave-length for the transition in question. For λ of the order of centimeters, and for any reasonable value of the temperature, this ratio is very nearly unity.

All this is simply to say that, on the assumption of thermal equilibrium between two very close fine-structure levels, the effect of incident resonant radiation is merely to produce absorption processes at a rate very nearly equal to the rate of induced emission processes. Thus, in such a case, one could not expect any observable result from an experiment like that described (in which one would measure changes in the intensity ratios of Balmer line components.) Such a conclusion needs by no means to be limited to this particular kind of experiment. Tolman¹⁴⁾ has pointed out that induced emission (or "negative absorption")

14) R. C. Tolman. Phys. Rev. 23, p. 700, 1924.

must necessarily consist of radiation coherent with the primary beam, and consequently that it must reinforce the primary beam to such an extent that the observed absorption may be considerably less than that which would be expected if induced emission were neglected. Tolman's concern was with absorption in the far infra-red between close levels of molecular rotation-oscillation spectra. Nevertheless the principle is the same; and, in fact, its application is of greater importance the longer the wave-length being absorbed. Certainly, given natural excitation and temperature equilibrium between the hydrogen levels $3p_{3/2}$ and $3d_{5/2}$, say, we could not expect to observe absorption of the characteristic wave-length (27.75 cm) by any means whatever, direct or otherwise.

Several papers (previously referred to) have been published on the absorption of ultra short radio waves in hydrogen, but none of them have included any discussion of this vital consideration except Schneider's paper¹⁵⁾, which concludes briefly that $N(\text{II})g(\text{I}) > N(\text{I})g(\text{II})$ in order to account for observed negative dispersion in excited hydrogen.

Certainly it is appropriate to investigate experimentally the dependence of level population upon excitation conditions. The validity of the plausible appearing assumption of thermal equilibrium between close levels must be tested. If it can be shown experimentally under what conditions the actual population of levels deviates markedly from that supposed in equation (10), then the indirect method of observing absorption in hydrogen offers much promise. If an "abnormal" level population proves unattainable, then such an experimental attempt is likely to be fruitless.

15) E. E. Schneider. loc. cit.

The theoretical ratio of intensities of the components for the several Balmer lines may be simply calculated from a knowledge of the A probability coefficients for all transitions. The actual intensity for a transition is proportional to the rate of spontaneous emission processes, given by (5). Then by the use of (10) and the various values of A, we may compute (in arbitrary units) the intensity corresponding to each transition. Finally, the intensities may be grouped (as were the transitions for H_{α}) into (1) short wave-length component and (2) long wave-length component. The ratio of the sum of the intensities for each group is taken as the required theoretical value. The ratio of short wave-length to long wave-length intensities (calculated by this method) is 0.805 for H_{α} and 0.92 for H_{β} . It is of interest to examine the actual calculated intensities for H_{α} , and to draw some conclusions therefrom, keeping in mind the fact that H_{α} is typical of all the Balmer lines. These intensities (in arbitrary units) are given in Table 3.

Table 3

| Shorter λ Component of H_{α} | | Longer λ Component of H_{α} | |
|---|-----------|--|-----------|
| Transition | Intensity | Transition | Intensity |
| $3d_{3/2} \rightarrow 2p_{1/2}$ | 3840 | $3d_{5/2} \rightarrow 2p_{3/2}$ | 6912 |
| $3p_{3/2} \rightarrow 2s_{1/2}$ | 1600 | $3d_{3/2} \rightarrow 2p_{3/2}$ | 768 |
| $3p_{1/2} \rightarrow 2s_{1/2}$ | 800 | $3s_{1/2} \rightarrow 2p_{3/2}$ | 150 |
| $3s_{1/2} \rightarrow 2p_{1/2}$ | 75 | | |
| Sum = 6315 | | Sum = 7830 | |
| Ratio of Components = $\frac{6315}{7830} = 0.805$ | | | |

If, under certain conditions of excitation, the measured value of the intensity ratio for H_{α} or H_{β} does not agree with the theoretical value, then one may take this fact as evidence that equation (10) is not rigorously true; i.e. that the upper levels of the line in question are not populated "normally" (according to the Maxwell-Boltzmann law.)

Several experimenters, in the course of analysing the fine structure of H_{α} , have noted intensity ratios considerably different from the theoretical value, when the pressure of the excited hydrogen was low. Others have observed intensity ratios which were normal, or nearly so. Bethe¹⁶⁾ gives a brief summary of all except the most recent ones of such observations. These results do not give any very coherent agreement. Most of the experimenters were not primarily interested in this problem, and hence did not trouble to record the pressure at which they worked.

At any rate, it is natural to expect an "ideal" equilibrium distribution at relatively high pressures. At pressures of the order, say, of 1 mm the mean time between collisions for hydrogen atoms is of the same order as the mean life of the upper excited states for the Balmer lines. Hence we might expect equilibrium between close levels, through a constant redistribution of energy in collisions.

At low pressures, on the other hand, any observed abnormality of intensity ratios must be accounted for as the preferential excitation

16) H. A. Bethe. Handbuch der Physik v. 24, part 1 2nd ed. p. 464.

of certain levels. From the inconclusive experimental data one may draw one fairly clear observation: all observed deviations from the theoretical intensity ratio were in the direction of an enhanced shorter wave-length component. A glance at Table 3 shows that such observations are most naturally attributable to a preferential excitation of the p levels (i.e. an overpopulation of these levels) at the expense of the s and d levels. This would lead to a greater intensity for the transitions ($3p_{3/2} \rightarrow 3s_{1/2}$) and ($3p_{1/2} \rightarrow 2s_{1/2}$), and to a lesser intensity for all the others. This interpretation will be discussed further near the conclusion of this paper, in connection with the results obtained in this research.

In the existing publications, little or no evidence is to be found concerning the intensity ratio for H_{ϵ} or the higher Balmer lines. Houston and Hsieh¹⁷⁾ found the ratios nearly normal for all the lines up to H_{ϵ} .

One might expect the behavior of H_{ϵ} at low pressures to parallel that of H_{δ} , since the structure of its upper levels is entirely analogous. As it will be seen later in this paper, this supposition has been experimentally verified.

This section should not be concluded without some mention of the finite width of an absorption line. It is not quite true that the incident radiation must be of just the wave-length calculated from Bohr's rule in order that it be absorbed. The wave train absorbed in

17) W. V. Houston and Y. M. Hsieh. Phys. Rev. 45, p. 263, 1934.

