Fine-Structure Analysis of $H^1\alpha$ and $H^2\alpha$

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Methods employed in applying corrections to an observed "doublet" interval to find the true interval and in relating the position of an intensity maximum to that of the components of which it is composed are critically discussed. The need for clearly distinguishing between the position of the center of gravity of even a nearly symmetrical intensity complex and that of its maximum is emphasized. A Fabry-Pérot interferometer was used to examine the fine structure of the $H^1\alpha$ and the $H^2\alpha$ lines. The interval between the main components of the "doublet" is found to be 0.308 cm^{-1} for $H^1\alpha$ and 0.321 cm^{-1} for $H^2\alpha$ as compared with 0.328 cm^{-1} indicated by theory. The relative intensities of the components as revealed by the analysis are approximately in agreement with theory.

THE Balmer lines of hydrogen are commonly referred to as "doublets," each of the two members of which, according to theory, is composed of two or more single symmetrical lines or components. The fine structure of these "doublets" has been studied by numerous investigators. Although roughly concordant results have been obtained experimentally in recent years for the $\Delta\nu$ interval between the two members of the doublets, the positions and relative intensities of the various components, especially the weaker ones, have been determined with only moderate accuracy and reliability. It is the purpose of this paper to discuss the methods of obtaining an analysis of the fine structure of the hydrogen lines, and to give the results of such an analysis for both $H^1\alpha$ and $H^2\alpha$.

The latest extensive paper upon the fine structure of H^1 lines was published by Kent, Taylor and Pearson.[1] They used crossed Lummer plates and an echelon grating as the resolving instruments, and a liquid-air-cooled Wood tube as a source. The crossed Lummer plates gave patterns which had to be measured visually, while the echelon grating gave patterns which could be measured both visually and with microphotometer curves. Corrections for the "shrinking effect"[2] were applied to the microphotometer curve results. Combining such corrected results with the visual measurements they obtained for $H^1\alpha$ a weighted average of 0.318 cm^{-1} for the "doublet" interval. Further, they analyzed the microphotometer curves to show the components predicted by theory.

In commenting upon their methods and results it may be pointed out that their microphotometer curves show grain variations comparable with the intensities of the weaker components, and that in their corrections and analyses these curves were used in their original form without reduction to intensity. Their shrinking effect correction amounted in some cases to as much as 9.6 percent of the measured interval. Both the size of this correction and their method of applying it are open to question. This correction is one to be made to the observed separation of intensity maxima of an incompletely resolved doublet composed of two similar and symmetrical components having approximately the same intensities. It is computed from the relative *intensity* of the "saddle" to that of either of the peaks, and when applied, changes the observed separation between intensity maxima to the true separation between two such components. For a given doublet, the relative saddle intensity and therefore the shrinking correction will be independent of photographic exposure. Kent, Taylor and Pearson made a shrinking correction on their *unreduced* curves, and hence obtained corrections that varied with the density of the photographic image. After applying this correction, they interpreted the interval thus determined as representing that between the centers of gravity of the two sets of components that form the "doublet." Several objections can

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[1] Kent, Taylor and Pearson, Phys. Rev. **30**, 266 (1927).
[2] Hansen, Ann. d. Physik **78**, 558 (1925).

be raised to such a procedure. As can be seen from their curves the "doublet" is not of the type to which such a correction can suitably be applied. If theory is at least approximately correct, the main components do not overlap each other sufficiently to produce any measurable shrinking. Whatever shifts occur in the maxima, so as to displace them from the peaks of the main components, are due to the minor components, and these shifts are in the same direction for both maxima. As a matter of fact, our results show that the *total saddle intensity*, made up of contributions from both major and minor components, is not sufficient to produce an appreciable correction of the type treated by Hansen, even if a correction of this sort were applicable. Since they used the original microphotometer curves from which to obtain fine-structure analyses, they were able to obtain results in harmony with theory only from plates having a limited range of blackening.

Kent and his colleagues gave values of the $\Delta\nu$ they obtained and compared them favorably with the theoretical values of the $\Delta\nu$ between the centers of gravity of the "doublet." Yet the $\Delta\nu$ measured was in reality that between maximum intensity peaks, to which interval, as has already been noted, a shrinking correction was erroneously applied in the case of measurements from the microphotometer records. However, when an intensity complex is made up of two or more simple components of such relative positions and intensities as is indicated by theory for each member of the $H^1\alpha$ "doublet," the position of the maximum intensity does not coincide with the center of gravity of that complex.

