be rotated about an axis passing through its center and parallel to the refracting edge. The prism could also be removed from the path of light without disturbing the vacuum. The introduction of the prism displaced the monochromatic images of the pinhole from their positions when formed by the grating alone. The tangent of the angle of deviation was then given by the ratio of this displacement to the perpendicular distance (20 cm) from the photographic plate to the prism.

When the prism was rotated about its center, each of the monochromatic images formed through the prism moved toward its corresponding undeviated image until the position of minimum deviation was reached. Rotating beyond this point caused the images to reverse their direction of motion. Thus rocking the prism through the positions of minimum deviation during the exposure gave a series of lines on the photographic plate. The ends nearest the spectrum formed by the grating alone represented the positions of the refracted monochromatic beams at minimum deviation. The index of refraction could then be expressed directly in terms of the angular displacement of the ends of these lines and the angle of the prism. Fig. 3 gives the index of refraction of lithium fluoride plotted against wave-length. The accuracy of the data is of the order of magnitude of three-tenths of one percent. As a check on the apparatus the values obtained for the index of refraction in the near ultraviolet were compared with those of Z. Gyulai.[5] His values are indicated by the crosses in Fig. 3.

Conclusions

Lithium fluoride in moderately thin pieces may be expected to transmit several percent of the light down to wave-lengths as short as 1100A, but this transmission cannot be assumed for a piece chosen at random. Impurities in the crystal, poor polish, and layers of foreign material on the surface may reduce the transmission in the Schumann region to a negligible quantity.

In conclusion the author wishes to express his gratitude to Professor T. Lyman for his continued interest in the progress of these experiments.

[5] Gyulai, Zeits. f. Physik **46**, 80 (1927).

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Intensity Distribution of the Continuous Spectrum of Hydrogen in Mixtures with Helium and with Neon*

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Shift of intensity in the continuous spectrum of hydrogen by admixture of rare gases. The continuous spectrum of hydrogen emitted in mixtures with helium and with neon was studied. The effect of these gases was to shift the maximum of intensity to longer wave-lengths. The ratio of intensity of the spectrum emitted in pure hydrogen to that emitted in the presence of helium as a function of the wave-length was determined by photographic photometry. In order to establish the reasons for this change in distribution of energy with wave-length in the continuous spectrum, a study of the intensity distribution of the many-line spectrum in the presence of helium was made. 20 cm of helium were sufficient to *reduce the vibration* in the excited states to practically zero. Hence the continuous spectrum emitted in the presence of helium must come from transitions from the *lowest vibrational level* of its upper state.

Measurement of intensity distribution of the continuous spectrum of hydrogen in the presence of helium. The wave-length distribution of energy in the continuous spectrum for 0.6 mm of hydrogen and 21 cm of helium was determined by comparison with the radiation emitted from the positive crater of the carbon arc, taken as the best available approximation of the ultraviolet black-body radiation. Under these conditions the maximum intensity of the continuous spectrum was in the neighborhood of 3200A in contrast with about 2500A for the spectrum under ordinary conditions. The position of this maximum is in agreement with the results of Finkelnburg and Weizel. The broadness of the maximum, however, does not agree with their results nor with the theoretical curves of James, Coolidge and Present. Another possible maximum noted at 4500A suggests that more than one electronic state contributes to the observed continuum.

* An extract from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Harvard University.

I. Shift of Intensity in the Continuous Spectrum of Hydrogen by Admixture of Rare Gases

A. Problem and previous work

The present research was chiefly concerned with the molecular continuum of hydrogen in the near ultraviolet region. However, the intimate relation which exists between the continuum and the discrete molecular spectrum made it necessary to study the intensity relations in the discrete spectrum with a view to a clear understanding of the elementary processes involved in the radiation of the continuum.

Richardson,[1] using the experimental results of Merton and Barratt,[2] found that the addition of helium to a hydrogen discharge reduced the intensity of the high vibrational bands relative to the low vibrational bands. Roy[3] made further observations on the effect of helium which confirmed the findings of Richardson. Because of the low intensities involved and because increasing the pressure of helium did not produce an observable change in the effects, the highest pressure of helium employed by Roy was 20 mm. He also found that the intensity of the continuous spectrum was apparently increased with respect to the discrete spectrum.

