THE DENSITIES OF HYDROGEN SPECTRAL LINES AS A FUNCTION OF THE ELECTRONIC VELOCITY OF EXCITATION

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Abstract

The densities of the principal lines of the singlet and triplet systems of molecular hydrogen, as well as H_α, H_β and H_γ were measured for electronic velocities in the range 19 to 220 equivalent volts, the electron emission and the gas pressure being kept constant. The triplet lines have no maximum density in this range but seem to be approaching one slightly below 19 volts. All the singlet lines show a decided maximum of density between 30 and 35 volts. The densities of H_α, H_β and H_γ decrease very rapidly below 30 volts indicating that the number of dissociating collisions which produce an excited atom must be very small at 19 volts. The use of curves showing the variation in the ratio of the densities of singlet and triplet lines with voltage is suggested as a method for finding the mean electronic velocities in certain types of gaseous discharges.

Introduction

DURING the past few years, the writer has been interested in studying the variation in intensity of lines of the secondary spectrum of hydrogen under different conditions of excitation. At the end of nearly every experiment, the conclusion was reached that after all, the electronic velocity of excitation was the most important factor influencing changes of intensity. So in view of our most recent knowledge of the origin of lines in the secondary spectrum,[1,2] it seemed desirable to get direct evidence of the influence of the electronic velocity of excitation on their intensity, by keeping all other conditions constant.

In 1923 Hughes and Lowe[3] performed some experiments very similar to the one proposed here. However, they were interested primarily in the Balmer lines and their data on the lines of the secondary spectrum were more or less fragmentary. Their measurements were confined to electronic velocities in the range 29 to 110 equivalent volts. In as much as marked changes in the intensity of the lines of the secondary spectrum seem to occur around 30 volts, the writer hoped to depress this lower limit as far as possible. Moreover, it was thought that somewhat more accurate results might be obtained by use of an equipotential source of electrons rather than the strip filament used by them. Finally, the writer hoped to confirm certain differences in behavior of the lines of the singlet and triplet systems of molecular hydrogen, which seemed to be indicated by their results.

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[1] O. W. Richardson and K. Das, Proc. Roy. Soc. A122, 688 (1929).

[2] O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. A123, 54 (1929).

[3] A. L. Hughes and P. Lowe, Phys. Rev. 21, 292 (1923).

Apparatus and Procedure

The experimental tube used is shown in Fig. 1. The observation chamber *a*, being essentially plate and grid in one, was semi-cylindrical in shape, approximately fitting the glass tube. The grid part was made of coarse nickel gauze (18×18 mesh of 18 mil wire) while the "plate" part was of fine gauze (60×60 mesh of 8 mil wire). Approximately 1 mm below the grid was the equipotential cathode *b*, backed by a semi-cylindrical sheet of nickel *c* which served as a shield and focusing cup for the electrons emitted by *b*. Both cathode and shield were held in place by springs *s*. The equipotential cathode[4] seemed to be simply an oxide coated nickel shell, having inside it a tungsten filament packed in alundum cement. Three wires were brought in through the ground joint, two of which furnished current to heat the cathode, while the third was connected to the shell of the cathode and the shield. Positive accelerating voltages were applied at *d*. Thus electrons emitted by the equipotential cathode were accelerated to the grid of the observation chamber and, passing through it into the field free space, produced radiation by col-
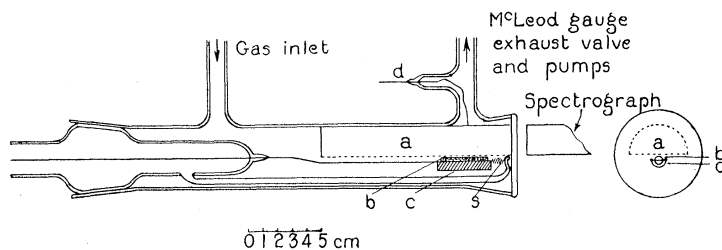

Fig. 1. Apparatus used to excite hydrogen by controlled electron impact.

lision with hydrogen molecules. This radiation was then photographed through an optical glass window sealed into the end of the tube.

Hydrogen was admitted to one end of the experimental tube by means of a platinum tube and was pumped out at the other end, thus insuring a continuous flow of pure hydrogen. The platinum tube was 20 cm long, 1 mm in diameter with 0.1 mm walls. It was surrounded by a glass jacket through which commercial hydrogen was flowed. On heating the platinum tube to a dull red heat (about 600°K) by passing a current of about 16 amperes through it, an adequate flow of hydrogen was obtained through the experimental tube. The pressure could be varied either by changing the temperature of the platinum tube or by means of a valve which regulated the rate of pumping. Pressures were measured by McLeod gauge.