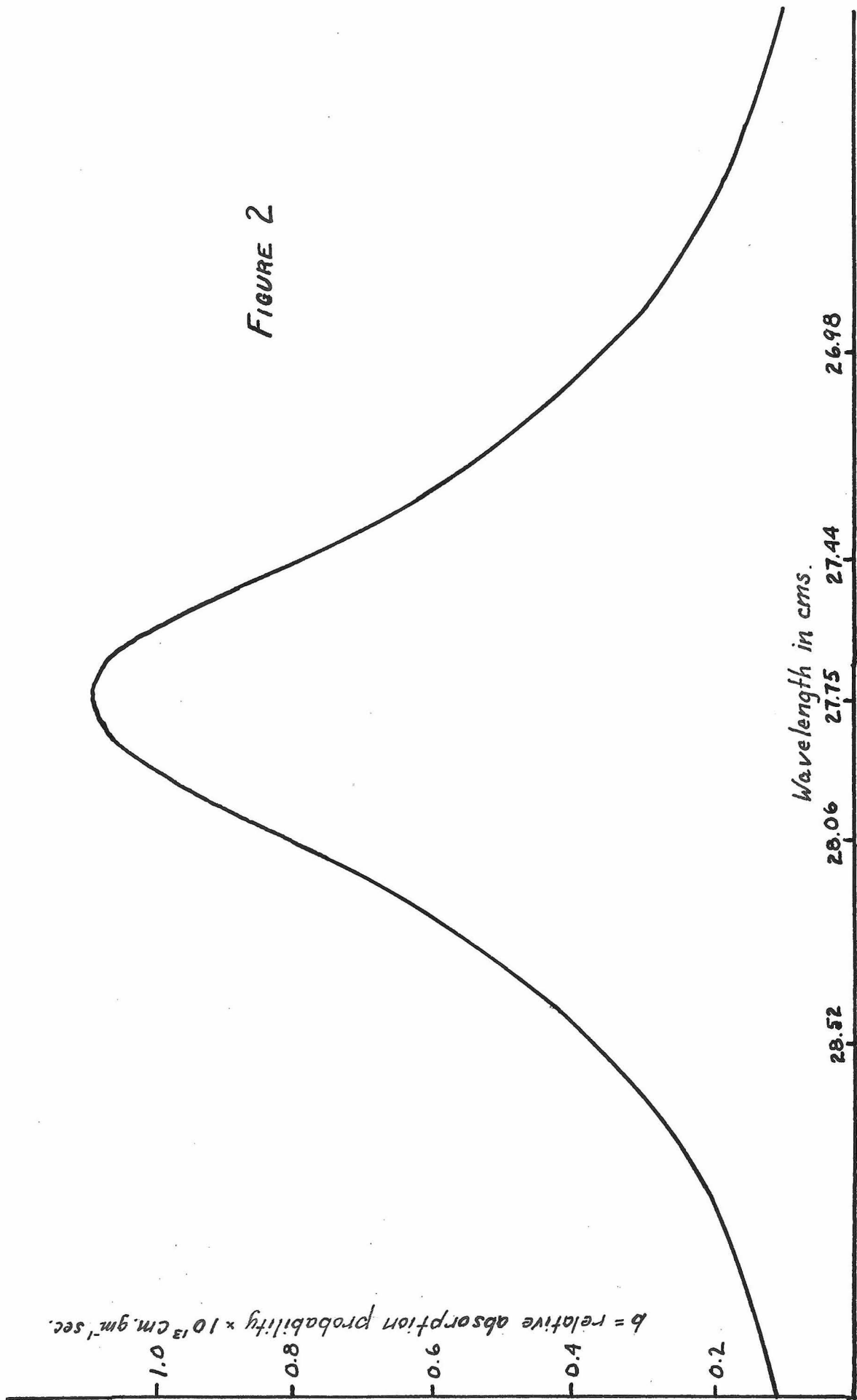


FIGURE 2

a single process is finite and not monochromatic when expressed as a sum of monochromatic waves with a Fourier integral. Weisskopf and Wigner¹⁸⁾ find that the probability of absorption in the wave number range $d\sigma$ at σ (where σ is measured from the wave number given by Bohr's rule) is

$$b = \frac{B}{\pi\sigma_0} \frac{1}{1 + (\sigma/\sigma_0)^2} \quad \text{where} \quad \sigma_0 = \frac{1}{4\pi c} \left(\frac{1}{\tau(I)} + \frac{1}{\tau(II)} \right)$$

The quantities $\frac{1}{\tau(I)}$ and $\frac{1}{\tau(II)}$ are, respectively, the mean lives of levels I and II, which are defined in the following fashion:

$$\frac{1}{\tau(I)} = \sum_c A(I \rightarrow c)$$

where the summation of the A's is extended over all states of lower energy. Figure 2 shows as an example of a broadened absorption line the theoretical curve for the transition ($3p_{3/2} \rightarrow 3d_{5/2}$).

This finite width of an absorption line does not affect the validity of any of the conclusions arrived at in the preceding paragraphs. Nevertheless, for any attempted experimental absorption observations, it must always be kept in mind.

DESCRIPTION OF THE APPARATUS

The source of light used in this experiment is a simple discharge tube having cylindrical aluminum electrodes at the ends. The

18) Weisskopf and Wigner. Ztschr. f. Phys. 63, p. 54, 1930.

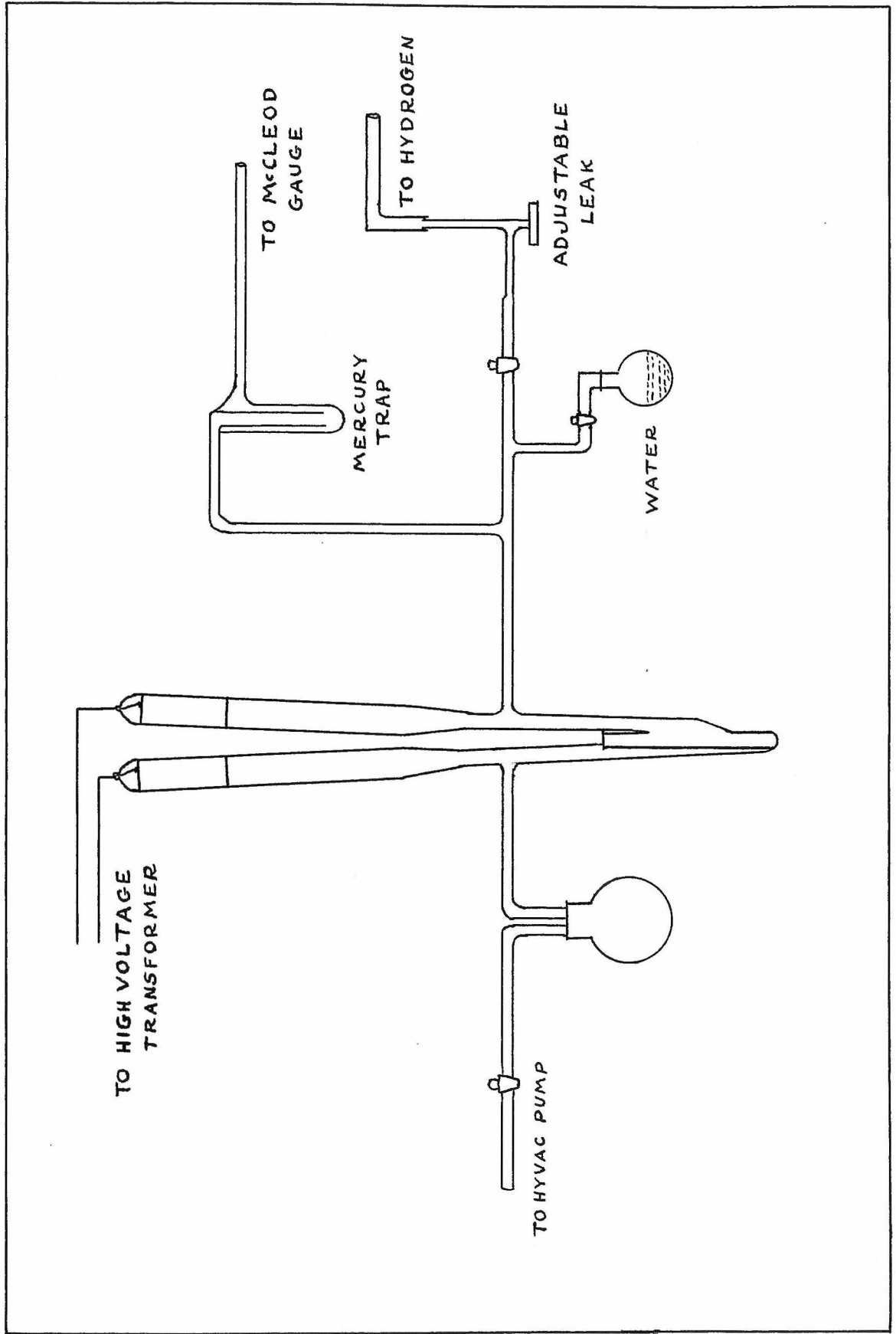


FIGURE 3

electrodes are 15. cm in length and 4 cm in diameter, and they fit the inside walls of the ends of the tube. The tube (of total length 220 cm) is bent in the form of a V, and the lower part is immersed in liquid air. A window was constructed so that one may look end on (at the portion of the discharge immersed in liquid air) for a distance of about 21 cm. The arrangement is indicated in Figure 3. The diameter of the immersed portion of the tube is 2.5 cm. By means of a mirror and a cylindrical lens, light from the cooled portion of the tube is thrown on the slit of the spectrograph.