In the theory of the hydrogen continuum proposed by Winans and Stückelberg[4] the spectrum originates in transitions from the $1s\sigma 2s\sigma\ {}^3\Sigma_g$ level as an upper state to the $1s\sigma 2p\sigma\ {}^3\Sigma_u$ level, discovered by Heitler and London,[5] as the lower state. The general mechanism of this theory has been established by the experiments of Finkelnburg and Weizel.[6] According to the theory we expect a change in the population of the vibrational levels of the upper state of the continuum to change the wave-length distribution of intensity. Thus the reduction of vibration by the addition of helium to a hydrogen discharge leads us to expect important changes in the continuous spectrum. The relative population of the vibrational levels of the upper state without helium present depends in a very complicated manner on the conditions in the discharge tube. The spectrum coming from each vibrational level can be calculated theoretically without too great difficulty. The relative magnitudes of these spectra, however, are unknown, for the population of the vibrational levels is unknown. Hence a quantitative check of the theory can be carried through only if the radiation originates from a definite vibrational level of the upper state. Then the excitation functions and other complicating relations need not be known.

Considerable progress has been made recently in the theory of the continuous spectrum. The *upper* level, its position and potential curve, is well known from the analysis of the discrete spectrum. For the *lower*, repulsive, level Winans and Stückelberg assumed a crude approximation. James and Coolidge[7] have developed new methods which enabled them to make great progress in the accurate computation of this level. If the vibration can be reduced to practically zero by the addition of high presssures of helium, the continuous spectrum under such conditions can be compared with the theoretical predictions. Consequently we studied the continuous spectrum emitted in the presence of helium and investigated the many-line spectrum in order to ascertain the effectiveness of helium in reducing vibration.

B. Experimental procedure

A discharge tube was constructed of Pyrex and arranged so that the capillary could be observed end-on from both ends. A thin window of Pyrex was blown on one end, and a thin quartz window was attached by means of a quartz-to-Pyrex graded seal to the other end so that simultaneous observations could be made with two spectrographs. A Hilger right-angle glass spectrograph was used to record the many-line spectrum situated largely in the visible, and a Hilger small quartz spectrograph was used to record the continuous spectrum in the ultraviolet. The electrodes were rolled from thin sheet

[1] O. W. Richardson, *Molecular Hydrogen and its Spectrum*, (Yale University Press, 1934).
[2] T. R. Merton and S. Barratt, Phil. Trans. Roy. Soc. **A222**, 369 (1922).
[3] A. S. Roy, Proc. Nat. Acad. Sci. **19**, 441 (1933).
[4] I. G. Winans and E. C. G. Stückelberg, Proc. Nat. Acad. Sci. **4**, 867 (1928).
[5] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).
[6] W. Finkelnburg and W. Weizel, Zeits. f. Physik **68**, 583 (1931).
[7] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933); H. M. James, A. S. Coolidge and R. D. Present, ibid. **4**, 187 (1936).

nickel and spot-welded so that they could be heated by an induction furnace to drive off occluded gases. The capillary, 3 mm inside diameter and 10 cm long, was platinized to enhance the molecular spectrum by aiding the recombination of hydrogen atoms. The tube was mounted in a water bath for cooling.

The tube was pumped out by means of a single-stage mercury diffusion pump backed by a Cenco Hyvac pump. The electrodes were raised to a bright red heat during pumping by means of an induction furnace, and the tube was baked out at 475°C.

Tank helium was purified by passing it slowly through activated charcoal at liquid-air temperature and then admitted to a misch metal arc. The helium was pure enough after passing through the charcoal trap to emit the helium bands quite strongly. However, the misch metal arc was run for ten or twelve hours before the helium was used.

Hydrogen, purified by diffusion through a hot palladium tube, was admitted to the discharge tube at a pressure of a few tenths of a millimeter. Exposures of varying times were then made with both the quartz and glass spectrographs. Pure helium was admitted at a few centimeters pressure, and another series of exposures on the same plates was made with the two instruments. The current was kept constant at 30 ma in both cases. Other plates were taken with the pressure of helium as high as 20 cm. Eastman ultraviolet sensitive plates were used with the quartz spectrograph while exposures made with the glass instrument were with Wratten type M panchromatic plates.

The same sort of experiment was then performed for mixtures of hydrogen and neon. The latter was purified by passing it through a charcoal trap in liquid air, but it was not so pure as the helium. Bands of OH and CO^+ were present. Also the line spectrum of neon was more strongly developed than that of helium in the previous case.

