

The Fine Structures of $H\alpha$ and $D\alpha$ Under Varying Discharge Conditions

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The fine structures of $H\alpha$ and $D\alpha$ have been observed under varying conditions of excitation in the discharge tube with pure hydrogen and pure deuterium maintained in each case at near liquid-air temperature, and with the aid of a Zeiss triple-prism spectrograph and a pair of Hilger quartz interferometer plates. The interference patterns obtained upon the photographic plates were analyzed with a Moll microphotometer. The microphotometer curves were reduced to intensity curves and to linear dispersion curves in the usual manner. From the final reduced curves analyses were made of the intensities and positions of the fine

structure components. Within the limits of error of the observations the positions of the fine structure components were found to be invariant with changing discharge conditions. The average interval between the two main components of the complex was found to be 0.319 cm^{-1} for $H\alpha$ and 0.321 cm^{-1} for $D\alpha$. The second and third most intense components were optically resolved from each other in $D\alpha$ but not in $H\alpha$. The average interval between these components was found to be 0.130 cm^{-1} . According to theory these intervals are respectively 0.328 cm^{-1} and 0.108 cm^{-1} .

INTRODUCTION

THE first recorded observation of the complex character of $H\alpha$ was made in 1887 by Michelson and Morley. They examined the visibility of the fringes of $H\alpha$ as formed by a Michelson interferometer, and concluded that the line possessed a doublet structure. The magnitude of this doublet interval has been reported by numerous investigators with values that differ widely.

In 1913 Bohr developed a theory for hydrogen, according to which the transitions of an electron from a quantized circular orbit having a quantum number 3 to one having a quantum number 2 is responsible for the $H\alpha$ emission. On this simple basis this transition would occur in only one way and the line would have no structure.

Refinements of the quantum theory and the advent of the relativistic wave mechanics have now resulted in a consistent picture of the formation of $H\alpha$, from which it is predicted that this line should consist of five components. Expressions for the relative positions and intensities of these components have been derived by Heisenberg and Jordan,¹ Darwin,² and Dirac.³ Computations of their relative intensities have been made by Sommerfeld and Unsöld,⁴ Kupper,⁵ and Saha and Banerji.⁶

The theoretical predictions agree in assigning to $H\alpha$ a fine structure as illustrated in Fig. 1. (The components are assigned numbers in the order of their intensities, and these numbers will be used in further reference to them.) Since deuterium is an isotope of hydrogen, the fine structure of $D\alpha$ is presumably the same, at least to a first approximation, as that of $H\alpha$. Fig. 2 shows the theoretical fine structure intensity pattern that should result for $D\alpha$ at a temperature of 100°K , if it is assumed that the line width is due solely to Doppler broadening. This is the chief factor affecting the shape of the spectral lines of either $H\alpha$ or $D\alpha$, since it is many times as great as the natural widths of the energy levels involved.

The pattern presented by the complex of the fine structure components of $H\alpha$ and $D\alpha$, as observed with high optical resolution, is generally called the *doublet* pattern. The two components chiefly responsible for the familiar doublet appearance are called the *major* components in this paper, while the three less intense ones are called *minor* components. The interval between the intensity maxima of the doublet pattern is called the doublet interval, or *peak-to-peak interval*. The intervals predicted by theory are those between the centers of the components, and are referred to as the *component-to-component* intervals. The doublet interval and the interval between the major components will usually differ slightly, because of the overlapping minor components. The term "center of gravity" is not

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¹ Heisenberg and Jordan, *Zeits. f. Physik* **37**, 263 (1926).

² Darwin, *Proc. Roy. Soc.* **A116**, 227 (1927).

³ Dirac, *Proc. Roy. Soc.* **A117**, 610 (1928).

⁴ Sommerfeld and Unsöld, *Zeits. f. Physik* **38**, 237 (1926).

⁵ Kupper, *Ann. d. Physik* **86**, 511 (1928).

⁶ Saha and Banerji, *Zeits. f. Physik* **68**, 704 (1931).

used in this paper, since there is usually no measurable point in an intensity complex corresponding to the ordinary definition of that term.⁷

Several investigations have been pursued in recent years with the object of checking experimentally the theoretical predictions of the positions and intensities of the fine structure components of both H α and D α . Since clear resolution has been obtained only for the two major components, comparable values can be listed only for the measured *doublet* interval. Table I lists the results of the more recent investigations.

EXPERIMENTAL PROCEDURE

A hydrogen discharge tube was used in which the pressure and current density could be measured, as well as the potential difference across the portion of the discharge from which the light was taken. It was believed that these

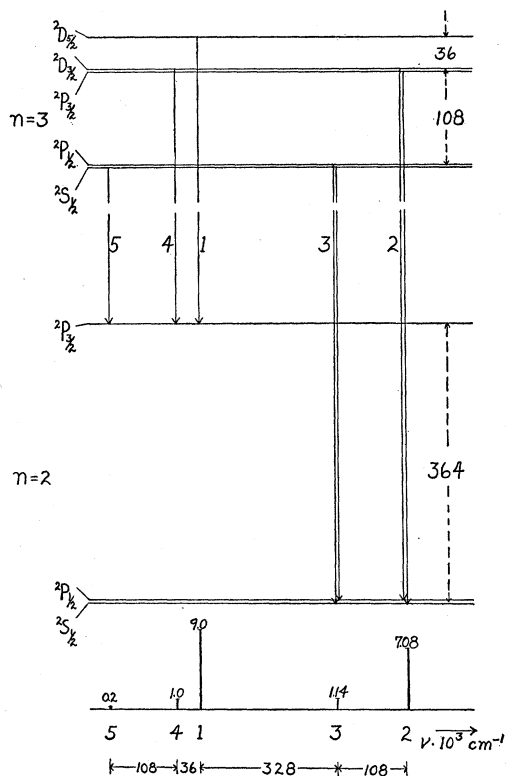


FIG. 1. Theoretical fine structure of H α .