Hydrogen is supplied continuously to the tube from a simple apparatus for the electrolysis of water. The hydrogen may be admitted to the system at any desired rate, by means of a variable leak, for whose suggestion and design my gratitude is due to Dr. W. R. Smythe¹⁸⁾.

In addition to hydrogen, water vapor may be admitted at will into the evacuated system from a sealed on bulb equipped with a stopcock. In practice it is found that the Balmer series comes out much more strongly when a considerable amount of water vapor is frozen on the inside of the walls in the cooled portion of the tube.

The pressure in the tube is measured by means of a MacLeod gauge which is connected (through a liquid air trap) to the tube in a place as close as possible to the portion of the tube seen from the spectrograph slit. In each run, the pressure was checked several times for constancy.

18) W. R. Smythe. Rev. Sci. Inst. 7, p. 435, 1936.

A steady flow of fresh hydrogen through the tube is maintained by constant pumping. A Hyvac oil pump is quite adequate since, with the intake leak nearly closed, the pressure soon becomes too low to allow any discharge.

Before each run the vacuum system was pumped down and flushed with hydrogen and distilled water vapor, so that the discharge (as seen through the spectrograph) was free from all impurities, such as air or mercury.

Excitation of the hydrogen is accomplished by means of a large neon sign transformer, which operates on the 60 cycle current and delivers 100 milliamperes. This transformer is rated at 15,000 volts, and is so compensated by a high-reactance secondary that it delivers practically constant current, even though the voltage output may vary to accommodate the load.

In designing the discharge tube, it was found to be very important that it include no sharp bends or constrictions, except the necessary one at the bottom. The tube first used (which has a 90° bend near each electrode) was melted through by cathode rays which originated in the cylindrical electrodes and were roughly focussed on the first bend in the tube. Although this effect occurred only at the lowest pressures, it had to be minimized, since it was of particular interest to make observations at these very pressures. The use of a very long, straight tube (the one described) and the practice of running the discharge intermittently at the lowest pressures proved to be a satisfac-

tory disposition of this difficulty.

The spectrographic apparatus is the usual arrangement for analysing hydrogen fine structure. A Fabry-Perot interferometer is included between the collimator lens and the prism in an ordinary prism spectrograph. The interferometer plates are 3.1 cm in diameter and their whole aperture is filled with light. Their separation is 7.3 mm. Just shortly before the interferometer plates were used in obtaining the results recorded in this paper, they were silvered by evaporation in an apparatus designed by Dr. J. D. Strong¹⁹⁾.

The slit of the spectrograph is only 9 mm long. This fact helps greatly in attaining uniform illumination of the slit. By the use of a camera of 55 cm focal length, however, the image of the slit was magnified about 3.3 times. In this way the effect of photographic plate grain was minimized.

If the spectrograms are to yield intensity ratios, intensity marks must be put on the photographic plates. This is accomplished by covering the slit of the spectrograph except a section 1 mm long in the center. The illumination of this very small area by an incandescent lamp placed about 40 cm away and operated on constant voltage D.C. results in a continuous spectrum on the photographic plate. Five such marks on each plate, corresponding to exposures of 1, 2, 4, 8, and 16 minutes gives an adequate intensity record for each wave-length. The times of these standard exposures are accurately measured by means of

19) J. D. Strong. Rev. Sci. Inst. 2, p. 189, 1931.

a stop watch. The exposures on the plate are so arranged that the intensity records are accurately lined up vertically (the plate holder being slid in a vertical track between exposures), and so that they fall between two pictures of the hydrogen spectrum which are to be analysed.

MEASUREMENTS AND RESULTS

The measurements consisted in making a microphotometer curve of each interference pattern and of the intensity marks put on each plate. This was done for H_{α} and for H_{β} at 5 different pressures, ranging from 0.70 mm to 0.043 mm. At pressures higher than 0.70 mm the structures did not come out very clearly, and there was considerable contamination of the pure Balmer spectrum by lines due to molecular hydrogen. The discharge could not be maintained at pressures lower than 0.043 mm with the voltage available from the transformer.

In order to interpret the peaks in the microphotometer curves it is first necessary to reduce their heights to numbers proportional to their intensities. Any convenient fiducial mark may be chosen as a base line from which to measure the height of the microphotometer curve. The heights of the curve for the various standard intensity marks are now plotted against the corresponding exposure times (1, 2, 4, 8, and 16 minutes), and a smooth curve is drawn through the five resulting points. Figure 4 is an example of such a curve. For convenience, the abscissae are plotted on a logarithmic scale. The

abscissae may now be taken as absolute intensities on an arbitrary scale, and curves such as Figure 4 serve as calibration curves for finding the absolute intensity equivalent to any measured height of the microphotometer curve. In this way, the height of every maximum in all the microphotometer curves was reduced to its corresponding intensity. In essence, this is a process of interpolation, the accuracy of which is enhanced by the fact that in every case only a small portion of the calibration curve was employed. The peaks of the microphotometer curves were measured on a comparator.

The average intensity ratio of the components of the line in question was now computed as follows: the peak intensity for each fringe was plotted against its distance from the center of the fringe system or from some other convenient zero. Figures 5 to 9 inclusive were plotted in this fashion. The points represented as circles represent the peaks corresponding to the short wave-length component, while the crosses correspond to the long wave-length component. A smooth curve was drawn through each group of points in each case (see Figs. 5 to 9), and the ratio of ordinates for each pair of curves was taken for six different abscissae. The mean of these six ratios is taken as the best value of the required result: namely, the intensity ratio of shorter wave-length component to longer wave-length component.

The results are summarized below:

| Pressure in millimeters of Hg. | Intensity Ratio | |
|---|-----------------|--------------|
| | Shorter | to Longer |
| 0.70 | 0.911 ± .007 | - |
| 0.43 | 0.967 ± .003 | 1 |
| 0.122 | 1.065 ± .005 | 1.112 ± .009 |
| 0.068 | 1.202 ± .024 | 1.125 ± .012 |
| 0.043 | 1.269 ± .004 | 1.131 ± .002 |

The uncertainties given are the means of the absolute values of the deviations. It should be noted that these results are the ratios of peak intensities, and hence are nearly, but not quite, an accurate measure of the ratio of integrated intensities.

DISCUSSION OF RESULTS

At least two conclusions of some importance may be drawn from the results recorded in the preceding section.

In the first place, they establish quite definitely that one may, with some hope of success, attempt the indirect method of observing absorption of ultra short waves in hydrogen. That the level populations must be definitely "abnormal" at all except the very highest pressures is evident from the results. At the lowest pressure, (0.043 mm) the observed intensity ratio for H_{α} is 1.27. This may be

