The Internal Intensity Ratio of H_{α} and of D_{α}

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A Geissler-Wood discharge tube was designed for use as the light source of H_{α} or D_{α} line. The tube was cooled in liquid air under low pressure to reveal the fine structure of the spectral lines. Four different separations, 7.6, 7.8, 8.0, and 8.2 mm, were used in the Fabry-Perot interferometer. Ten spectroscopic plates were measured for H_{α} and ten others for D_{α} . The internal intensity ratio of H_{α} and of D_{α} was found to be 0.808 ± 0.004 and 0.803 ± 0.003 , respectively, as compared to the theoretical value of 0.806. This study indicates that the experimental value of the intensity ratio between the two main component groups agrees with the theoretical value when pure hydrogen or pure deuterium gas is used in the discharge tube and the discharge is at its maximum intensity.

I. INTRODUCTION

`HE theoretical relative intensities of the fine structure components of the first Balmer line of hydrogen, H_{α} , were calculated by Sommerfeld and Unsöld¹ on the basis of Schrödinger's wave mechanics. In applying Dirac's relativistic quantum theory of electron to determine the intensity distribution of the H_{α} components, Saha and Banerji² obtained identical results. At least to the first approximation, the fine structure of D_{α} , 6561A, may be assumed to be the same as that of H_{α} , 6563A, because deuterium is an isotope of hydrogen. Detailed description of the theoretical structure of the H_{α} and D_{α} lines, including the separations of the components, has been published.³ Experimentally, only two main components were clearly and definitely resolved from the five components predicted in the theory. It was found by some observers⁴ that the relative intensities of the two main components depended largely upon the conditions of excitation and had little relationship to the theoretical value. In some cases, the intensity of the supposed weaker component was observed to be equal to or even

greater than that of the stronger component of the theory.

This paper describes a further study on the intensity ratio between the two main component groups of the H_{α} and D_{α} lines.

II. THE LIGHT SOURCE FOR H_{α} OR D_{α}

In the first stage of this work, an electrodeless hydrogen discharge tube⁵ excited by a high frequency oscillator was tried. It was found to have several disadvantages. One of these was observed in trying to photograph the H_{α} line through a Fabry-Perot interferometer. The hydrogen discharge tube was not able to provide an H_{α} line of sufficient intensity to give a satisfactory interferometer spectrogram. Furthermore, the discharge in the tube produced a circular image on the spectrograph slit, which caused the latter to be unevenly illuminated. A third disadvantage arose from the large bore of the tube. Its diameter of one inch was too large for efficient cooling of the hydrogen gas inside, and the H_{α} line thus obtained was not as sharp as desired. Therefore, another hydrogen discharge tube was designed.

A. The Discharge Tube and Its **Cooling Method**

There appears in Fig. 1 the new hydrogen discharge tube inside a Dewar flask. It resembled a Geissler tube in that its central part consisted of a 6-cm long capillary. To insure a rapid cooling of the tube in liquid air, a thin-walled capillary

^{*} Now at the Research Laboratory, U. S. Naval Ord-¹ A. Sommerfeld and A. Unsöld, Zeits. f. Physik **36**, 259

^{(1926);} **38**, 237 (1926). ² M. Saha and A. C. Banerji, Zeits. f. Physik **68**, 704

^{(1931).} ³ W. V. Houston and Y. M. Hsieh, Phys. Rev. 45, 271

⁶ W. V. Houston and Y. M. Hsten, Phys. Rev. **45**, 271 (1934); R. C. Williams, Phys. Rev. **54**, 559 (1938); J. W. Drinkwater, O. Richardson, and W. E. Williams, Proc. Roy. Soc. **A174**, 165 (1940). ⁴ W. V. Houston, Astrophys. J. **64**, 88 (1926); R. C. Williams, Phys. Rev. **54**, 563 (1938); J. W. Drinkwater, O. Richardson, and W. E. Williams, Proc. Roy. Soc. **A1**74, **175** (1040)

^{175 (1940).}

⁶ C. W. Hsueh, Rev. Sci. Inst. 14, 251 (1943).

having a bore of 3 mm and outer diameter of 5 mm was chosen. By concentrating the discharge in a narrow space, the capillary had the advantage of increasing the intensity of H_{α} . The new tube also had some of the features of a Wood's discharge tube in being longer than the Geissler tube and having a smaller diameter. A transformer was used to run it. The voltage drop across the tube was about 1200 volts, and the power consumed by the tube was approximately 20 watts. The tube was protected from overheating by means of two 9000-ohm resistors connected in series.