The spectrograph used for photographing the radiation was a three prism Steinheil instrument having an opening $f/3.0$ and giving a dispersion of 113A per mm at H_α, 31.3A per mm at H_β and 13.5A per mm at H_γ. Ilford Special Rapid Panchromatic Plates were used for all exposures.
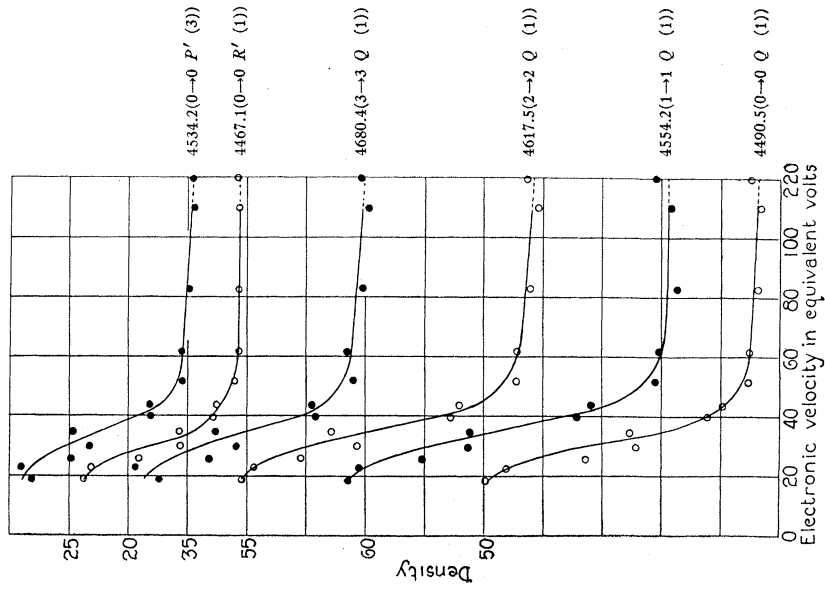
Fig. 3. Density-voltage curves for the $4^3\Pi \rightarrow 2^3\Sigma$ system.
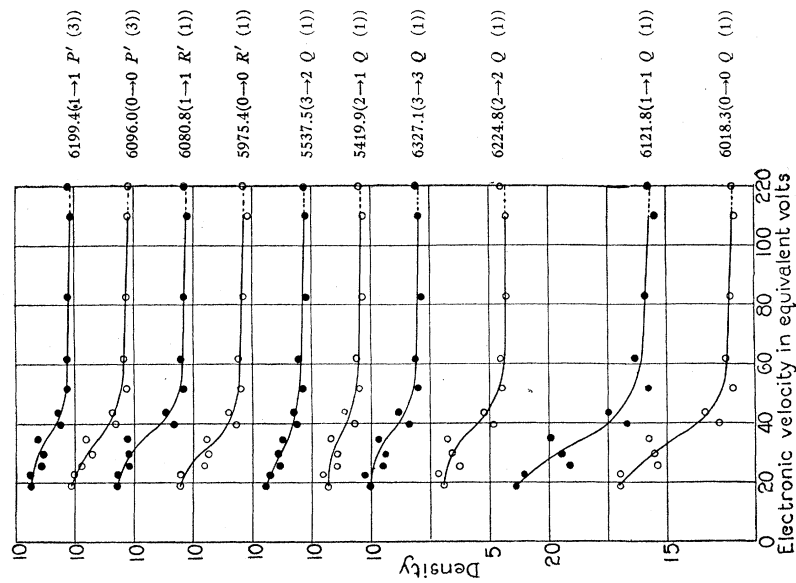