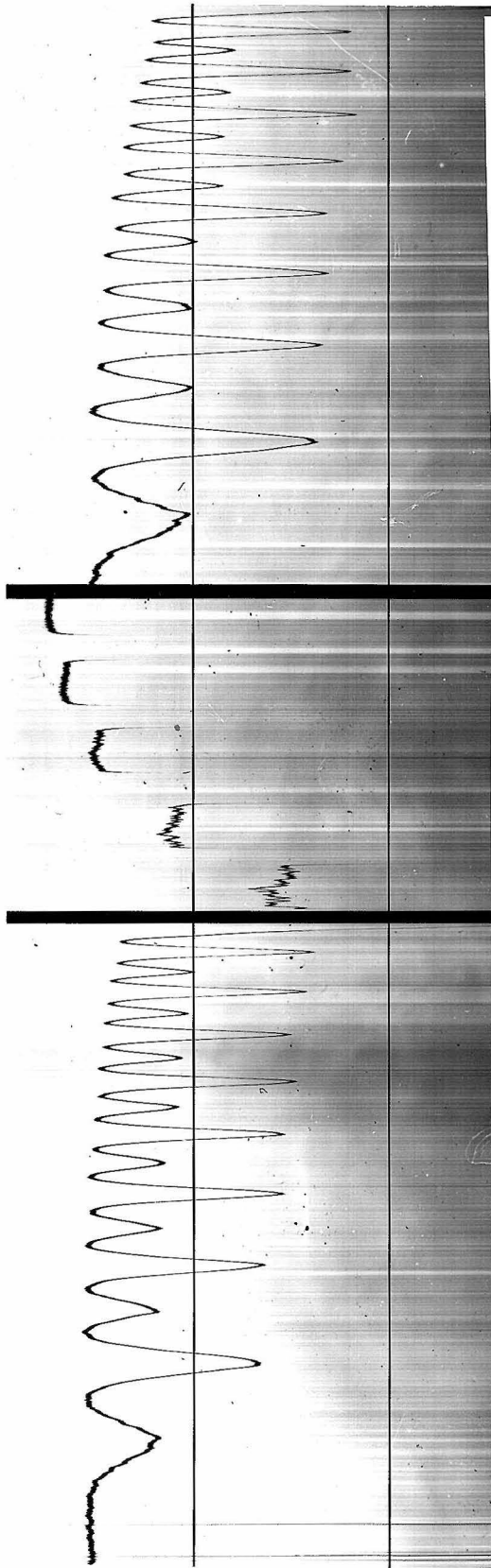
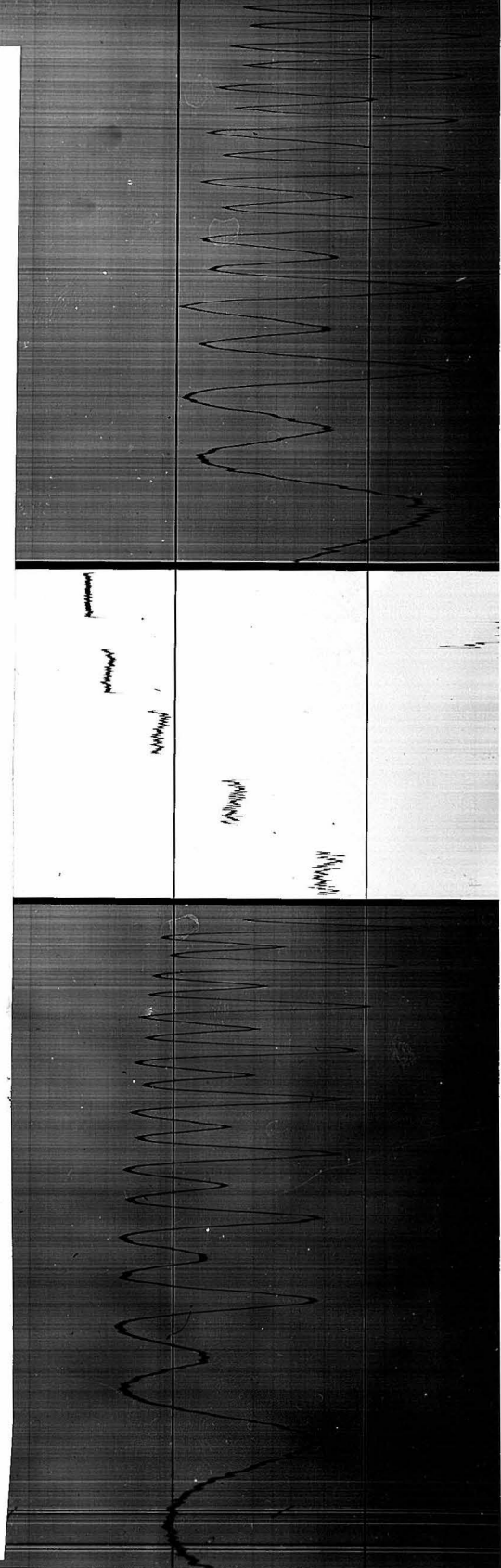


PLATE I MICROPHOTOMETER CURVES

Upper Left: H alpha at 0.043 mm. Upper Right: H alpha at 0.70 mm.
Lower Left: H alpha at 0.122 mm. Lower Right: H alpha at 0.068 mm.



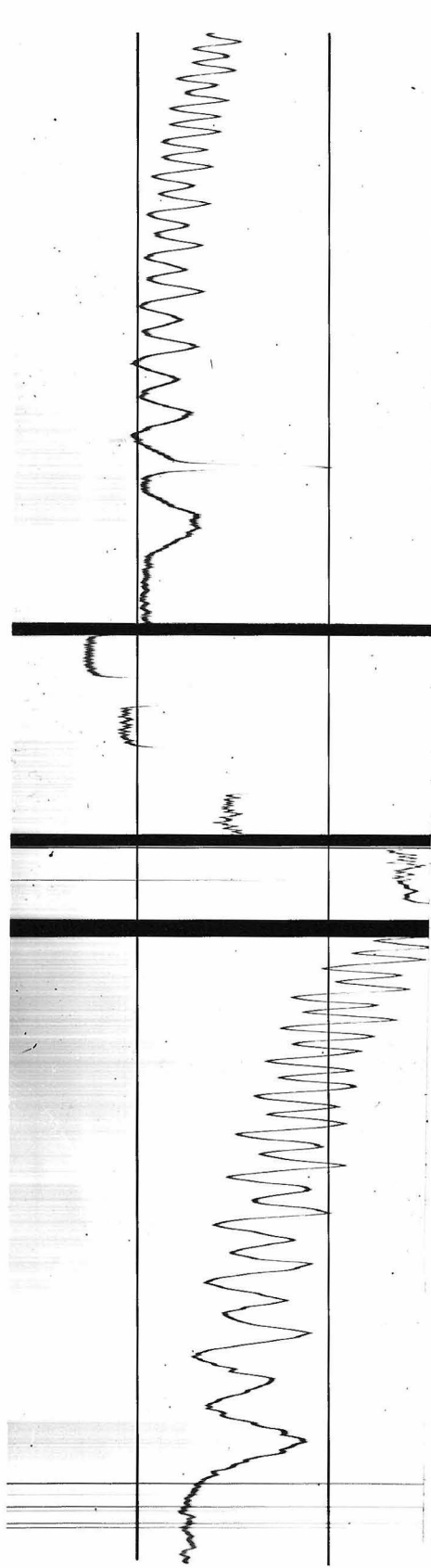
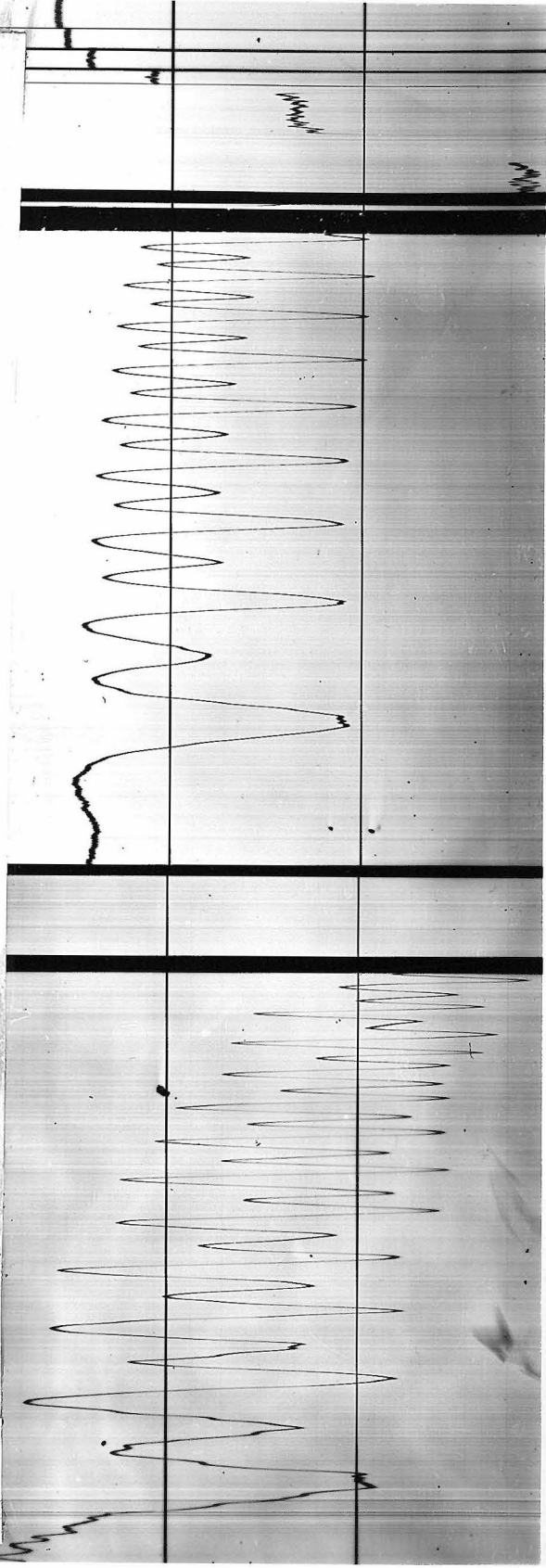