Inasmuch as the light emitted from the capillary discharge was used for taking spectrograms, the construction of the capillary needed special consideration. In general, when a discharge is run by a transformer or a generator, the hottest part of the tube is around the electrodes. Hence, to diminish the heating effect of the discharge on the central capillary of the tube, it is better to have the electrodes far away from the capillary. This was one of the features from the Wood's tube, which was adopted in our modification. To decrease the Stark effect at the capillary, the two ends of the tube were bent towards the same side of the capillary. The electric lines of force which joined the two electrodes would concentrate on one side of the tube without passing through the capillary, and, thereby, the electric field around the capillary was reduced.

In order to subdue the Doppler-effect broadening of the H_{α} and D_{α} lines and to make their fine structure observable, the discharge tube was cooled in rapidly evaporating liquid air which, because of its low temperature, cut down the temperature motion of the atoms. A schematic diagram of the cooling arrangement is shown in Fig. 1. Liquid air was contained in a Dewar flask of 4.5-liter capacity. The opening of the flask was closed with a brass cap and sealed airtight with layers of rubber tape and paintings of G. E. Glyptal No. 1202. A layer of wood, 2 cm thick, was placed under the cap to improve the heat insulation of the system. On top of the cap are connections to vacuum pumps and to the manometer, leads to the transformer, inlet for hydrogen or deuterium gas, and holes for pouring in liquid air. Experience proved that rapidly evaporating liquid air not only provided much

lower temperature than liquid air at atmospheric pressure but also lasted longer. This apparent paradox can be explained in the following way. The speed of evaporation of the liquid air in a Dewar flask depends upon the rate at which the surrounding heat is conducted into the liquid air. When liquid air is under low pressure and thus protected by a better insulation, the heat absorbed is less than that under atmospheric pressure.

The light of the capillary discharge situated at the bottom of the liquid-air flask was transmitted to the outside through a high vacuum window which was an evacuated and sealed glass pipe, 27 cm long and 5 cm in diameter. This highly evacuated window had the desirable quality of being a good transmitter of light and an excellent heat insulator at the same time. The lateral side of the glass pipe was covered with a layer of black tape to cut off stray light. The capillary of the discharge tube was placed under the vacuum glass pipe, perpendicular to the long axis of the latter. Thus, the line of observation was normal to the direction of the discharge current. Since observation was made in a direction perpendicular to the motion of the light-emitting atoms, the Doppler-effect broadening of the spectral line was further reduced.

Several precautions in the use of the tube may be mentioned. No liquid, like acids, alcohol, or water, should be used to clean the Geissler-Wood discharge tube, because liquid contaminates the tube and decreases the efficiency of producing the H_{α} line. After the tube had been used for a long time a decrease in intensity of the H_{α} line was also observed. This was due to accumulation



FIG. 1. The Geissler-Wood hydrogen discharge tube cooled in liquid air under reduced pressure.



FIG. 2. Generator for the deuterium gas.

of impurities condensed inside the tube. Sometimes the efficiency can be recovered by evacuating the tube at room temperature. If this method fails, then it is better to make a new tube since a good glass blower can make a new Geissler-Wood tube in a few hours. Because mercury vapor interferes seriously with the emission of a strong H_{α} line, care should be exercised to prevent mercury vapor from entering into the tube by means of an efficient liquid-air trap. The current used in exciting the tube was chosen in accordance with the time of exposure and the amount of hypersensitizing of the spectroscopic plate. For example, when the plate was baked for 26 hours at 50°C and the exposure time was 30 minutes, the discharge current for a newly made tube was around 14 milliamperes.