⁷ See Williams and Gibbs, *Phys. Rev.* **45**, 475 (1934) for a discussion of the distinction between the position of the center of gravity and the position of the maximum intensity of a complex spectral pattern.

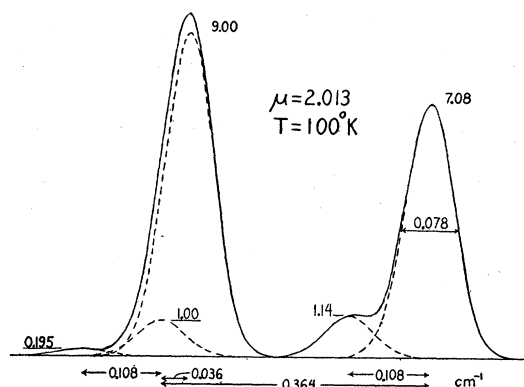


FIG. 2. The fine structure intensity pattern of D α at a temperature of 100°K. The pattern is drawn from the theoretical positions and intensities of the components.

three variables would have the chief influence, if any, upon the component separations and intensities, although the effect of the addition of a large percentage of helium gas to the pure hydrogen gas, and the effect of a longitudinal magnetic field were also investigated. A primary consideration in this investigation was to insure that enough plates be taken for each discharge condition to eliminate the possibility of any real variations being masked by accidental errors of measurement. Since each plate contained enough fringes to allow six independent determinations of the peak-to-peak interval to be made, it was decided that four plates for each discharge condition would be sufficient. Three values of pressure in the discharge tube were selected, and for each value of the pressure, two values of the current density. Nearly the same pressure and current density values were used for both pure hydrogen gas and pure deuterium gas.

The source of radiation was a liquid-air-cooled, modified Wood tube of 8 mm internal diameter, which is described in detail in an earlier publication.⁸ Two electrodes were inserted through the glass at the ends of the U-section from one side of which the light was taken in order to allow the potential difference across this part of the tube to be measured. An electrostatic voltmeter was used to measure the potential difference, and consequently the discharge was not appreciably affected while the readings were being taken.

The discharge tube was connected through a liquid-air trap to a McLeod gauge by means of

⁸ Williams and Gibbs, *Phys. Rev.* **45**, 475 (1934).

TABLE I. *Recent measurements of the doublet interval in H α and D α .*

| INVESTIGATOR | YEAR | DOUBLET INTERVAL IN CM ⁻¹ | |
|--|-----------|--------------------------------------|------------|
| | | H α | D α |
| Houston and Hsieh ¹ | 1934 | 0.312 | |
| Williams and Gibbs ² | 1934 | 0.304 | 0.317 |
| Kopfermann ³ | 1934 | | 0.323 |
| Spedding, Shane and Grace ⁴ | 1934 | 0.314 | 0.318 |
| Williams and Gibbs (Unpublished) | Dec. 1934 | 0.314 | 0.318 |
| Heyden ⁵ | 1937 | | 0.331 |

¹ Houston and Hsieh, *Phys. Rev.* **45**, 263 (1934).

² Williams and Gibbs, *Phys. Rev.* **45**, 475 (1934).

³ Kopfermann, *Naturwiss.* **22**, 218 (1934).

⁴ Spedding, Shane and Grace, *Phys. Rev.* **47**, 38 (1935).

⁵ Heyden, *Zeits. f. Physik* **106**, 499 (1937).

which the pressures in the tube were determined. Both hydrogen and deuterium were available in very nearly 100 percent concentrations, and reservoirs containing these were attached either separately or jointly to the discharge tube through two stopcocks. The pressure of the gas in the tube could be regulated very easily, and maintained over a long period at any desired value.

The source of excitation was a 20,000 volt Thordarson transformer with a variable resistance in series with the primary. An a.c. milliammeter was placed in the secondary circuit in series with the tube, so that the current values could be recorded. Thus it is seen that the three important variables: pressure, current density, and potential gradient were known for every discharge condition.

The optical equipment was a triple-prism spectrograph made by Zeiss, with a Hilger quartz Fabry-Perot étalon placed in the parallel beam of the collimator. Eastman 4-C photographic plates were used, which proved to be relatively fast and almost entirely free from grain. It was the general experience that more trouble was caused in the microphotometering process by dust settling on the plates while drying than by plate grain. The Eberhard effect was eliminated practically by using fine-grain plates and agitated development, and by keeping the density of the photographic image moderately low.

In order to calibrate the plates for their density-intensity relation, an arrangement was provided for impressing intensity marks upon each plate. This was done by placing in front of the slit a box containing an electric lamp, and

having a window covered with two layers of ground glass. The intensity of illumination on the plate was controlled by varying the slit widths. This method is a standard one⁹ and needs no justification other than to point out that the slit readings must be reduced by 0.02 mm to allow for the diffraction losses at the slit jaws, and that slit readings less than 0.06 mm should not be used. For the readings lower than this, the intensity is not proportional to the slit readings as corrected above. When the slit openings are large there is considerable overlapping of regions of the spectrum fairly far apart, and if the spectral intensity distribution in the region used is far from uniform, serious error can be introduced by using too wide a slit. In the spectral region used for intensity marks in this investigation ($\lambda 6600$ — $\lambda 6300$) the combined effects of intensity-lamp energy distribution, transmission of the spectrograph, and sensitivity of the plate produced a region of nearly uniform effective sensitivity, and consequently little error was introduced by using a slit as wide as 1 mm.