The ratio of the intensity of the continuous spectrum emitted by pure hydrogen to that emitted in the presence of helium was then determined. An enlarged image of the capillary of the discharge tube described above was focused by means of a quartz condensing lens on the slit of a quartz spectrograph. A series of exposures of constant time and current was made with the tube filled with hydrogen at 0.6 mm and 21 cm of helium. The intensity of each exposure was decreased a known amount from the preceding one by the interposition of wire gauze screens which had been calibrated with a photoelectric cell. Since the screens were not used in combinations, they were not shuffled as recommended by Harrison.[8] The tube was run from a 3000-volt rectifier with a large series resistance in the output circuit. Then, without disturbing the optical system, the tube was pumped out and filled with 0.6 mm of pure hydrogen. Several exposures were made with the current and time the same as for the first set of exposures and with the intensity reduced by very dense screens which had been calibrated by Dr. Rieke and kindly loaned for these experiments.

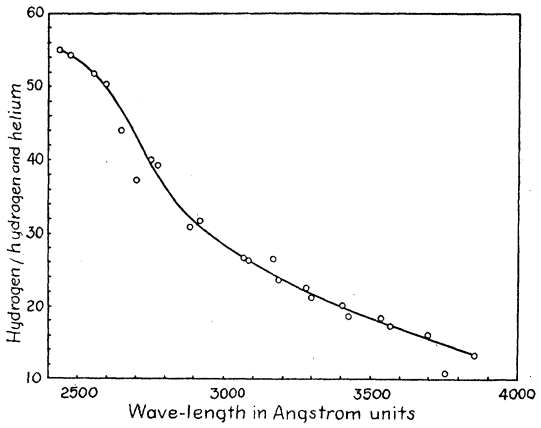

FIG. 1. Ratio of the intensity of the continuous spectrum in pure hydrogen at 0.6 mm to that in a mixture of 0.6 mm of hydrogen and 21 cm of helium, as a function of wave-length.

At each wave-length used, the relation between intensity and density of the photographic image was obtained from microphotometer readings taken from the first set of exposures. Then from these curves the ratio of intensity of the two continuous spectra was obtained from data taken from the second set of exposures. The ratio of the two intensities as a function of wave-length is shown in Fig. 1. With four exceptions the points fit a smooth curve nicely. An accuracy of better than 5 percent cannot be

[8] G. R. Harrison, J. O. S. A. & R. S. I. **18**, 492 (1929).

expected for a single measurement in photographic photometry. It should be pointed out, however, that in photometering a continuous spectrum we have the advantage of determining a smooth curve and not a definite number of points.

C. Results

These plates showed that the wave-length distribution of the continuous spectrum was changed to a marked degree by the addition of helium. The intensity in the longer wave-lengths was relatively enhanced (see Fig. 1). The discrete spectrum was greatly simplified—most of the energy being in the Fulcher bands in the yellow and red—but the dispersion was too small to allow a detailed study. Many lines of helium appeared on the plates, and at the highest pressures used a faint helium band appeared at 4648A. The results for neon were qualitatively the same as those found for helium.

Chalonge[9] has determined the relative changes in distribution produced by various pressures of hydrogen and various currents. Similar results have just been published by Gonsalves[10] in a report of an investigation of the conditions under which the hydrogen discharge may serve as a standard source for ultraviolet radiation. These changes are much less pronounced than the effects caused by the addition of helium.

D. Many-line spectrum in mixtures with helium

In order to interpret the shift of intensity reported, it was necessary to determine the extent of the modification of the vibration of the hydrogen molecule produced by the helium. For this purpose the discharge tube and auxiliary equipment were moved to a concave grating of ten-foot radius which gave a dispersion of about 5.2A/mm in the first order. Eastman type I–F plates were taken with the discharge in pure hydrogen and then with mixtures with various pressures of helium up to 40 cm.

It was found that the vibration was reduced to practically zero at pressures of helium of the order of 20 cm. Transitions ending on the $1s\sigma 2s\sigma\ {}^3\Sigma_g$ and the $1s\sigma 2p\pi\ {}^3\Pi_{ab}$ levels were studied in particular, for the $1s\sigma 2s\sigma\ {}^3\Sigma_g$ state is the upper level of the continuous spectrum. The ${}^3\Pi_{ab}$ state is of interest because it lies only 0.02 volt higher and combines with the ${}^3\Sigma_g$ state. Because of the small difference in energy between the states, transitions emitting radiation are extremely improbable. However, we expect radiationless transitions to occur—probably induced by collisions with other molecules or atoms.