Many workers on the D_{α} line used only the vapor of heavy water (D_2O) in their discharge tube. Nevertheless, according to the author's experience, pure deuterium gas gave much stronger D_{α} line than the heavy water vapor, especially when cooled in liquid air. This was also true with the hydrogen line. Moreover, the intensity ratio of the two main component-groups would have almost the theoretical value when gas, rather than water vapor, was admitted to the tube. The work of Spedding, Shane, and Grace⁶ supported this fact. Therefore, pure deuterium and hydrogen gases were used throughout this work.

B. Preparation of the Deuterium Gas

The hydrogen gas used in the discharge tube was obtained from the electrolysis of water to which ten percent of concentrated sulfuric acid was added. The gas was purified by being passed through a liquid-air trap. In view of the scarcity of heavy water during the war, it did not seem feasible to prepare deuterium gas by means of electrolysis of heavy water, because too much of it was needed to fill the available electrolysis apparatus. Hence, another method of preparing the deuterium gas had to be developed.

Figure 2 shows the apparatus for generating deuterium gas from the reaction of deuterium oxide with sodium. The sodium metal was supplied by the Mefford Chemical Company of Los Angeles, and was kept in an airtight tin can free from oil. A few pieces of sodium were placed in the glass basket, 5 cm above the surface of heavy water. When the vapor of the deuterium oxide came into contact with the sodium metal, a chemical reaction took place liberating deuterium gas and depositing sodium deuteroxide (NaOD) on the surface. The sodium deuteroxide, similar to sodium hydroxide, has the property of absorbing water vapor. So the reaction continued until all the sodium which could be reached by the heavy water vapor changed into deuteroxide. The chief advantage of this method over the electrolysis procedure mentioned above was the economical use of heavy water. Only one gram of



FIG. 3. Photograph showing the interferometer spectrogram of the D_{α} , Cd, and Ne lines and the intensity marks. White color on the photograph corresponds to black color on the plate.

⁶F. H. Spedding, C. D. Shane, and N. S. Grace, Phys. Rev. 47, 39 (1935).

heavy water was required each time, thereby generating deuterium gas sufficient for ten days' work or longer.

The general procedure used for preparing deuterium gas is as follows: First, the apparatus was cleaned by evacuation until it was free from water or organic vapor. One gram or less of heavy water was poured into the deuterium generator, and two grams of clean sodium in small pieces were put in the glass basket. After replacement of the stopcock, the reaction chamber was partially immersed in liquid air which froze the heavy water and stopped the reaction. The apparatus was then evacuated again to remove any air enclosed. Removal of the liquid-air bath gave rise to generation of the deuterium gas. After sufficient gas was obtained, the apparatus was cooled again in liquid air. In so doing, the heavy water could be preserved for future use.

III. PROCEDURE FOR TAKING SPECTROGRAMS

The spectrograph used for taking spectrograms had a camera lens of 200 cm focal length. The dispersing system consisted of a plane reflection grating of 48,000 lines per inch, which was crossed by a resolving system consisting of a Fabry-Perot interferometer. In the interferometer were two circular optical flats which were 11.5 cm in diameter and heavily silvered. For studying the internal intensity ratio of the H_{α} and D_{α} lines, four different interferometer gaps, 7.6, 7.8, 8.0, and 8.2 mm, respectively, were used.