Plates were taken of H α and D α at pressures of 1.2×10^{-1} , 3.1×10^{-1} , and 2.5 mm of mercury. For each pressure, plates were taken for two values of the current density: 15 and 40 ma/cm². It was found that a discharge could not be maintained at a pressure appreciably below 1.2×10^{-1} mm, and for a pressure greater than 2.5 mm the α -lines were so weak that usable pictures could not be obtained. Exposures varied from 2 to 55 minutes. The nominal étalon spacing was 5 mm for the H α and the D α plates, and was obtained with great accuracy from interference fringes of neon lines.

In analyzing an intensity complex, a proper choice of étalon separation is most important. Inasmuch as both the resolving and dispersive power of the interferometer increases with increasing plate separation, as large a value as possible of this quantity should be used. But if so large a spacing is used that the fringes begin to overlap, the resultant confusion of intensities makes the analysis most difficult. Accordingly a separation was selected just large enough that the intensity complex of a given interference order does not overlap appreciably on the pattern of the next order. In the case of H α

⁹ G. R. Harrison, *J. Opt. Soc. Am.* **24**, 59 (1934).



FIG. 3. Interferometer fringes of D α obtained with a 5 mm étalon spacing.

and D α , the total measurable width of the complex is about 0.750 cm^{-1} and 0.650 cm^{-1} respectively. An étalon separation of 5 mm results in a $\Delta\nu$ between orders of 1.0 cm^{-1} . Hence the H α or D α patterns will not overlap on adjacent interference orders, and the intensity of the fringe pattern will approach zero very closely between orders. The result of this selection is shown in Fig. 3, which is a photograph of a fringe pattern of D α . Fig. 4 shows a microphotometer record of such a pattern. As can readily be seen, the intensity pattern is at the constant value zero for a considerable interval on both sides of the complex. Of course, a 5 mm étalon does not have the optical resolving power of a 7.8 mm étalon as used by other investigators. But for a reflectivity of 90 percent from the silvered plates, the resolving power of a 5 mm étalon is at least 400,000. Because of the broadening of the H α and D α fringes by thermal agitation in the discharge, however, the maximum resolving power that can be obtained for D α is about 150,000, and for H α , about 90,000. Hence a highly silvered 5 mm étalon has a resolving power considerably in excess of the necessary minimum.

MEASUREMENT OF THE PEAK-TO-PEAK INTERVALS

The interval between components 1 and 2 of the H α or D α intensity complex was determined by measuring the peak-to-peak interval, and then applying certain corrections made necessary by the overlapping minor components. The separation in cm^{-1} in the fringe system of a Fabry-Perot étalon between two fringes is $\Delta\tilde{\nu} = \Delta p / 2d \cos \theta$, where Δp is the difference in order of interference between the two fringes, d is the spacing of the étalon plates in cm, and θ is the mean angle that the fringes make in the case of close fringes with the center of the fringe system as viewed from the camera objective. Since d and θ are known or can be measured, $\Delta\nu$ is determined after Δp is known. The dispersion of the Fabry-Perot étalon

fringe system is not linear, but varies in such a way that the linear distance on the photographic plate between a fringe and the center of the fringe system is very nearly proportional to the square root of the order difference between the fringe and the center of the system.

Actually, however, the relation connecting orders of interference with radii of fringes is not an exact square-root relation, because of possible optical distortions in the optical system. An accurate, although laborious, method of determining the Δp between two fringes of the same integral order of interference is to use an equation of the type

$$y = A + Bx + Cx^2 + Dx^3 + \dots,$$

where y represents the order of interference of a certain wave-length λ_1 , counted from an arbitrary zero fringe, and x the corresponding linear distance on the plate of the fringe measured from the same zero. Three fringes of λ_1 , are selected at a time, and the three constants A , B and C determined. It has been found by repeated trial that the value D is negligible with the Zeiss spectrograph used. With the constants determined for a set of three orders of interference, the fractional order of interference (Δp) between λ_1 and another fringe of a slightly differing wave-length can be determined by solving for y in the above equation.

This method supposes the experimental curve connecting order number with fringe diameter to be parabolic in short sections, when the value of

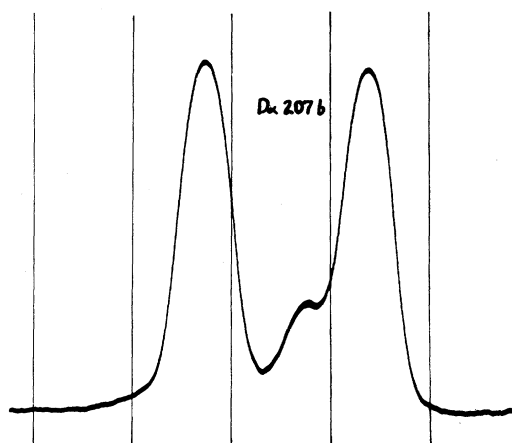


FIG. 4. Microphotometer tracing of part of the fringe pattern shown in Fig. 3.