For a complex of n symmetrical spectral components, of intensity I_0, I_1, I_2, $\cdots$ I_n, the displacement x_c of the *center of gravity* of the components from the I_0 component is defined by the equation:

$$x_c = -(1/I_0)\{I_1(x_c - x_1) + \cdots + I_n(x_c - x_n)\}$$
$$= -(1/I_0)\sum_{k=1}^{k=n} I_k(x_c - x_k) \quad (1)$$

where x_1, x_2, $\cdots$ x_n are respectively the distances of the center of each component from that of the component chosen as I_0.

Let us now consider the displacement of the *position of maximum intensity* of the complex composed of similar and symmetrical components from the component chosen as I_0. Let the distance of the center of each component from that of I_0 be respectively x_1, x_2, $\cdots$ x_n as before, and the corresponding intensities be I_1, I_2, $\cdots$ I_n. Then the resultant intensity curve of the complex will be:

$$I = I_0 e^{-cx^2} + I_1 e^{-c(x-x_1)^2} + \cdots + I_n e^{-c(x-x_n)^2}, \quad (2)$$

where c is defined by the equation $\log_e 2 = c(\text{half-line-width}/2)^2$. The stationary points of the complex are obtained by differentiating the above expression with respect to x, and equating the result to zero. Then the displacements x_m of the maxima and minima, from I_0, are given by the values of x_m which satisfy the equation:

$$x_m = -(e^{cx_m^2}/I_0)\sum_{k=1}^{k=n} I_k(x_m - x_k)e^{-c(x_m - x_k)^2}. \quad (3)$$

By using the theoretical positions and intensities of the components of the high frequency member of the $H^1\alpha$ "doublet" as an illustration, it is found from Eqs. (1) and (3) that the center of gravity of the two components is displaced 0.014 cm^{-1} from the stronger one while the intensity maximum, with a value of c determined from our half-line-width, is shifted 0.007 cm^{-1}. This clearly indicates that in a doublet, either member of which contains one or more components, the position of maximum intensity cannot be identified in general with the position of the center of gravity. A careful analysis of an experimental intensity curve, an illustration of which will be given later, for $H^1\alpha$ fine structure will yield information to which Eq. (3) can be applied as a check.

In obtaining the $H^1\alpha$ interference fringes the source of radiation was a liquid-air-cooled Wood tube bent in the form of a modified U, with suitable precautions to insure the complete immersion in liquid air of the portion of the tube from which light was taken. The radiation was analyzed by a Zeiss three-prism spectrograph, with a Fabry-Pérot etalon in the collimated beam. The discharge in gaseous hydrogen was maintained by a 3000-volt transformer, and the pressure and current were held at such values that the discharge was maintained only very weakly. The exposures were from 30 seconds to 1 minute of actual exposure time, the discharge being run only 5 seconds in every 20. Intensity marks were placed on the plates by using a continuous uniform source and varying the slit widths.

Eastman 4-C and 5-C plates, which are very fine grained and quite sensitive in the $H\alpha$ region, were used. As an example of the type of record obtained from these plates, an original microphotometer curve taken of $H^2\alpha$ with a 3 mm etalon on a 4-C plate is shown in Fig. 1.

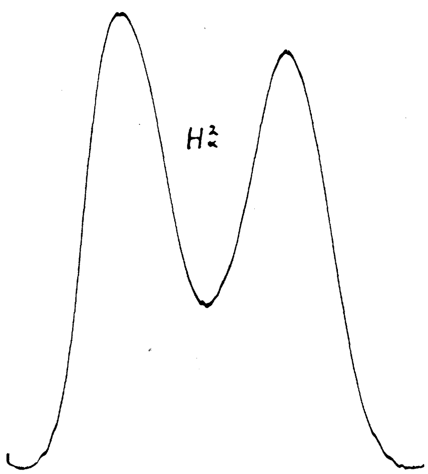

FIG. 1. Microphotometer curve of $H^2\alpha$ (3 mm etalon).

Such curves together with the intensity mark records were obtained on a Moll microphotometer. These curves were then enlarged fourfold upon cross-section paper by a transmission projector, the uniformity of whose field had been checked. The curves were next reduced to densities by the usual logarithmic formula, and were further reduced to intensities by the density-intensity curve obtained from the intensity mark records. A satisfactory check on this procedure was obtained by drawing intensity curves for both an overexposed and an underexposed pattern. Although the original microphotometer curves were quite unlike, the intensity curves of the two were practically identical.