All exposures were made on the Eastman spectroscopic plates, type 103-H_{α} and size 5 in. \times 7 in. To increase the speed of the plates, each plate was hypersensitized by means of heat treatment⁷ a few hours before use. In the heat treatment, the plate was wrapped in layers of black paper and tin foil and packed in a cardboard box, which was placed in an electric oven kept at a temperature of 50°C for a period of about 26 hours. The exposure time for H_{α} or D_{α} was 30 minutes, during which time the temperature of the interferometer remained constant to within 1/20 of a degree centigrade. Immediately after that, the plate was exposed for another 30 minutes to the intensity-mark maker described in Section IV. Then it was developed in a high contrast Kodak ⁷ I. S. Bowen and L. T. Clark, J. Opt. Soc. Am. 30, 508 (1940).

developer, D-19, for 3.5 minutes with constant agitation. A short development time was chosen in order to reduce the fog or the background of the spectrogram to a minimum. Figure 3 shows a sample of the spectrogram. When not in use the red-sensitive spectroscopic plates were stored in a refrigerator in order to keep them from fogging.

IV. CALIBRATION OF SPECTROSCOPIC PLATES

The relation between the blackness of a photographic plate and the intensity of the incident light which caused that blackness is usually expressed by the characteristic curve of the plate, also called the H and D curve. This curve is determined by means of calibration with intensities of known ratio. One of the methods for producing the various intensities is the stepweakener. The stepweakener used in this work consisted of twelve holes on a brass block, 1.75 inches wide, 2.00 inches long, and 1.50 inches high. The diameter of the holes varied from 0.537 mm to 6.312 mm. The intensity of the light which reached the plate was proportional to the area of the hole through which passed the light, or to the square of its diameter. Each hole was covered by a small lens having a focal length equal to the height of the block, and on top of the twelve small lenses was a larger lens which covered all the twelve holes. Above the block was an illuminated square at a distance from the large lens equal to its focal length. Under the block was the spectroscopic plate to be calibrated. An image of the illuminated square was formed under each hole on the emulsion of the plate. After sufficient exposure and development, twelve or less photographs of the square appeared on the plate, each



FIG. 4. Arrangement for photographing intensity marks to calibrate the spectroscopic plate.

Plate no.	Interferometer separation, mm.	Intensity ratio I(23)/I(145)	Plate no.	Interferometer separation, mm.	Intensity ratio $I(23)/I(145)$
75	7.6	0.816	12	7.6	0.794
76	7.6	0.820	13	7.6	0.800
72	7.8	0.824	33	7.8	0.804
73	7.8	0.810	34	7.8	0.815
77	7.8	0.822	21	8.0	0.809
80	8.0	0.789	22	8.0	0.817
81	8.0	0.800	27	8.0	0.807
62	8.2	0.798	44	8.2	0.809
63	8.2	0.814	47	8.2	0.791
64	8.2	0.789	48	8.2	0.787
	Ν	√lean 0.808±0.004		I	Mean 0.803 ± 0.003

TABLE I. Internal intensity ratio for the H_{α} line.

displaying different degrees of blackness corresponding to the light intensity received. A sample of the intensity marks is shown at the bottom of Fig. 3.

The characteristic curve of a spectroscopic plate depends upon the time of exposure, development of the plate, and the wave-length of the incident light. In order to find the intensity of the H_{α} and D_{α} components accurately, the time of exposure for H_{α} or D_{α} and for the intensity marks was the same. The development factor also was expected to be identical because they were on the same plate. The light used to illuminate the square came from a G. E. 25-watt Mazda ruby lamp through a Wratten No. 29 F red filter. The spectrum of this red light source showed that the light from such an arrangement consisted of a narrow band with a central maximum at the H_a line, 6563A. Hence it was suitable for use in calibrating the plate in the spectral region around the H_{α} line. The red light was further covered



FIG. 5. Typical calibration curve of the spectroscopic plate 103-H_{α}.

with opal and ground glass to cut down the light intensity from the ruby lamp. This was required to match the intensity of the band emitted by the Mazda lamp with that of the H_{α} line. The detailed arrangement for photographing the intensity marks is illustrated in Fig. 4.

TABLE II. Internal intensity ratio for the D_{α} line.