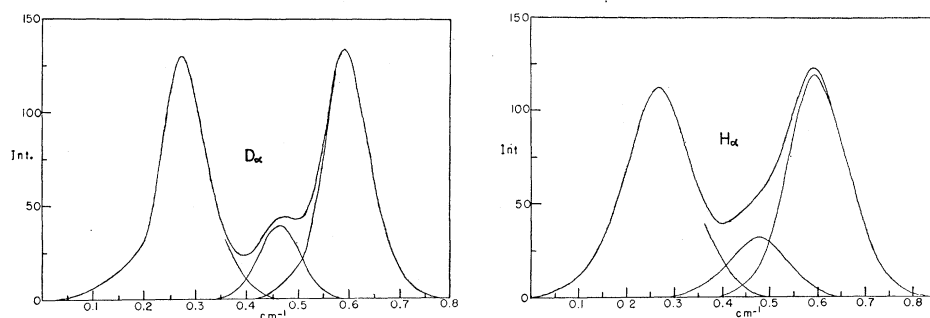


FIG. 5. Typical intensity curves obtained for $H\alpha$ and $D\alpha$.

D is neglected, but allows the equation of the parabola to change at every set of three fringes used. Less serious error will be introduced by this method of computing, in case the fringe system is not strictly parabolic, than will be introduced in computing by the so-called "standard" method, or by the one suggested by Tolansky.¹⁰

The fringe radii were determined by measuring their diameters and dividing by two. A Moll microphotometer was used as a measuring engine, and diameter readings taken at the position of maximum deflection of the galvanometer. This method of measurement proved surprisingly accurate as judged by the smallness of accidental errors, chiefly owing to the fine grain of the plates and the proper exposures of the photographic images.

REDUCTION OF MICROPHOTOMETER CURVES TO INTENSITY CURVES

From each series of five plates taken under identical discharge conditions, two sets of fringes were selected to be microphotometered. The fringe selected was number 3 in most cases, since it was found that the intensity distribution along the length of the slit image was sensibly constant at fringe 3. Microphotometer records were obtained in the usual fashion. The same width of thermocouple slit was used that was used in the measurement of the peak-to-peak intervals. The microphotometer curves were re-traced by use of an enlarging camera on cross-section paper. The density-intensity curve was placed on the same sheet of paper, and the reductions to intensity curves made. These

curves were corrected to linear dispersion in the usual fashion, and resulting typical curves for $H\alpha$ and $D\alpha$ are shown in Fig. 5.

COMPONENT-TO-COMPONENT INTERVALS

The purpose of plotting true intensity curves of the $H\alpha$ and $D\alpha$ complexes is to determine values of relative intensities, and to determine line shapes, from both of which corrections for displacements may be computed to apply to the measured peak-to-peak interval in order to yield the major component-to-component interval. The problem of corrections is the most critical one in the determination of component intervals, and unfortunately is a problem not susceptible to precise nor definite calculation. The corrections can be arrived at only after certain rather limited assumptions are made which are not directly open to test.

The method of analyzing the curves so as to obtain the corrections to the measured peak-to-peak intervals is fairly completely described in a previous article,¹¹ and was modified in the present research only in one major respect: Inasmuch as the $D\alpha$ patterns showed a resolution of components 2 and 3, the intensity complexes of this isotope were analyzed first. This increased resolution has made possible for the first time the direct measurement of the interval between components 2 and 3. The interval so found for $D\alpha$ was used in the analysis of the patterns of $H\alpha$, since these components were not resolved for the latter isotope. This differs from the previous work, in which this interval was taken as about 0.108 cm^{-1} , from theoretical considerations.

The general results of this investigation are

¹⁰ Tolansky, *J. Sci. Inst.* **8**, 223 (1931).

¹¹ Williams and Gibbs, *Phys. Rev.* **45**, 475 (1934).

TABLE II. *Component separations in H α .*

| PLATE No. | PRES-SURE (mm Hg) | CURRENT DENSITY (A/cm ²) | P.D. (V/cm) | DOUBLET INTERVAL (cm ⁻¹) | HALF-INT. BREADTH (cm ⁻¹) | INTENSITIES RELATIVE TO THEORY | | CORRECTIONS | | | | INTERVALS | | |
|-----------|-------------------|--------------------------------------|-------------|--------------------------------------|---------------------------------------|--------------------------------|----------------|---------------------|--------|---------------------|--------|-----------|--------|---|
| | | | | | | I ₁ | I ₃ | COMP. 1 | | COMP. 2 | | | | |
| | | | | | | | | (cm ⁻¹) | DUE TO | (cm ⁻¹) | DUE TO | | | |
| 201a | 0.12 | 0.015 | 20-30 | 0.3153 | 0.150 | 0.67 | 1.70 | -0.0039 | 4 | +0.0050 | 3 | 0.316 | | |
| 201b | | | | 0.3130 | | | | +0.0010 | 3 | | | | | |
| 201c | | | | 0.3148 | | | | -0.0039 | 4 | | | | 0.0045 | 3 |
| 201e | | | | 0.3140 | | | | +0.0010 | 3 | | | | | |
| 202b | 0.12 | 0.040 | 20-40 | 0.3149 | 0.160 | 0.70 | 1.45 | -0.0039 | 4 | 0.0045 | 3 | 0.318 | | |
| 202c | | | | 0.3178 | | | | +0.0012 | 3 | | | | | |
| 202d | | | | 0.3162 | | | | -0.0041 | 4 | | | | 0.0042 | 3 |
| 202e | | | | 0.3183 | | | | +0.0011 | 3 | | | | | |
| 204a | 0.31 | 0.015 | 20-25 | 0.3090 | 0.165 | 0.79 | 1.80 | -0.0041 | 4 | 0.0082 | 3 | 0.316 | | |
| 204b | | | | 0.3108 | | | | +0.0015 | 3 | | | | | |
| 204c | | | | 0.3108 | | | | -0.0041 | 4 | | | | 0.0082 | 3 |
| 204d | | | | 0.3113 | | | | +0.0015 | 3 | | | | | |
| 205a | 0.31 | 0.040 | 24 | 0.3134 | 0.165 | 0.82 | 1.85 | -0.0041 | 4 | 0.0082 | 3 | 0.319 | | |
| 205b | | | | 0.3136 | | | | +0.0015 | 3 | | | | | |
| 205c | | | | 0.3153 | | | | -0.0041 | 4 | | | | 0.0082 | 3 |
| 205d | | | | 0.3119 | | | | +0.0015 | 3 | | | | | |
| 203a | 2.50 | 0.040 | 100 | 0.3096 | 0.180 | 0.90 | 1.90 | -0.0042 | 4 | 0.0090 | 3 | 0.315 | | |
| 203b | | | | 0.3060 | | | | +0.0028 | 3 | | | | | |
| 203c | | | | 0.3074 | | | | -0.0043 | 4 | | | | 0.0100 | 3 |
| 203d | | | | 0.3077 | | | | +0.0030 | 3 | | | | | |