These observations led to results which are of interest in connection with the many-line spectrum itself and which will be reported in another paper.

We are led to expect, in consequence of these results from the many-line spectrum, that the continuous spectrum emitted in the presence of helium arises largely from the *lowest vibrational level* of the $1s\sigma 2s\sigma\ {}^3\Sigma_g$ state.

II. Measurement of Intensity Distribution of the Continuous Spectrum of Hydrogen in the Presence of Helium

A. Experimental procedure

The result of the experiments described is of great interest for a quantitative comparison with the quantum theory. The ordinary electric discharge through hydrogen emits a continuous spectrum to which various vibrational levels contribute energy in an uncontrollable way. Only when the upper state is restricted to a definite vibrational level can a quantitative test of the theory be carried through.

The principal difficulty is due to the lack of a standard source for comparison of intensities in the ultraviolet. At the temperature easily available in the laboratory, black-body radiation is vanishingly small. No calibrated tungsten lamp was available. However, the positive crater of a carbon arc emits radiation that corresponds over a range of at least 1000A to a definite black-body temperature. Henning and Heuse[11] measured the temperature at two wave-lengths, 6560A and 5450A, and found it to be constant at 3703°K. Recently Chaney, Hamister, and Glass[12] of the National Carbon Co. determined the arc tem-

[9] Daniel Chalonge, Ann. de physique **1**, 123 (1934).
[10] V. E. Gonsalves, Physica **2**, 1003 (1935).
[11] F. Henning and W. Heuse, Zeits. f. Physik **32**, 799 (1925).
[12] N. K. Chaney, V. C. Hamister and S. W. Glass, Trans. Electrochem. Soc. **67**, 201 (1935).

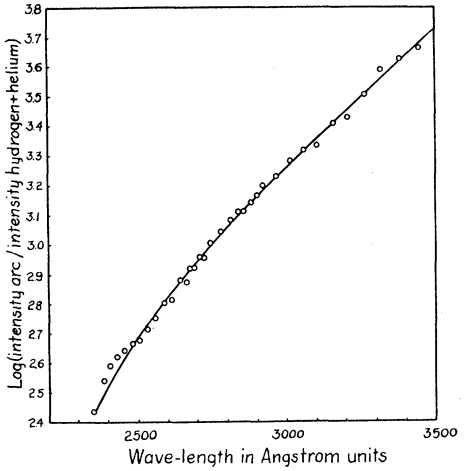

FIG. 2. Logarithm of the ratio of intensity of the carbon arc to the continuous spectrum with 0.6 mm of hydrogen and 21 cm of helium, as a function of the wave-length.

perature to be 3810°K. For the present experiment an arc with the same type of carbon was used as a standard.

In order to prevent fogging of the plate by scattered visible light two filters were used, a Corning red-purple Corex glass filter for the range from 4000A down to 2800A and a filter of bromine vapor down to 2400A.

An aluminum mirror on a turntable reflected the light of either the arc or the capillary into a quartz lens which formed an image of the source on the slit of a quartz spectrograph. The calibrated screens and filter were placed immediately in front of the lens.

The discharge tube, filled with 0.6 mm of hydrogen and 21 cm of helium, was run at 80 ma on a 3000-volt rectifier until quite steady. Only exposures of constant time were compared. For this purpose intensities were reduced by calibrated screens and a rapidly rotating sector.

From a set of exposures with the discharge tube and calibrated screens, the curves showing the relation of intensity and density at each wave-length were determined with a microphotometer. From these and the exposures of the arc, the relative intensity of the two sources was then obtained as a function of the wave-length.

B. Results

The logarithm of the ratio of intensity is plotted as a function of the wave-length in Fig. 2.

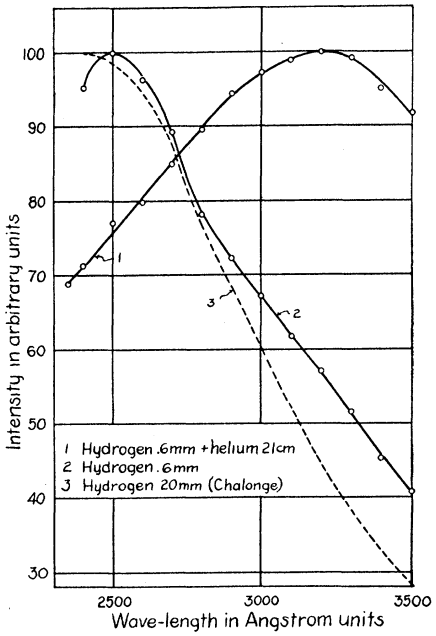

FIG. 3. Curves showing intensity of the continuous spectrum as function of wave-length.