In general, the H and D curve is obtained by plotting the optical density against the common logarithm of exposure. However, the purpose of this calibration was to find the relative intensity of the H_{α} and D_{α} components. For the sake of avoiding unnecessary steps such as reduction of the microphotometer readings to optical density and multiplication of the light intensity by the exposure time to get the value of exposure, the following simple procedure was adopted in obtaining the calibration curve of the spectroscopic plates. The intensities produced by the stepweakener were proportional to the area of the holes, and only the relative values of the various intensities were known. For convenience in plotting on the graph paper, the intensity through the largest hole was taken as 10 and the relative value of the intensity through the other holes was reduced in proportion to the square of their respective diameters. In measuring the blackness of the intensity marks, a microphotometer reading was taken for each square when the average reading of the background surrounding that black mark was made zero. In this way, the blacker intensity marks had larger microphotometer readings. Figure 5 shows a typical calibration curve of the spectroscopic plate, type $103-H_{\alpha}$. It was plotted on the log-log graph paper with the microphotometer reading as ordinate and with the relative intensity as abscissa.



FIG. 6. Microphotometer curve of the H_{α} line.

V. METHOD FOR FINDING THE INTENSITY RATIO

After the microphotometer curve of an H_{α} line or D_{α} line was made, the blackness of the intensity marks on the same plate was measured immediately on the microphotometer without changing any of its adjustments. With the microphotometer readings thus obtained, the calibration curve of the said spectroscopic plate was plotted according to the method described in Section IV.

Figures 6 and 7 show, respectively, the microphotometer curve of the H_{α} line and the D_{α} line. There are, in general, eight or ten orders of the interferometer pattern on each microphotometer curve. Each order of the interferometer pattern reveals the two main components of the line, which were clearly resolved. The two components were identified by measuring their respective wave-lengths. The red of the two apparent components which has a longer wave-length is called the (145) component group and the violet which has a shorter wave-length, the (23) component group. Explanation for this denomination will be given in Section VI. The wave-lengths in air of the apparent H_{α} components are 6562.85A for the component (145) and 6562.72A for (23), and those of the D_{α} components are 6561.07A for the component (145) and 6560.93 for (23).

The white line at the bottom of Figs. 6 and 7 gives the common background of the spectroscopic plate, and the height of the microphotometer curve above the white line represents the blackness of the spectral line. For each order of a line on the microphotometer tracing, the heights of the two maxima above the line of common background were measured. The mean maximum height of all the orders on one plate gave the average degree of blackness for the component-groups (145) and (23) respectively.



FIG. 7. Microphotometer curve of the D_{α} line.

The intensity corresponding to each average maximum height was found from the calibration curve of that spectroscopic plate, and from these intensity values the intensity ratio was computed. The values of the intensity ratio for the H_{α} and D_{α} lines appear in Tables I and II.

As pointed out by Williams and Gibbs,8 the intensity maximum of a complex spectral pattern does not always coincide with its center of gravity. For the component-group (23) of H_{α} , they computed the position difference as being equal to 0.007 cm^{-1} in comparison with their observed half-intensity width of 0.180 cm⁻¹. It appears then that the position difference is about 1/25 of the half-intensity width. For example, suppose the half-intensity width of a pattern shown on the microphotometer curve be 5 mm. The position difference between the center of gravity and the intensity peak of that pattern would be⁹ approximately 0.2 mm which, being of the same order of the experimental error in taking the microphotometer readings, may be neglected. Furthermore, in the neighborhood of the intensity maximum the variation of intensity is nearly zero. Therefore, as far as the measurement of the H_{α} or D_{α} intensity from the microphotometer curve is concerned, the intensity of the center of gravity may be considered to be identical with the intensity at the peak of the curve. In view of this fact, the procedure used in this study for finding the intensity ratio is justified.