PLATE II MICROPHOTOMETER CURVES

Upper Left: H beta at 0.068 nm.
 Lower Left: H alpha at 0.043 nm.

Upper Right: H beta at 0.122 nm.
 Lower Right: H alpha at 0.043 nm.



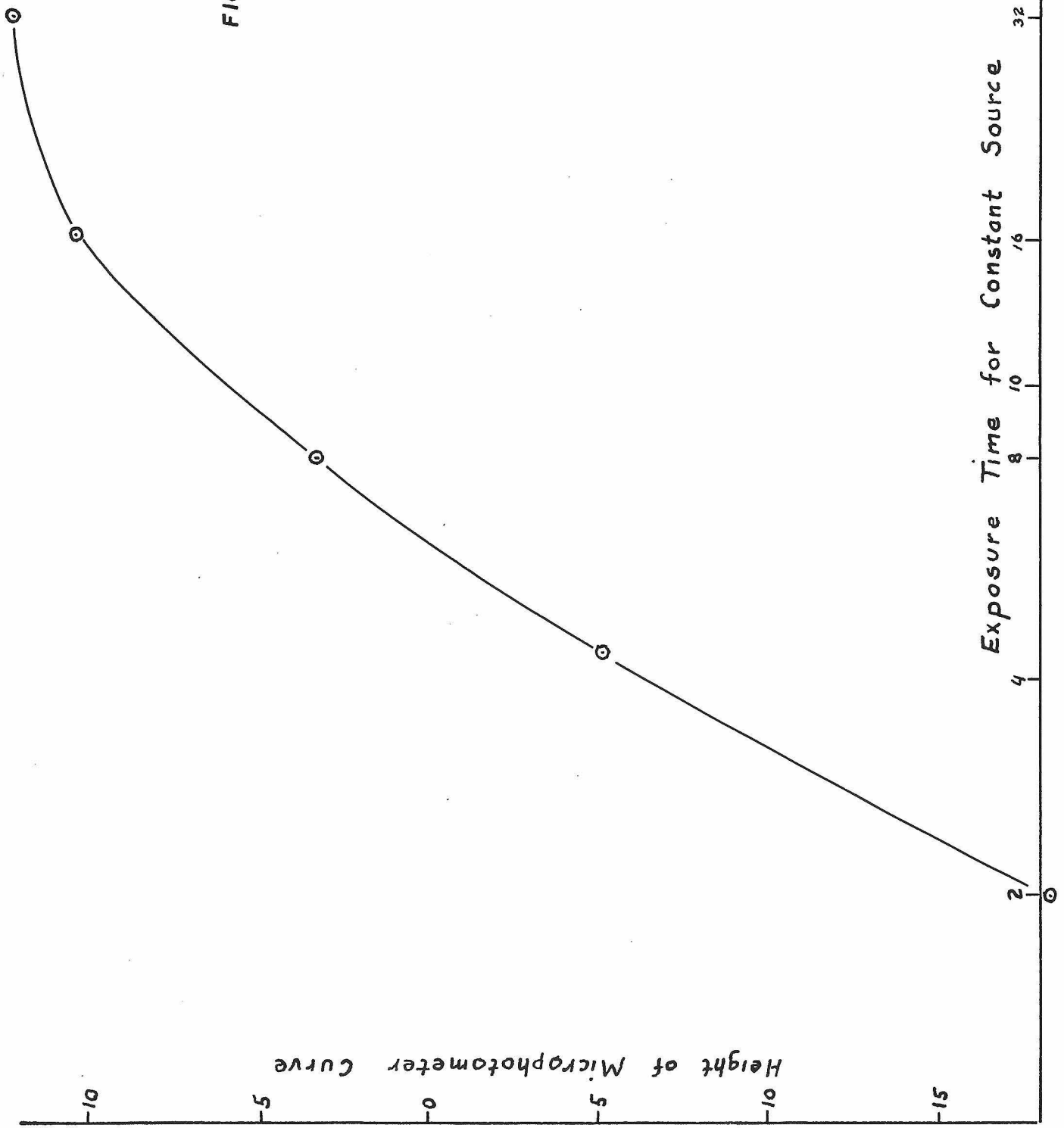


FIGURE 4.