TABLE III. *Component separations in D α .*

| PLATE No. | PRESSURE (mm Hg) | CURRENT DENSITY (A/cm ²) | P.D. (V/cm) | DOUBLET INTERVAL (cm ⁻¹) | HALF-INT. BREADTH (cm ⁻¹) | INTENSITIES RELATIVE TO THEORY | | CORRECTIONS | | | | INTERVALS | | | |
|-----------|------------------|--------------------------------------|-------------|--------------------------------------|---------------------------------------|--------------------------------|----------------|---------------------|--------|---------------------|--------|-----------|--------|---|-------|
| | | | | | | I ₁ | I ₃ | COMP. 1 | | COMP. 2 | | | | | |
| | | | | | | | | (cm ⁻¹) | DUE TO | (cm ⁻¹) | DUE TO | | | | |
| 210a | 0.14 | 0.015 | 20-30 | 0.3224 | 0.120 | 0.74 | 2.3 | -0.0038 | 4 | +0.0015 | 3 | 0.134 | | | |
| 210b | | | | 0.3224 | | | | -0.0038 | 4 | | | | 0.0015 | 3 | 0.132 |
| 210c | | | | 0.3229 | | | | -0.0038 | 4 | | | | 0.0015 | 3 | |
| 210d | | | | 0.3260 | | | | -0.0038 | 4 | | | | 0.0015 | 3 | |
| 209a | 0.14 | 0.030 | 20-40 | 0.3218 | 0.125 | 0.75 | 2.1 | -0.0038 | 4 | 0.0020 | 3 | 0.133 | | | |
| 209b | | | | 0.3220 | | | | -0.0037 | 4 | | | | 0.0011 | 3 | 0.135 |
| 209c | | | | 0.3230 | | | | -0.0037 | 4 | | | | 0.0011 | 3 | |
| 209d | | | | 0.3221 | | | | -0.0037 | 4 | | | | 0.0011 | 3 | |
| 207a | 0.31 | 0.015 | 20 | 0.3217 | 0.120 | 0.79 | 2.2 | -0.0038 | 4 | 0.0015 | 3 | 0.135 | | | |
| 207b | | | | 0.3212 | | | | -0.0038 | 4 | | | | 0.0012 | 3 | 0.126 |
| 207c | | | | 0.3221 | | | | -0.0038 | 4 | | | | 0.0012 | 3 | |
| 207d | | | | 0.3212 | | | | -0.0038 | 4 | | | | 0.0012 | 3 | |
| 206a | 0.31 | 0.040 | 24 | 0.3205 | 0.127 | 0.89 | 2.0 | -0.0038 | 4 | 0.0020 | 3 | 0.135 | | | |
| 206b | | | | 0.3208 | | | | -0.0038 | 4 | | | | 0.0019 | 3 | 0.136 |
| 206c | | | | 0.3200 | | | | -0.0038 | 4 | | | | 0.0019 | 3 | |
| 206c | | | | 0.3226 | | | | -0.0038 | 4 | | | | 0.0019 | 3 | |
| 208b | 2.50 | 0.040 | 100 | 0.3179 | 0.155 | 0.94 | 2.4 | -0.0041 | 4 | 0.0045 | 3 | 0.136 | | | |
| 208c | | | | 0.3177 | | | | +0.0008 | 3 | | | | | | |
| 208d | | | | 0.3186 | | | | -0.0041 | 4 | | | | 0.0035 | 3 | 0.137 |
| 208e | | | | 0.3171 | | | | +0.0008 | 3 | | | | | | |

contained in Tables II and III. Column 1 is plate number, and columns 2, 3 and 4 give the pressure, the current density, and the potential gradient in the discharge tube. Column 5 contains the measured peak-to-peak intervals in cm^{-1} . Each entry in column 5 is an average of the measurements of 6 fringes. Column 6 gives the half-intensity breadth in cm^{-1} , computed for those plates whose fringes were subjected to an intensity analysis. Column 7 contains the intensities of components 1 and 3, in terms of their theoretical intensities. Component 2 has here been taken arbitrarily as having standard intensity. Column 8 lists the corrections in cm^{-1} that are applied to the positions of the peaks to obtain positions of maxima of major components. These are listed in two sub-columns as corrections to peak 1, and corrections to peak 2. There is also listed after each correction the minor component to whose effect the correction is due. Column 9 gives the measured interval in cm^{-1} between the centers of components 2 and 3 for $D\alpha$. The last column contains the final value for the separation in cm^{-1} between the centers of component 1 and component 2. This column is, of course, the sum of column 5 and column 8.