VI. RESULTS AND CONCLUSION

All the spectrograms of H_{α} and of D_{α} employed in determining the intensity ratio were made

⁸ R. C. Williams and R. C. Gibbs, Phys. Rev. **45**, 476 (1934). ⁹ See the Appendix.

when the discharge in the Geissler-Wood tube was at its maximum intensity. That condition was ascertained by the purple red color of the capillary discharge and by the strong intensity of the red H_{α} or D_{α} line as viewed with a directvision spectroscope. Moreover, the resistance of the discharge tube was at the lowest value, because the discharge current was at its maximum as measured with a milliammeter when the voltage across the tube was set at a desired value and the gas pressure in the tube was varied. Ordinary hydrogen discharge is bluish in color, but when the discharge is strong the color becomes purple red. The pressure of the hydrogen gas in the discharge tube was observed to be about 0.4 mm Hg during the period of maximum discharge.

On the basis of either Sommerfeld's fine structure formula or Dirac's quantum theory of electron, it has been theoretically predicted that the H_{α} or D_{α} line should consist of five components. In agreement with Williams's assignment,¹⁰ they are named the components 1, 2, 3, 4, and 5 in the decreasing order of their intensity. However, on account of overlapping of the components, caused chiefly by the Doppler-effect broadening, only two groups of components can be clearly resolved. The group with the stronger intensity is composed of the components 1, 4, and 5 and has longer wave-length, while the weaker group is composed of the components 2 and 3 and has shorter wave-length. According to the theory, the value of the intensity ratio is given bv^{11} I(23)/I(145) = 0.806, where I(145) and I(23) denote the intensity of the center of gravity of the component groups (145) and (23), respectively.

For finding the experimental value of the intensity ratio, the method given in Section V was applied. The results are tabulated in Tables I and II, in which the deviation measure was computed by using an expression described in Holman's book.¹² The deviation measure is equal to the average deviation from the mean divided by the square root of the number of measurements.

The results of measurements on the intensity ratio between the two apparent main components of the H_{α} and D_{α} line indicate the following conclusion: The value of the internal intensity ratio obtained experimentally agrees with the theoretical value, when the discharge tube is filled with pure hydrogen or pure deuterium gas and the discharge is at its maximum intensity.

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APPENDIX

In the work done by Williams and Gibbs,⁸ the abscissa of their intensity curve denoted the wave number and the unit was cm⁻¹. As we were working on the microphotometer curve directly and the abscissa represented the radius of the interferometer fringes, the unit was mm. The relation between the wave number n and the radius R of the corresponding interference fringe can be expressed by the equation

$$n = (q/2df)(f^2 + R^2)^{\frac{1}{2}}, \qquad (1)$$

where q is the order of interference, d the gap of the Fabry-Perot interferometer, and f the focal length of the camera of the spectrograph. Differentiate n with respect to R, and we get

$$dn/dR = (q/2df)R(f^2 + R^2)^{-\frac{1}{2}}.$$
 (2)

Let Δn and ΔR be the half-intensity width of the intensity curve and of the microphotometer curve, respectively; let dn and dR be the position difference between the center of gravity and the intensity peak of the two respective curves. According to Eq. (2), we have approximately

$$\Delta n / \Delta R \approx (q/2df) R (f^2 + R^2)^{-\frac{1}{2}}$$
$$\approx dn/dR, \qquad (3)$$

where R represents the radius of interference fringe at the intensity peak. The approximation is due to the fact that Δn and ΔR are finite quantities and are not infinitesimal in comparison with R. From Eq. (3), we obtain

$$dR/\Delta R \approx dn/\Delta n. \tag{4}$$

 ¹⁰ R. C. Williams, Phys. Rev. 54, 559 (1938).
¹¹ W. V. Houston and Y. M. Hsieh, Phys. Rev. 45, 271 (1934).

¹² S. W. Holman, Discussion of the Precision of Measurements (John Wiley and Sons, Inc., New York, 1904), second edition, p. 18.



FIG. 3. Photograph showing the interferometer spectrogram of the D_{α} , Cd, and Ne lines and the intensity marks. White color on the photograph corresponds to black color on the plate.



FIG. 6. Microphotometer curve of the H_{α} line.



FIG. 7. Microphotometer curve of the D_{α} line.