FIGURE 5

Intensities for H_{α}

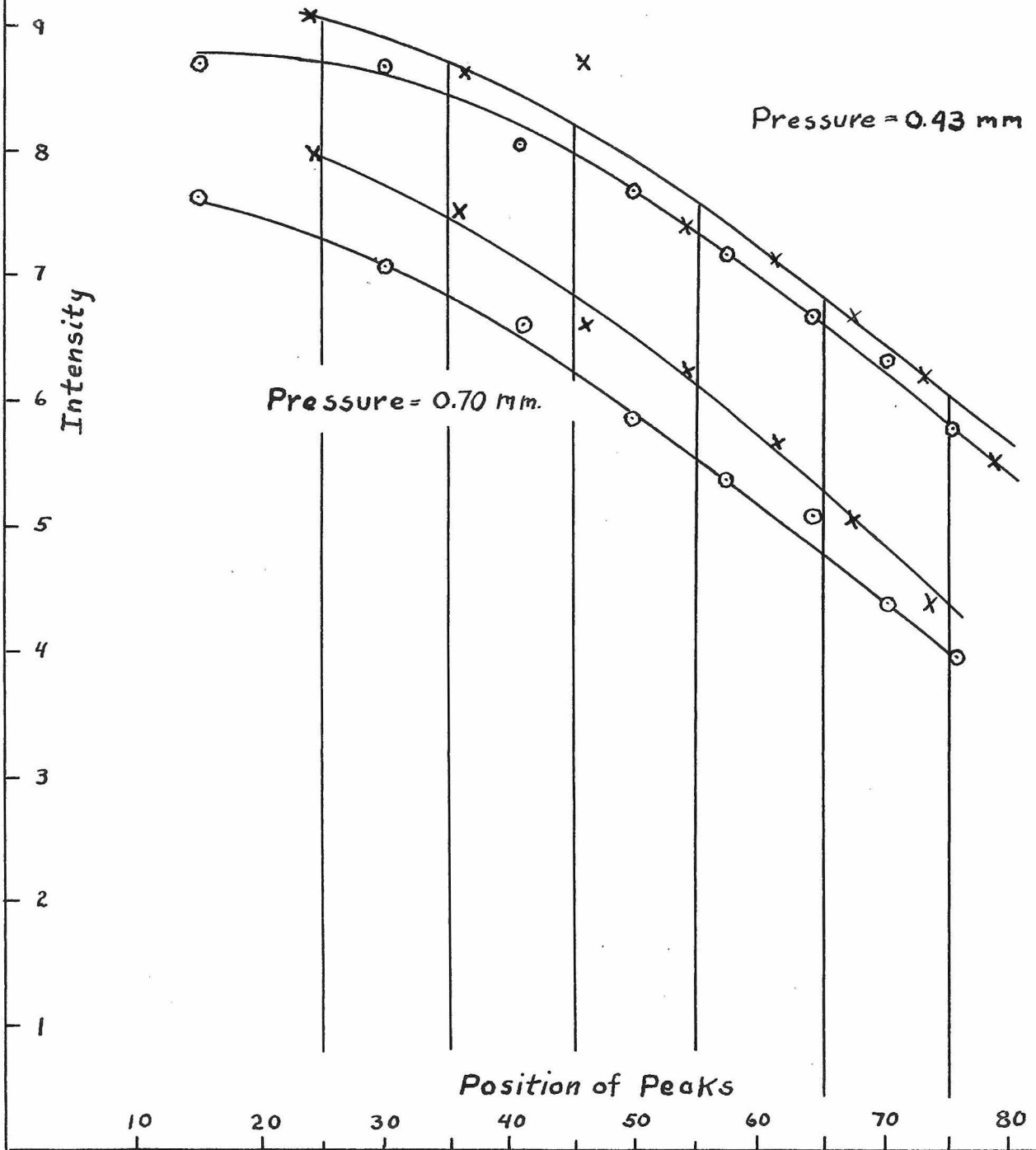


FIGURE 6

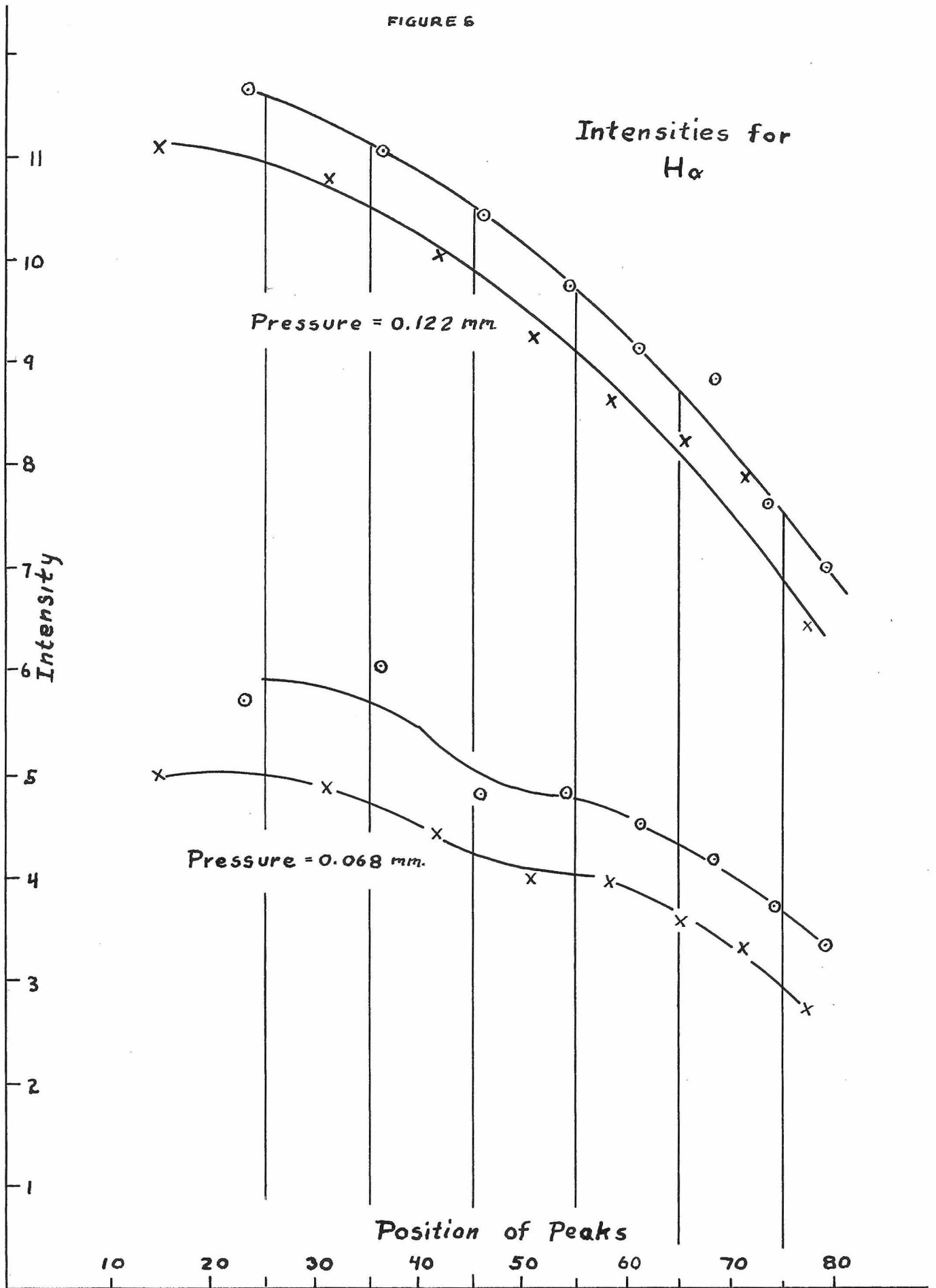


FIGURE 7