The values were obtained from two plates well overlapped as to the wave-length ranges. One plate covered the range between 3500A and 2650A, while the other extended from 2900A to 2350A. The points fit the smooth curve shown except in the region below 2500A. In this region there is a strong carbon line along with some faint lines of silicon. Consequently we may consider the curve below 2480A as an extrapolation.

By comparison with the spectrum from the arc, the intensity distribution with wave-length of the helium-hydrogen mixture was calculated. These values are plotted in Fig. 3 with the maximum intensity arbitrarily set at 100. By using the values for the ratio of intensities of the spectrum of pure hydrogen and of hydrogen and helium, the intensity distribution for pure hydrogen was obtained. This relation is also shown in Fig. 3, again with the maximum intensity arbitrarily set at 100. The dotted curve is the one found by Chalonge[9] for a discharge in pure hydrogen at 20 mm. The smoothness of these curves arises from the fact that they were determined from other smooth curves, and hence

they are not indicative of the experimental error. These curves rest on the data shown in Fig. 1 and Fig. 2.

C. Discussion of results

The random error exhibited in the curves is satisfactorily small. We must look carefully, however, for possible sources of error which are functions of the wave-length.

It should be noted that the slit of the spectrograph was not illuminated in the same way by the images of the capillary and of the crater of the arc, for the image of the arc is sensibly a disk and that of the capillary is a truncated cone. This difference of image shape might well cause an incorrect determination of the ratio of intensities, but it is not likely to cause an error which varies appreciably with the wave-length.

The sector used to reduce the intensity was rotated at 1800 revolutions per minute. From the work of Webb[13] and a discussion by Harrison[14] we expect the error in the reduction of intensity at this speed to be small. Moreover it is the way in which this error varies with wave-length that concerns us. Hence if a small error does occur, it is a second-order effect and will not disturb our measurements.

An obvious source of uncertainty is the use of the arc as a black-body, for we are extrapolating the properties of the arc from the visible into the near ultraviolet. An increase in the temperature of the arc would shift the position of the maximum for the hydrogen continuum toward the shorter wave-lengths. A small error of this sort would not, however, affect the essential character of the results. The deviation of the carbon spectrum from the black-body spectrum seems the main source of error which cannot well be estimated as long as no reliable standard source is available.

We believe that the observed continuum cannot be appreciably due to the helium molecule because of the low excitation potential of the hydrogen continuum—11.8 volts compared with about 20 volts for helium.

The intensity curve for pure hydrogen at 0.6 mm is in fair agreement with Chalonge's curve for 20 mm and is deformed in the way he predicts for the difference in pressure.

The position of the maximum at 3200A for the hydrogen-helium mixture is in agreement with the work of Finkelnburg and Weizel, but the broadness is not. Also this broadness does not agree with the theoretical predictions of James, Coolidge and Present.[15] If electronic states other than $1s\sigma 2s\sigma\ ^3\Sigma_g$ give rise to continua in the observed range, the curve shown in Fig. 3 should not be compared with the theoretical predictions. On the plates taken with mixtures of helium and of neon what appeared to be another maximum of intensity in the continuous spectrum was observed at about 4500A. However, the appearance of a maximum might be caused by the varying sensitivity of the plate. This maximum is in the region where Brasefield[16] found a new continuum in an electrodeless discharge at low pressures of hydrogen and is possibly related to it. The high excitation potential of helium would allow a large population in the high electronic states of the hydrogen molecule.

The principal result of the experiments reported here is that helium and neon by reducing vibration produce a major change in the continuous spectrum of hydrogen. Under these conditions a large portion at least of the continuum arises from the lowest vibrational level of the $1s\sigma 2s\sigma\ ^3\Sigma_g$ state.

The author wishes to express his sincere appreciation to Professor O. Oldenberg for his interest in the work and for his numerous helpful discussions and suggestions.

[13] J. H. Webb, J. Opt. Soc. Am. **23**, 157 (1933).
[14] G. R. Harrison, J. Opt. Soc. Am. **24**, 59 (1934).
[15] A. S. Coolidge, H. M. James and R. D. Present J. Chem. Phys. **4**, 193 (1936).
[16] C. J. Brasefield, Phys. Rev. **33**, 925 (1929).