Before discussing the results of the investigation the assumptions underlying the measurements and the probable upper limits of error will be noted. The chief source of error in the measurements is the evaluation of the corrections. The peak-to-peak interval can be measured with the photometric comparator to an estimated maximum error of 0.0005 cm^{-1} in the mean from a set of four plates. The mean is apparently affected only by accidental errors of measurement, for no systematic differences can be regularly observed from fringe to fringe, or from plate to plate.

The corrections necessary to reduce the position of an intensity peak to the center of the component almost directly under it are dependent upon four factors: The relative intensity of all components, the separations of the components, the value of the half-intensity breadth, and the similarity to a Doppler curve of the actual intensity curve of a component. It is assumed that the components are single in structure, all have approximately the same half-intensity breadth, and all have a shape somewhat similar to that of a Doppler curve.

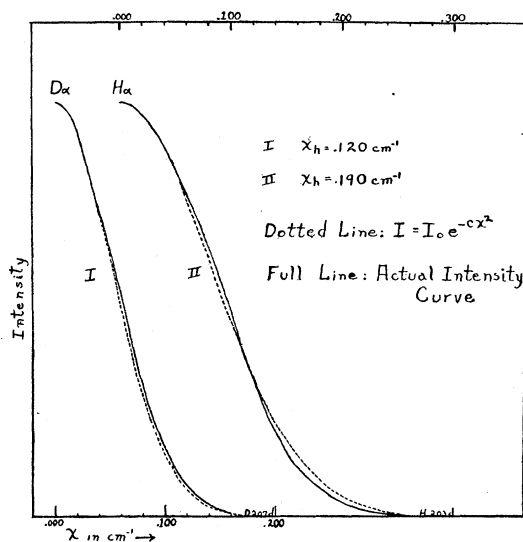


FIG. 6. A comparison of the intensity curves of the high frequency sides of $H\alpha$ and $D\alpha$ with Doppler curves of the same half-intensity breadth.

The intensities and positions of components 2 and 3 for $D\alpha$ are obtained by symmetry and subtraction, as mentioned previously. With the above assumptions granted, these values for $D\alpha$ are quite accurate. The positions and intensities of these components for $H\alpha$ are based on the hypothesis that the interval from component 2 to component 3 is the same for $H\alpha$ as for $D\alpha$. The assigned position of component 4 relative to component 1 for both $H\alpha$ and $D\alpha$ is a pure assumption that the theoretical value is reasonably correct. The intensity of this component is taken as the theoretical intensity relative to component 2, which has been arbitrarily considered as standard.

Neither the position nor intensity of component 5 would have any appreciable effect on the position of the intensity peaks, if the actual position and intensity of this component are even approximately those predicted by theory.

The assumption of singleness and similarity of all five components cannot be tested. The similarity of the actual curve to the theoretical Doppler curve has been tested by comparing the undisturbed, high frequency side of the $H\alpha$ and $D\alpha$ complexes with a Doppler curve of the same half-intensity breadth. The result of this is shown in Fig. 6. Comparisons are here shown for the smallest and the largest half-intensity breadth met with in this research. It is seen

that the two curves are practically the same, particularly near their tops. It must be remembered that the slope of these curves enters into the corrections, and in places where the slope is almost zero the percent difference in slope between the theoretical and actual curve could be quite large. In the region of small values of the slope near the top of the curves the slope is approximately proportional to the displacement from the center of the component. Hence a 100 percent deviation of the true slope from the Doppler curve slope would introduce an error of $\pm 0.007 \text{ cm}^{-1}$ in the correction of peak 2 and a $\pm 0.003 \text{ cm}^{-1}$ in the correction of peak 1 for H α , and considerably less than half these values for D α . The actual corrections for peaks 1 and 2 are opposite in sign, however, and thus it would seem that the net maximum error due to this cause would be on the order of $\pm 0.004 \text{ cm}^{-1}$ for H α and $\pm 0.002 \text{ cm}^{-1}$ for D α .

The errors in the corrections to peak 1 would be largely due to the error introduced in the placing of component 4 relative to component 1, and in assigning to it a theoretical intensity. The magnitude of the errors of the corrections, for both H α and D α , can be estimated from Table IV, where corrections are computed for various assumed values of the ratio of intensity of component 1 to component 4, and of the interval between components 1 and 4. The single-lined rectangle represents the most likely range

TABLE IV. Corrections to Component 1 due to Component 4. (Various hypotheses relative to intensity and separation are used.)