The intensity curves were analyzed for fine structure as will be later explained, and after this analysis the $\Delta\nu$ between the centers of the main components could be obtained as follows. It is readily seen that the position of a maximum on the microphotometer record coincides with the position of the corresponding maximum on the intensity curve. For a particular plate the displacements of the centers of the two main components from the positions of the respective intensity maxima were obtained from a fine-structure analysis, and checked by Eq. (3). These displacements being known, the interval between the peaks of the original microphotometer curve of that plate could be used in determining the $\Delta\nu$ between main components. Of course a fine-structure analysis had to be made for each plate in order to discover whether any change in relative intensities occurred due to changing discharge conditions, for this would affect the displacements mentioned above. However, in the results here reported there were noted no relative changes of intensity of sufficient size to affect the displacements appreciably. By using the curves obtained from several plates, an average interval between main components was determined with an estimated error of not more than 0.002 cm^{-1}.

Some investigators have used an etalon spacing such that the members of the "doublet" are spaced just one-half of an interference order apart, in order to neutralize the Eberhard and shrinking effects. The Eberhard effect can be minimized by rapid brush development or by the use of light exposures on fine-grained plates as were used in this study. The shrinking effect, which is not readily corrected for in the case of visual measurements, must be taken into account when the interval between resolved components is small, but as has been already pointed out, it is negligible for the $H\alpha$ "doublets." Accordingly, since in this study a positive analysis of the intensity curves was desired, an etalon spacing such as to reduce the intensity between successive interference orders to a very low value was used. Thus, in the light of the theoretical analysis, the intensity distribution on the high frequency side of the "doublet" pattern coincides with the true intensity curve of the corresponding main component over most of its high frequency side, which makes it possible to determine the constant in the intensity equation of all components for any chosen position and maximum intensity of this component. Consequently a 5 mm etalon spacing was selected for $H^1\alpha$.

The analysis of the experimental intensity curve was performed as follows. As already explained, all but the top portion of the high frequency side of the pattern is the actual shape of the intensity curve for one of the main components. A center position and a height for this component were tentatively chosen. From these the half-line-width and the related constant c in the equation $I=I_0e^{-cx^2}$ could be found. Then the approximate position of the low frequency main component (which was restricted within relatively narrow limits by the shape of the intensity distribution), was tentatively chosen. The separation of each minor component from its major component was taken so that the ratio of such intervals to that between the two main components was approximately the same as the corresponding ratio predicted by theory. This choice of intervals will be discussed later. All the components were then drawn in, in such a way as to satisfy the three simultaneous conditions: (a) The curve for each component had to satisfy the intensity equation with the same value for c; (b) the component curves had to add up to the original intensity distribution at every point; (c) the positions of all the maxima and minima of the complex as fixed by the tentative analysis had to satisfy Eq. (3). Successive trials were made until these conditions were all closely fulfilled.

Fig. 2 shows the analyzed intensity curve for $H^1\alpha$, with an interval[3] between intensity peaks of 0.304 cm^{-1}, which is an average value obtained from several microphotometer curves. The observed half-line-width is 0.180 cm^{-1}. The theoretical separations and intensities for $H^1\alpha$ are shown in Fig. 3. The analysis, made as described above, gives $\Delta\nu=0.308$ cm^{-1} as the separation of the main components, while $\Delta\nu=0.328$ cm^{-1} is expected theoretically. The theoretical intensities have been computed by Sommerfeld and Unsold,[4] by Saha and Banerji[5] and by Kupper.[6] The analysis was not sufficiently critical to establish either the existence or non-existence of the 5th component which theory predicts to be very weak. Accordingly in Figs. 2 and 4 no attempt has been made to show this component.

Experimental work on $H^2\alpha$ was started with a sample of hydrogen containing about 1 part

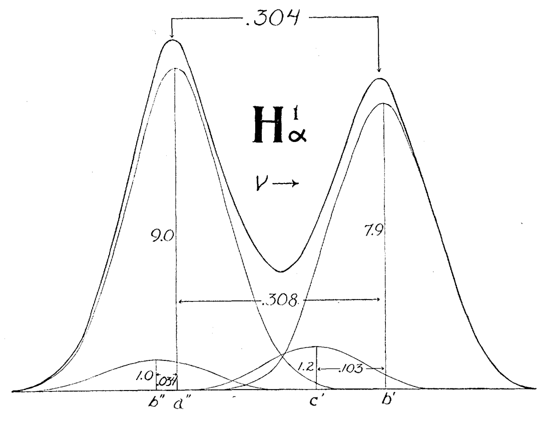

FIG. 2. Analysis of $H^1\alpha$ (intervals in cm^{-1}).