Fig. 2. Density-voltage curves for the $3^3\Pi \rightarrow 2^3\Sigma$ system.
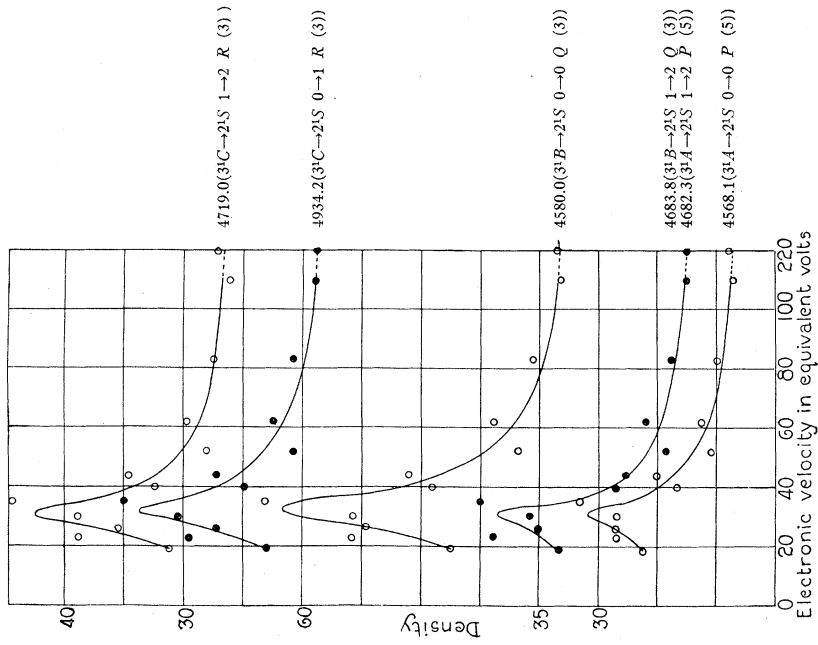
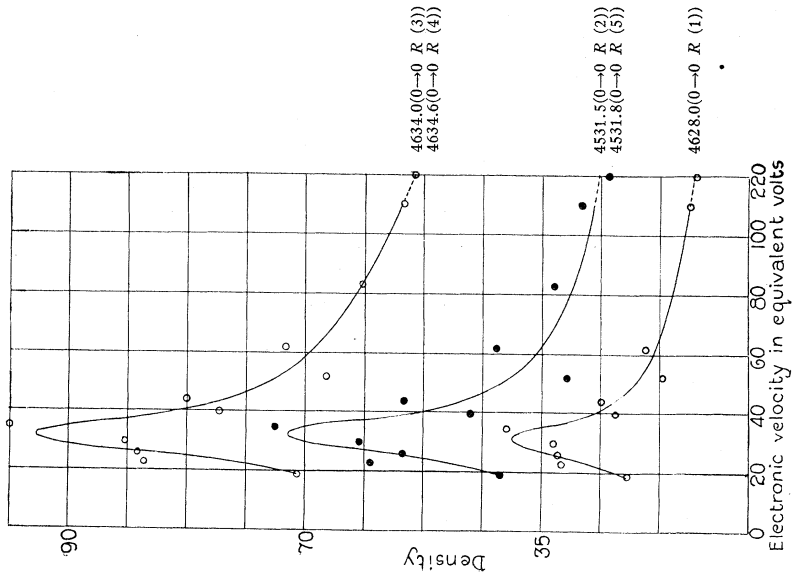Fig. 5. Density-voltage curves for the singlet systems.

Fig. 4. Density-voltage curves for the $3^1C \rightarrow 2^1S$ system.

During all exposures the electron emission was kept constant at 20 milliamperes and the pressure constant at 0.03 mm. At this pressure, the electronic mean free path[5] in hydrogen is about 2 cm, so that the chance of an electron making more than one collision is very small. Two plates were taken on which all exposures were of one hour duration. On the first plate the accelerating voltages were 23, 35, 62, 110, 83, 44 and 30; on the second plate the voltages were 19, 26, 40, 52 and 220. Below 19 volts the radiation was too feeble to photograph successfully in one hour.

Microphotometric traces were then made of all the spectra by means of a Moll self-registering microphotometer. From these traces the density of any line could be obtained by use of the relation: density $= \log d/d - h$, where d is the total galvanometer deflection in the absence of a line and h is the height of the peak on the trace corresponding to the line. Curves were then plotted showing the variation of the density of a line with the electronic velocity in equivalent volts.

RESULTS

The density-voltage curves for the principal lines of the triplet system of H_2 are shown in Figs. 2 and 3, and for the singlet system in Figs. 4 and 5. They are all plotted on the same scale and one density value is given for each curve. It will be noticed that densities at 23, 35 and 62 volts are uniformly high while densities at 26, 30, 40 and 52 volts are slightly low. In other words if photographs had been taken at constantly increasing voltages, the density values would probably have fallen on a smooth curve. But it is doubtful whether such a curve would have been as true a picture of conditions as the mean curve obtained by this method.

These density-voltage curves show that there is a decided difference in the behavior of singlet and triplet lines. The triplet lines have no maximum but seem to be approaching one slightly below 19 volts. On the other hand, all the singlet lines show a decided maximum of density between 30 and 35 volts. This, then, should be an excellent criterion for assigning an unknown line to either the singlet or triplet system. And, incidentally, it is also a nice confirmation of Richardson's analysis of the lines of the secondary spectrum.

The writer did not go to the trouble of calibrating the plates so that density values could be changed into intensity values, for after all, we are most interested in the voltages at which a maximum occurs and this should be the same for intensities as for densities. There are, however, two possible sources of error which might cause a shifting of the curves. In the first place, no account was taken of the distribution of velocities of the electrons going through the grid; the effect of this would probably be very small. However, the second source of error may be more serious. It will be remembered that it was the total electron emission to grid *and* plate which was kept constant, rather than the number of electrons penetrating through the grid. Thus if the ratio of the number penetrating through the grid to the total number collected varies appreciably with voltage, the result would be a shifting of the maxima to slightly lower voltages.

[5] Handbuch der Experimental Physik Vol. XIV, 192 et seq.