| I_1/I_4 | FOR HALF-WIDTH = 0.160 cm^{-1} (H) | | | | | | | |
|---|---|--------|--------|--------|--------|--------|--------|--------|
| | FOR HALF-WIDTH = 0.115 cm^{-1} (D) | | | | | | | |
| 4 | H | 0.0053 | 0.0055 | 0.0059 | 0.0064 | 0.0068 | 0.0070 | 0.0070 |
| | D | 0.0052 | 0.0056 | 0.0063 | 0.0068 | 0.0071 | 0.0074 | 0.0075 |
| 5 | H | 0.0044 | 46 | 49 | 51 | 54 | 55 | 56 |
| | D | 0.0044 | 47 | 51 | 55 | 58 | 60 | 61 |
| 6 | H | 0.0038 | 40 | 42 | 44 | 46 | 47 | 47 |
| | D | 0.0039 | 42 | 45 | 47 | 49 | 50 | 52 |
| 7 | H | 0.0033 | 34 | 36 | 38 | 40 | 41 | 41 |
| | D | 0.0034 | 36 | 39 | 41 | 43 | 44 | 45 |
| 8 | H | 0.0029 | 31 | 32 | 34 | 35 | 36 | 36 |
| | D | 0.0031 | 33 | 35 | 37 | 38 | 39 | 40 |
| 9 | H | 0.0027 | 27 | 28 | 29 | 30 | 32 | 32 |
| | D | 0.0028 | 30 | 31 | 32 | 33 | 35 | 36 |
| 10 | H | 0.0023 | 24 | 25 | 26 | 27 | 28 | 28 |
| | D | 0.0025 | 27 | 28 | 29 | 31 | 32 | 33 |
| Separation of I_1 and I_4 in cm^{-1} | | 0.030 | 0.032 | 0.034 | 0.036 | 0.038 | 0.040 | 0.042 |

of values, and it can be seen that the maximum error would probably be not over $\pm 0.002 \text{ cm}^{-1}$ for either H α or D α .

A possible source of error in the measurement of the separation of the components of D α would be the presence of an appreciable quantity of ordinary hydrogen in the discharge. A plate was taken to determine the relative abundance of hydrogen and deuterium. With a discharge current sufficient to expose D α in one second without the étalon in place, H α did not appear on the plate in a two-minute exposure. Evidently, then, the concentration of H α was considerably less than 1 percent. The pure deuterium gas used was graciously given to Cornell University by Professor H. C. Urey of Columbia University, and the completion of this research was made possible largely through his generosity.

On combining all these estimates and assumptions, the probable *maximum* error for the interval between components 1 and 2 is about $\pm 0.005 \text{ cm}^{-1}$ for H α and $\pm 0.003 \text{ cm}^{-1}$ for D α . The interval between components 2 and 3 of D α is probably known to the same degree of accuracy; namely, about $\pm 0.003 \text{ cm}^{-1}$. It is for the reason that the correction errors are so potentially large that no estimation of the relatively small probable error based solely on peak-to-peak measurement is given.

The most striking aspect of the data in Tables II and III is the large percent deviation from theory in the interval from component 2 to component 3. This interval should be 0.108 cm^{-1} by theory, and thus a deviation of about 20 percent is indicated. The other measurable interval is the main interval between components 1 and 2. The most likely statement that can be made at this time regarding this important interval is that it is sensibly invariant with changing discharge conditions for either H α or D α , that the H α interval seems consistently about 0.002 cm^{-1} less than the D α interval, and that either interval is about 0.009 cm^{-1} to 0.011 cm^{-1} less than the theoretically predicted one.

The results of this investigation indicate one reason for the chief discrepancies of the work of some of the previous investigators, including the previous work of the author. Without exception the assumption has always been made that

component 3 was in its theoretical position, because until the present research, this component had never been resolved from component 2. (Resolution is here defined as that degree of separation of two components such that the resultant intensity complex has two maxima and a minimum.) But component 3 is actually considerably removed from its theoretical position, and its intensity is far greater than predicted. Consequently, corrections based on the theoretical position and intensity of the component will be different from the corrections based on its observed position and intensity.

The relative intensities of the components listed in Tables II and III are seen to vary rather greatly from the theoretical predictions in agreement with the results of previous investigators. It is interesting to note that component 1 can be either more intense or less intense than component 2, but that it never quite reaches its theoretical relative intensity. Component 3 has an intensity relative to component 2 always considerably larger than it should have according to theory.

The most recent work on the structure of $D\alpha$ is that reported by Maria Heyden in 1937.¹² An interval of 0.3312 cm^{-1} is found between component 2 and the "Schwerpunkt" of components 1 and 4, which compares favorably with the predicted interval of 0.3321 cm^{-1} . From the microphotometer records reproduced in this paper it is difficult to determine whether or not component 3 is resolved, because of the very large grain of the plates. It is unfortunate that no examples of the resolution of components 2 and 3 are shown, as would be expected on those plates for which half-intensity breadths of less than 0.080 cm^{-1} are reported. As is shown in Fig. 2, a half-intensity breadth of 0.078 cm^{-1} results in a clear resolution even in the case of theoretical positions and intensities.

TABLE V. Test for lack of symmetry of hyperfine structure.

| PLATE | PRESSURE (mm Hg) | CURRENT DENSITY (A/cm ²) | PEAK-TO-PEAK INTERVAL (cm ⁻¹) | |
|-------|---------------------|--|---|-------------------|
| 211a | 0.31 | 0.030 | 0.3200 | Magnetic field |
| 211b | 0.31 | 0.030 | 0.3206 | |
| 211a | 0.31 | 0.030 | 0.3215 | No magnetic field |
| 211b | 0.31 | 0.030 | 0.3213 | |

¹² Maria Heyden, *Zeits f. Physik* **106**, 499 (1937).