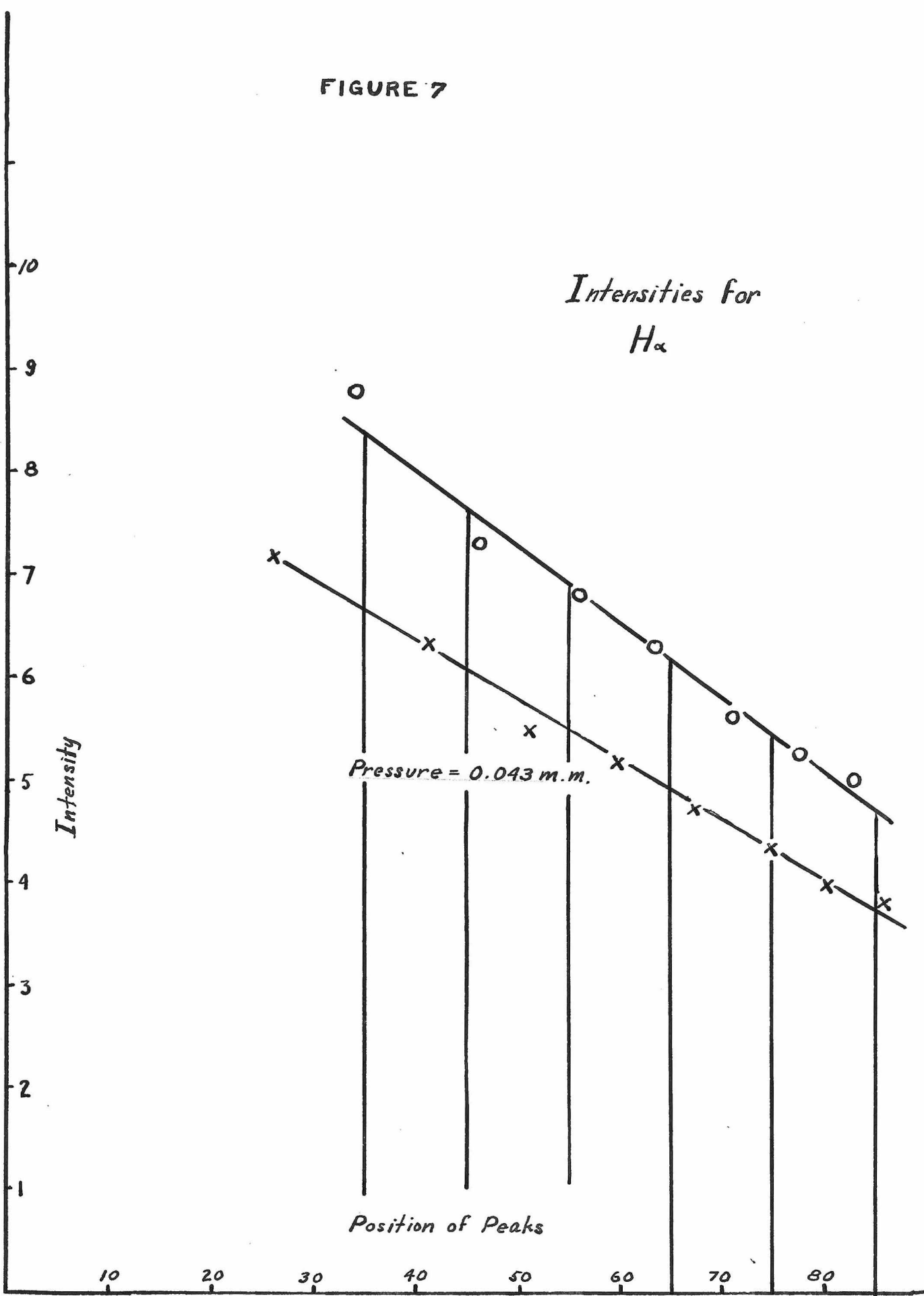


FIGURE 8

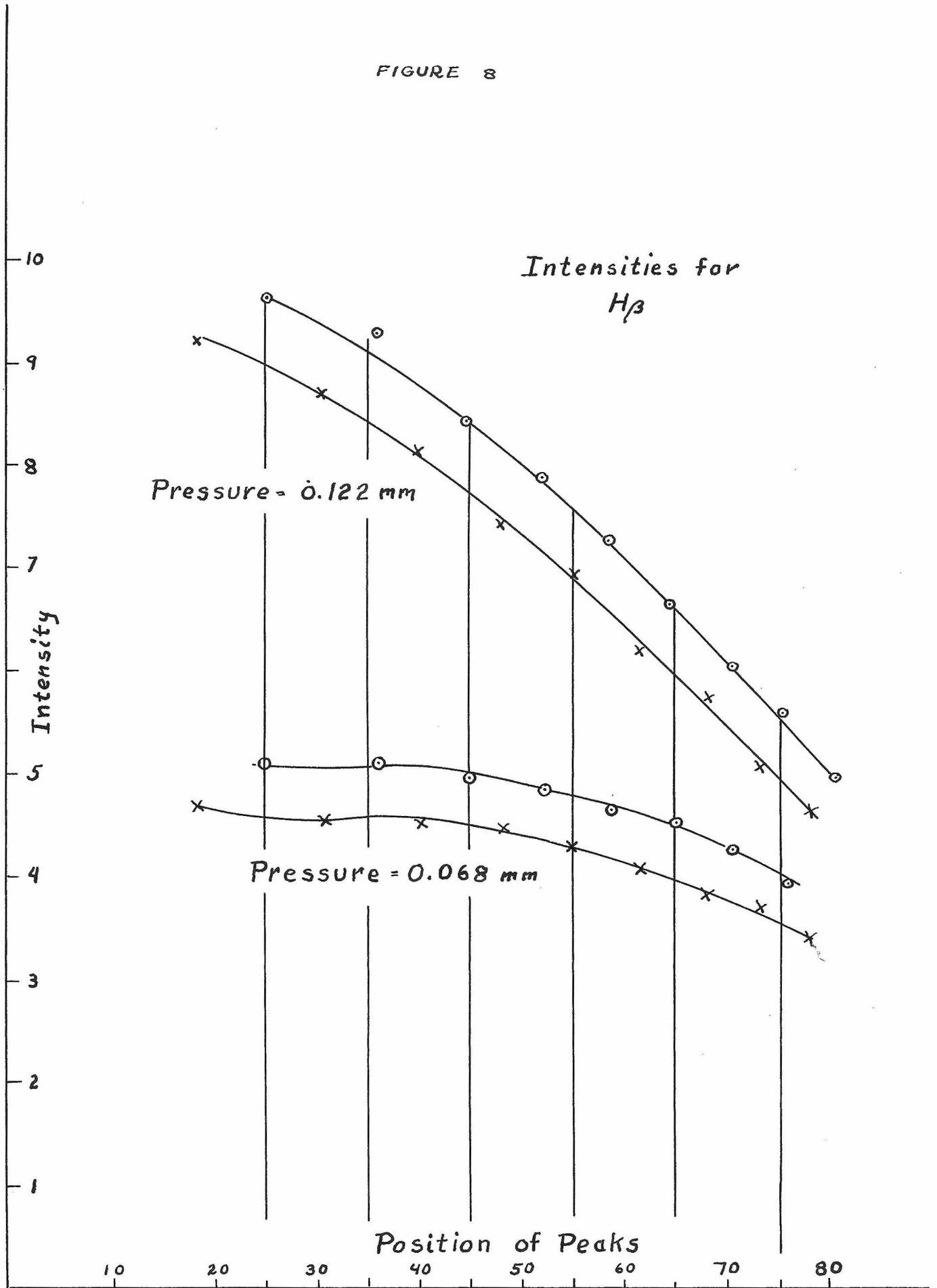
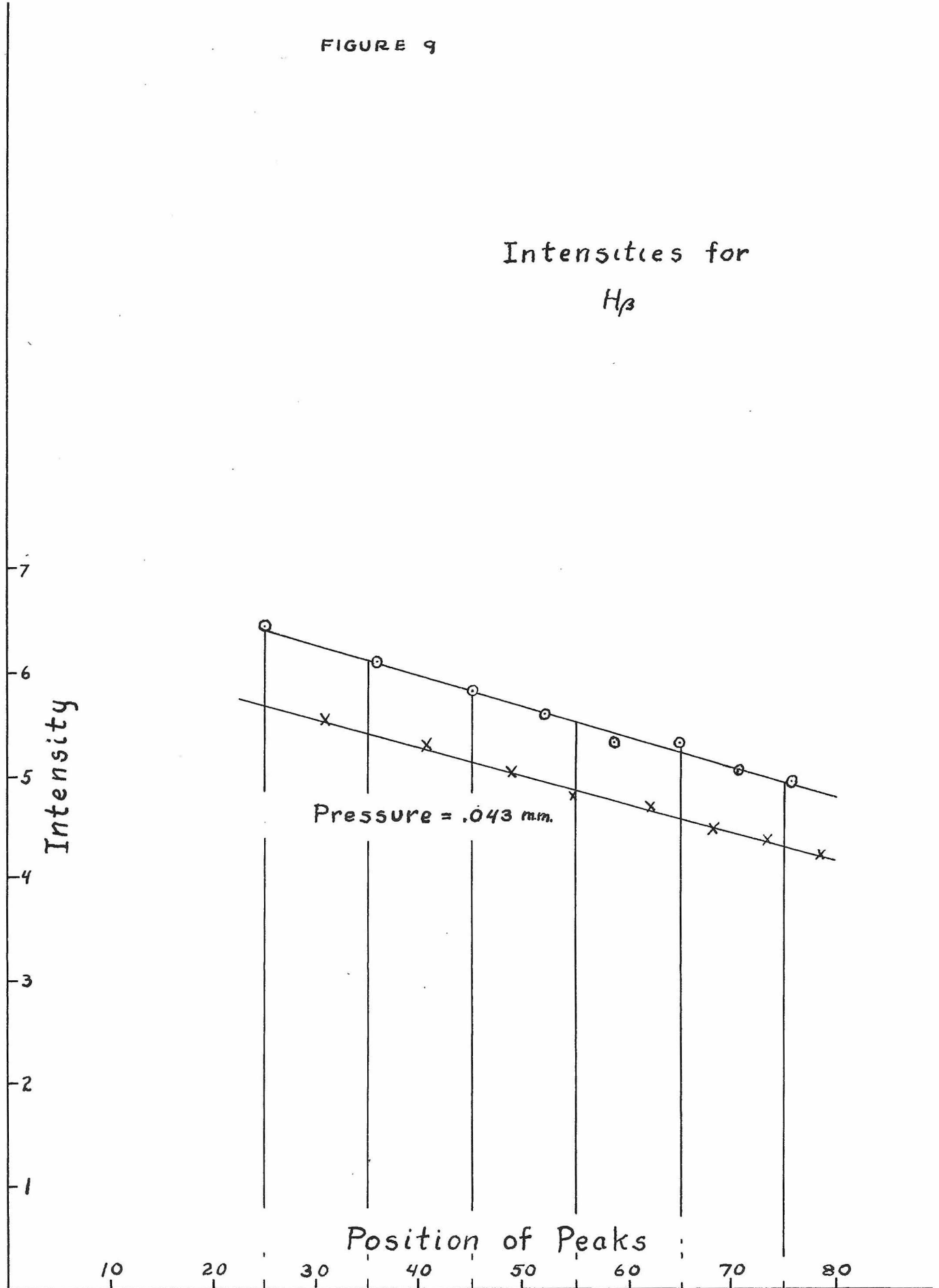