In Fig. 6 are shown the density-voltage curves for H_α, H_β and H_γ. The curves for the most intense lines of the singlet and triplet systems are also shown to give an idea of relative densities. As a matter of fact, H_α and H_β were really too intense on the photographic plates for an accurate measurement of density; for this reason the points at high densities fluctuated rather badly and only the mean curves are shown. The only reason for showing these curves is to indicate the rapid fall in density of H_α, H_β and H_γ at low voltages. From this we conclude that the number of dissociating collisions
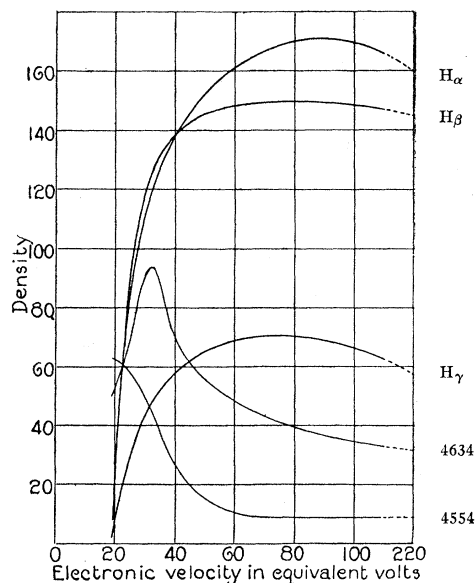
Fig. 6. Density-voltage curves for H_α, H_β and H_γ; also for the most intense lines of the singlet (4634) and triplet (4554) systems of H_2.

which produce an excited atom must be very small at 19 volts; for at these small electron currents there is little chance of an electron colliding directly with a hydrogen atom.

DISCUSSION

It is interesting to see how the ratio of the densities of singlet and triplet lines vary with voltage. Four such curves are shown in Fig. 7. They are in accordance with Ornstein and Burger's selection principle[6] which states that at high electronic velocities, impacts causing transitions between singlet and triplet states are improbable in the same way that transitions between such states to produce radiation are improbable.

These curves have been obtained by finding the densities of certain lines at known voltages of excitation. The writer ventures to suggest that they might also be used to find the mean electronic velocity of excitation when the densities of the lines are known. For these curves are independent of the

[6] L. S. Ornstein, H. C. Burger and W. Kapuscinski, Zeits. f. Physik 51, 45 (1928).

time of exposure and of the current density since both numerator and de-
nominator of the ratio would be multiplied by the same factor. They are also
independent of the kind of plate used for they are so close together that the
change in sensitivity of the plate from one to the other would be inappreci-
able. Finally, Lowe's curves[7] giving the variation of intensity of secondary
lines with pressure show that these curves should be independent of pressure
for electron velocities above 35 volts; and they should hold at least qualita-
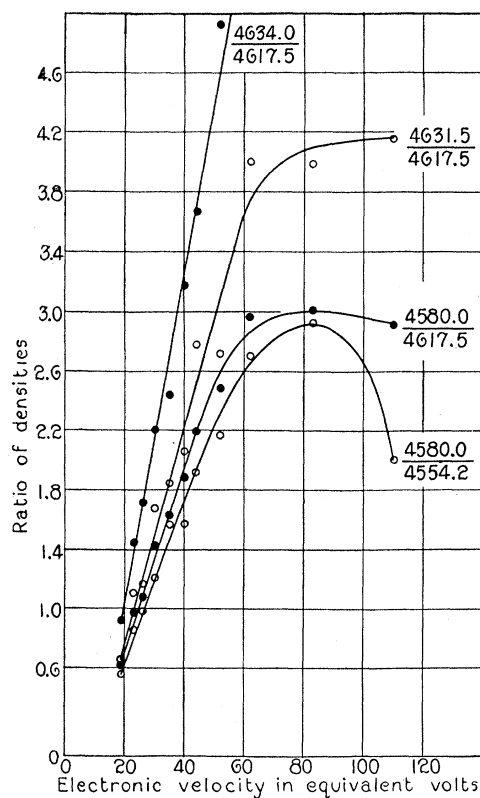tively for voltages below this.

Fig. 7. Variation in the ratio of densities of singlet and triplet lines with the electronic velocity.

An example of such an application of these curves is the following. During
the course of some work on an electrodeless ring discharge in hydrogen, the
writer estimated that the mean electronic velocity was 15 volts at 0.08 mm
pressure and greater than 30 volts at 0.0025 mm pressure. By use of the
curves of Fig. 7 it now appears that these values should have been 30 and 36
volts respectively. It is in just such cases as the electrodeless discharge that
the writer feels that the method outlined here would be more suitable for
measuring electronic velocities than the exploring electrode method.

[7] P. Lowe, Trans. Roy. Soc. Can. **20**, 217 (1926).