POSSIBLE CAUSES OF DEVIATION FROM THEORY

It was suggested by Professor H. Bethe that possibly the hyperfine structure of the $H\alpha$ and $D\alpha$ lines would be large enough to account for the observed deviations from theory. If the hyperfine structure splittings are unsymmetrical with respect to the fine structure levels and are sufficiently large, a shift of the peak of the observed intensity pattern from that of the theoretical pattern would result. Bethe¹³ shows that the hyperfine structure splittings for the $2s \ ^2S_{1/2}$ level is equal to

$$\frac{8\alpha^2 g(i)(i+\frac{1}{2}) Z^3 R}{3 \cdot 1838 n^3},$$

where $g(i)$ is the nuclear splitting factor believed to be 2 for deuterium, and i is the nuclear spin quantum number.

If a magnetic field is impressed, the hyperfine structure levels will be perturbed. If the magnetic field is strong enough, the fine structure levels will also be perturbed, and the normal Zeeman triplet structure will result. However, it is possible to keep the magnetic field weak enough (60–100 gauss) not to perturb the fine structure levels appreciably, and yet be strong enough to alter completely the hyperfine structure levels. If the hyperfine structure levels are unsymmetrically placed, this complete alteration should affect the observed intensity pattern.

To test whether or not an unsymmetrical hyperfine structure existed the apparatus was so modified that a magnetic field of about 100 gauss could be impressed along the axis of the discharge tube. This was done by wrapping wire around the tube, connecting to a source of direct current, and immersing the tube and wire in the liquid air. Two plates were taken of $D\alpha$ operating under ideal discharge conditions, and on each plate there was an interference pattern photographed with and without the magnetic field. If the hyperfine structure is important in shifting the peaks, the peak-to-peak interval should differ noticeably between the two cases. The results of these measurements are given in Table V. It is seen that the peak-to-peak intervals differ only slightly, and certainly the

¹³ Bethe, *Handbuch der Physik*, Vol. 24, p. 273.

change is far too small to account for the observed deviations from theory. It may be safely said that the hyperfine structure is not an important factor in the observed fine structure pattern of $D\alpha$. A paper by Bechert and Meixner¹⁴ has appeared which shows that there should be neither fine structure nor hyperfine structure differences between $H\alpha$ and $D\alpha$, and consequently the magnetic field result for $D\alpha$ can be safely assumed to hold for $H\alpha$. Furthermore, this paper shows that the hyperfine structure splitting should be symmetrical about the position of the fine structure components, so that no shift in the position of the intensity peaks due to hyperfine structure is to be expected.

At the suggestion of Professor J. Franck the possible effect of weak-field Stark-effect was considered. For an electric field sufficiently weak that the Stark-effect splitting is small compared with the separations of the fine structure levels, it has been calculated^{15, 16} that each fine structure level is split up into $2J+1$ equidistant levels. The separation of these levels from each other is proportional to the first power of the electric field, as long as the field is small. Bethe¹⁷ gives an equation relating field-strength and Stark-effect splittings, which shows that in order to produce a splitting of an amount that would appreciably distort the fine structure complex, a field of 100 volts per cm is required. There is little possibility that the potential difference across the discharge tube causes a field large enough to explain the observed discrepancies, since potential gradients generally existing in the discharge tube were less than 50 volts per cm.

In order to test whether or not there existed interionic fields of sufficient magnitude to produce the observed discrepancies, a series of plates were taken with the same pressure and widely differing current densities. Current densities as high as $0.050\text{A}/\text{cm}^2$ and as low as $0.005\text{A}/\text{cm}^2$ were taken. Within an estimated experimental error of 2 percent, the interval between components 2 and 3 did not change with current density, but continued to remain at about

0.130 cm^{-1} . This indicates that either Stark-effect is not responsible for the observed deviations from theory, or that the particular kinds of fields involved do not change much with changing current densities.

OBSERVATIONS WITH HELIUM IN THE DISCHARGE TUBE

It was considered barely possible that the presence of helium in the discharge tube would so modify the ionic field that appreciable differences could be observed between the fine structure pattern of pure deuterium and that of deuterium when helium was present. There exists a slight evidence of this in the results of Spedding, Shane and Grace, who found for 2 plates a 3 percent larger interval between components 1 and 2, when helium was abundantly present in the discharge tube, than they found for their other 3 plates when pure hydrogen and deuterium were present.

A source of He was provided, and although the nitrogen always present in commercial He could be removed by a liquid-air-cooled charcoal trap, the ordinary hydrogen also present could not be removed without difficulty. Consequently, a 3 mm étalon was used to avoid distortion of the $D\alpha$ pattern by that of $H\alpha$. The deuterium was admitted only as an impurity in the He gas in the discharge, but due to their low excitation potential, the Balmer lines came out with great brilliance. The hydrogen molecular spectrum was almost entirely suppressed. Plates were taken of the fine structure pattern, with and without He present, and with the constant current density value of $19\text{ ma}/\text{cm}^2$. These plates were measured on the microphotometer, and no change in interval between components 1 and 2 could be detected, within an estimated average error of $\frac{1}{2}$ percent. Consequently, the apparent change of interval with He present, indicated by the results of Spedding, Shane and Grace, was not substantiated.

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¹⁴ Bechert and Meixner, *Ann. d. Physik* **22**, 525 (1935).

¹⁵ Rojansky, *Phys. Rev.* **33**, 1 (1929).

¹⁶ Schlapp, *Proc. Roy. Soc.* **119**, 313 (1928).

¹⁷ Bethe, *Handbuch der Physik*, Vol. 24, p. 416.



FIG. 3. Interferometer fringes of $D\alpha$ obtained with a 5 mm étalon spacing.