FIGURE 9

Intensities for
 $H\beta$



accounted for as a preferential excitation of the p levels by assuming a population for the p levels about 2.51 times the theoretical value. On this assumption Table 3 is rewritten as follows:

Table 4

| Shorter Transition | Component Intensity | Longer Transition | Component Intensity |
|---------------------------------|------------------------|---------------------------------|------------------------|
| $3d_{3/2} \rightarrow 2p_{1/2}$ | 3840 | $3d_{5/2} \rightarrow 2p_{3/2}$ | 6912 |
| $3p_{3/2} \rightarrow 2s_{1/2}$ | 4022 | $3d_{3/2} \rightarrow 2p_{3/2}$ | 768 |
| $3p_{1/2} \rightarrow 2s_{1/2}$ | 2011 | $3s_{1/2} \rightarrow 2p_{3/2}$ | 150 |
| $3s_{1/2} \rightarrow 2p_{1/2}$ | 75 | | |
| | Sum = 9948 | | Sum = 7830 |

$$\text{Intensity Ratio} = \frac{9948}{7830} = 1.27$$

Under such conditions it is easy to understand how Betz and Schneider might have observed directly the absorption of the 27.75 cm wave-length; for the reinforcement of the primary beam by induced emission could never completely compensate for absorption.

In connection with accounting for the observed intensity ratio at the lowest pressure, it is very interesting to examine the consequences of a suggestion made to the writer by Dr. I. S. Bowen concerning the theoretical mechanism of excitation. It is natural to suppose that (at the lowest pressures) the effect of collisions of excited

atoms in distributing them among the excited levels is practically nil. Supposing also that the excitation is accomplished in some non-preferential way, we may try the assumption that the rate at which atoms are supplied (through excitation) to any given level is simply proportional to the statistical weight of that level. Now, since no collisions while in excited states are allowed, the total intensities of transitions from each upper level must be proportional to the rate at which atoms are supplied to that level, and hence to the statistical weight of that level. This leads to the following table of intensities:

Table 5

| Shorter Transition | Component Intensity | Longer Transition | Component Intensity |
|---------------------------------|---|---------------------------------|------------------------|
| $3d_{3/2} \rightarrow 2p_{1/2}$ | 3840 | $3d_{5/2} \rightarrow 2p_{3/2}$ | 6912 |
| $3p_{3/2} \rightarrow 2s_{1/2}$ | 4608 | $3d_{3/2} \rightarrow 2p_{3/2}$ | 7768 |
| $3p_{1/2} \rightarrow 2s_{1/2}$ | 2304 | $3s_{1/2} \rightarrow 2p_{3/2}$ | 1536 |
| $3s_{1/2} \rightarrow 2p_{1/2}$ | 768 | | |
| | Sum = 11520 | | Sum = 9216 |
| | Intensity Ratio = $\frac{11520}{9216} = 1.25$ | | |

The intensities in this table are, of course, expressed in arbitrary units. The well known intensity rule which requires that

$$\frac{I(3s_{1/2} \rightarrow 2p_{1/2})}{I(3s_{1/2} \rightarrow 2p_{3/2})} = \frac{I(3d_{3/2} \rightarrow 2p_{1/2})}{I(3d_{5/2} \rightarrow 2p_{3/2}) + I(3d_{3/2} \rightarrow 2p_{3/2})} = \frac{1}{2}$$

has also been applied.

It is interesting to note that the ratio 1.25 obtained on the basis of these assumptions is almost exactly the ratio observed for the lowest pressure.

Finally, it is of importance to predict the nature of the change in intensity ratio which one might expect to occur as a result of absorption of the wave-length 27.75 cm, say. Let us suppose that in the beginning the intensity ratio is the observed value 1.27. Now the application of the 27.75 cm wave-length can in the most favorable case do no more than redistribute the atoms in the levels $3p_{3/2}$ and $3d_{5/2}$ in the ratio of the statistical weights of the levels. This state of affairs requires, then, that

$$\frac{I(3p_{3/2} \rightarrow 2s_{1/2})}{I(3d_{5/2} \rightarrow 2p_{3/2})} = \frac{1600}{6912}$$

where I stands for the intensity of the transition. If we apply this condition to Table 4, keeping the total intensity constant, we obtain

$$I(3p_{3/2} \rightarrow 2s_{1/2}) = 2054$$

$$I(3d_{5/2} \rightarrow 2p_{3/2}) = 8880$$

This changes the ratio of total intensities in Table 4 from 1.27 to

0.814. If, on the other hand, we suppose that the true explanation of abnormal intensity ratio is contained in Table 5, then we obtain (for this table)

$$I(3p_{3/2} \rightarrow 2s_{1/2}) = 2166$$

$$I(3d_{5/2} \rightarrow 2p_{3/2}) = 9354$$

This changes the ratio of total intensities in Table 5 from 1.25 to 0.779.

Thus, which ever interpretation one prefers to give to the observed abnormal intensity ratios, it certainly should be possible, given a sufficiently intense source of ultra short waves, to produce an appreciable change in this ratio.

A simple calculation gives an idea of the order of magnitude for the energy density of radio waves necessary to produce an appreciable effect. Again we will consider the absorption of 27.75 cm waves. Let us denote the level $3p_{3/2}$ by the subscript 1, the level $3d_{5/2}$ by the subscript 2, and the level $2p_{3/2}$ by the subscript 3. Then

$$N b_{21} = \text{number of absorption processes } (3p_{3/2} \rightarrow 3d_{5/2})$$

$$N_2 b_{21} = \text{number of induced emission processes } (3d_{5/2} \rightarrow 3p_{3/2})$$

$$N_2 A_{23} = \text{number of spontaneous emission processes } (3d_{5/2} \rightarrow 2p_{3/2})$$

$$\rho = \text{radiation density of 27.75 cm waves.}$$

The value of b_{21} (the relative absorption probability) is taken from Figure 2.

Let us take as the experimental ratio

$$\frac{N_1}{N_2} = \frac{4}{6} \times 2.51$$

and let us use the theoretical values

$$b_{12} = 1.08 \times 10^{13} \text{ cm. gm}^{-1} \text{ sec} = \frac{6}{4} b_{21}$$

$$A_{23} = 0.643 \times 10^8 \text{ sec}^{-1}$$

Now let us suppose the extremely favorable case

$$\rho (N_1 b_{12} - N_2 b_{21}) = 10 \times N_2 A_{23}$$

i.e. the net rate of transitions to level 2 as a result of absorption is ten times the rate of transitions in the strong spontaneous emission ($3d_{5/2} \rightarrow 2p_{3/2}$). Solving this equation gives

$$\rho = 5.9 \times 10^{-5} \text{ ergs per cm}^3$$

for the required energy density of the radiation field. Certainly the required intensity for a source of continuous ultra-short waves is not of too large an order of magnitude.

In conclusion, the results of this work have shown that it appears entirely feasible to carry out the experiment for which this work lays the foundation: namely, the observation of intensity-ratio changes in the Balmer line fine structure as a result of the absorption of ultra short waves.

ACKNOWLEDGMENTS

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