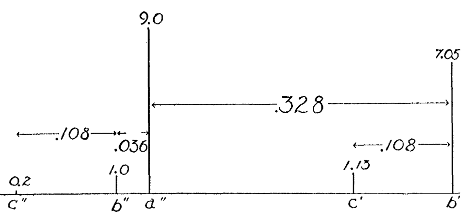

FIG. 3. Theoretical structure of $H^1\alpha$ (intervals in cm^{-1}).

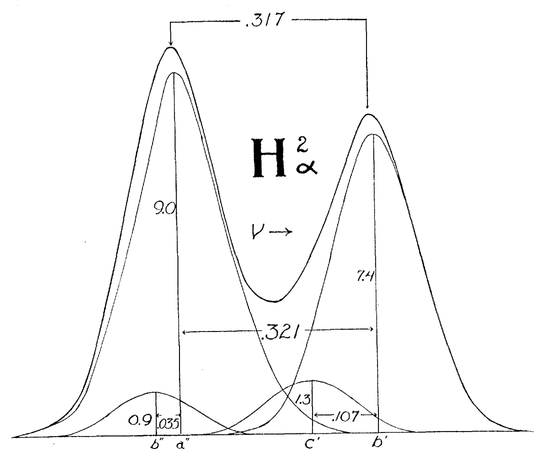

FIG. 4. Analysis of $H^2\alpha$ (intervals in cm^{-1}).

[3] Gibbs and Williams, Phys. Rev. **45**, 221 (1934).
[4] Sommerfeld and Unsold, Zeits. f. Physik **38**, 237 (1926).
[5] Saha and Banerji, Zeits. f. Physik **68**, 704 (1931).
[6] Kupper, Ann. d. Physik **86**, 511 (1928).

in 80 of H^2, kindly supplied by Professor H. C. Urey of Columbia University. Later a sample of water, whose hydrogen content was nearly 50 percent H^2, was generously furnished by Professor G. N. Lewis of the University of California. A discharge in the water vapor of this latter sample actually produced the $H^2\alpha$ line only about 1/3 as intense as the $H^1\alpha$ line, probably due to ordinary hydrogen contamination in the discharge tube. An etalon spacing of 3 mm was used, for this allowed the $H^2\alpha$ and $H^1\alpha$ fringes to be distinctly separated, although they were overlapped $2\frac{1}{2}$ orders of interference. This spacing has a resolving power of over 400,000 when the etalon plates have a reflectivity of 92 percent. With a resolution as great as this, or greater, the shape of the $H\alpha$ intensity curves is almost solely determined by the thermal Doppler effect, and consequently not much is to be gained from greater optical resolution. In order to determine whether much resolution is lost by the use of 3 mm plates, the $H^1\alpha$ fringes were photographed with etalon spacings of 3, 5 and 7 mm. No measurable decrease in half-width with increase in etalon spacing was observed.

Fig. 4 shows the analyzed intensity curve for $H^2\alpha$, with an averaged interval[3] between intensity peaks of 0.317 cm^{-1}. The observed half-width is 0.171 cm^{-1}. Had $H^2\alpha$ been observed from a discharge in gas, at the same temperature as was $H^1\alpha$, its half-width should have been 0.127 cm^{-1}. The maintaining of the water-vapor discharge in a liquid-air-cooled tube required an increased current and thus increased the effective temperature of the H^2 discharge.

The interval between main components for $H^1\alpha$ is about 6 percent below that expected theoretically. This is in approximate agreement with the most recent results of Houston and Hsieh.[7] Furthermore, the average of the intervals between intensity peaks given by Kent, Taylor and Pearson from direct measurements of their microphotometer curves, before any "shrinking-correction" was applied, is found to be 0.306 cm^{-1}. This is in close agreement with our value of 0.304 cm^{-1} for the same interval.

The observed interval between peaks is for $H^1\alpha$ considerably less and for $H^2\alpha$ somewhat less than that predicted by theory. This smaller interval may be due chiefly to a shift toward lower frequencies of the c' and b' components, each of which is made up in part of a radiated frequency involving a transition to the $2s\,{}^2S_{1/2}$ level, for of the levels involved in $H\alpha$ this level is most likely to be displaced by a departure from a coulomb field or from a spherically symmetrical field near the nucleus. These observations and considerations may perhaps suggest some modification in our choice of intervals between components b' and c' and between a'' and b''. However, before these questions can be definitely determined, it will be necessary to secure interference patterns with considerably smaller half-line-widths.

Spedding, Shane and Grace[8] have published microphotometer curves which by their asymmetry indicate the presence of the same components for $H^2\alpha$ as are revealed by this study.

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[7] Houston and Hsieh, Phys. Rev. **45**, 132A (1934).

[8] Spedding, Shane and Grace, Phys. Rev. **44**, 58 (1933).