# THE IONIZATION OF HYDROGEN BY SINGLE ELECTRON IMPACT

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Abstract

From an analysis of the theoretical potential energy curves for the $H_2$ molecule as outlined by Condon the theoretical predictions for the types of ions resulting from primary impacts with electrons are described. These predictions include the formation of $H_2^+$ at 15.25 volts, $H^+$ at 17.9 volts, $H_2^+$ at about 30 volts which then dissociates with several volts kinetic energy, and $H_2^{++}$ at about 50 volts which also dissociates with kinetic energy. Using a mass spectrograph the experimental results of a study of the primary ions in hydrogen indicate the formation of $H_2^+$ at $15.4 \pm 0.1$ volts, $H^+$ at $18.0 \pm 0.2$ volts, and $H^+$ at 26 to 30 volts, the last having various amounts of kinetic energy.

Curves are given showing the relative number of each of these types of ions from which it appears that at the higher velocities about 92 percent of the total number of ions formed is of the $H_2^+$ type, 1 percent of the $H^+$ corresponding to the 18 volt potential, and 7 percent of the $H^+$ having kinetic energy. The probability of ionization for all types together as a function of the electron velocity is given by a curve, plotted to an arbitrary scale, which exhibits a well-defined maximum at 60 volts.

## Introduction

THE ions produced by electron impact in hydrogen have been studied by the method of positive ray analysis so many times and by so many investigators that it might, at first sight, seem useless to try to make much more progress in this direction. As early as 1916 Dempster[1] designed a mass spectrograph with which he studied the ions produced in hydrogen by 800 volt electrons. Since that time somewhat similar experiments have been carried out by Smyth,[2] Hogness and Lunn,[3] Kallmann and Bredig,[4] Dorsch and Kallman,[5] and Brasefield.[6] The consensus of opinion of these observers is that their experiments have failed[7] to show that any ion other than $H_2^+$ may result from a single impact with an electron. The evidence from the experiment to be described[8] points toward a different conclusion. Moreover certain aspects of the theory of the hydrogen molecule predict several possible modes of production of the $H^+$ ion at a single impact.

[1] A. J. Dempster, Phil. Mag. **31**, 438 (1916).

[2] H. D. Smyth, Proc. Roy. Soc. **A105**, 116 (1924), and Phys. Rev. **25**, 452 (1925).

[3] T. R. Hogness and E. G. Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924), and Phys. Rev. **26**, 44 (1925).

[4] H. Kallmann and M. A. Bredig, Zeits. f. Physik **34**, 736 (1925), and Zeits. f. Physik **43**, 16 (1927).

[5] K. E. Dorsch and H. Kallmann, Zeits. f. Physik **44**, 565 (1927).

[6] C. J. Brasefield, Phys. Rev. **31**, 52 (1928).

[7] In their first papers both Smyth, and Hogness and Lunn (see references 2 and 3) reported $H^+$ as a primary process but later both reported these results as inconclusive.

[8] W. Bleakney and J. T. Tate, Phys. Rev. **35**, 658 (1930) (Abstract).

## Theory

Before the present experiment was undertaken Professor Condon drew up an outline of the results one might expect to find in making an $e/m$ analysis of the primary ions in hydrogen. The essential ideas of this outline have been discussed by Condon,[9] and Condon and Symth,[10] and the particular points pertinent to the present experiment will be reviewed here in some detail.

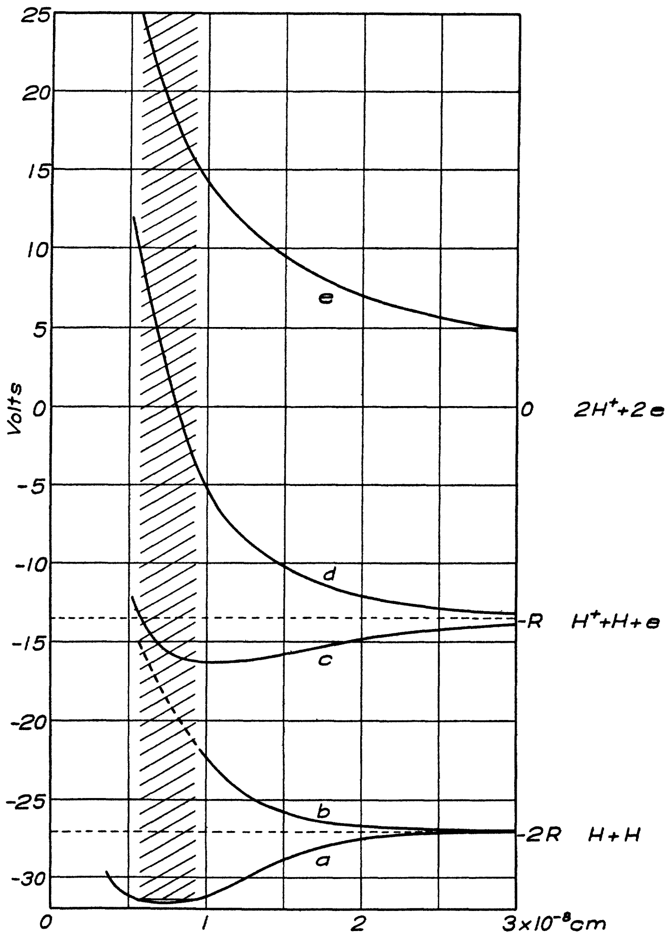


Fig. 1. Potential energy curves for the $H_2$ molecule.

In Fig. 1 are represented some of the theoretical potential energy curves for the hydrogen molecule. The potential energy in volts is plotted as a function of the nuclear separation in Angstrom units. Curves $a$ and $b$ represent the two solutions for the problem of bringing two H atoms in the normal state near each other to form an $H_2$ molecule as calculated by Sugiura[11] from the theory of Heitler and London.[12] Curve $a$ has been altered slightly in order to

[9] E. U. Condon, Phys. Rev. **35**, 658 (1930) (Abstract).

[10] E. U. Condon and H. D. Smyth, Proc. Nat. Acad. Sci. **14**, 871 (1928).

[11] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[12] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

fit the data as given by Birge and Jeppesen[13] and $b$ has been lowered somewhat in the dotted region. In like manner curves $c$ and $d$ represent the two solutions for the problem of the formation of the $H_2^+$ molecular ion from a normal H atom and a proton. Curve $c$ is that calculated by Burrau[14] and $d$ is from the paper by Morse and Stueckelberg.[15] Curve $e$ represents the potential energy of the $H_2^{++}$ molecule due to the Coulomb force of repulsion between the two protons. The width of the shaded band corresponds to the range of nuclear separations executed by the hydrogen molecule in its lowest vibrational state.[16] The effect of rotational energy has been disregarded since it would add the same amount of energy to all the curves.

Now if a normal $H_2$ molecule is transformed by an electron impact from its lowest energy level on $a$ to one of the states represented by the other curves it will, according to the Franck-Condon principle, suffer meanwhile little change in nuclear separation. Immediately after the transition, therefore, there is a high probability that the point representing the energy state of the molecule will lie within the shaded area. Hence, transitions are represented in this diagram by vertical or nearly vertical jumps from one state to another. Transitions from the normal to the state $b$ would result in subsequent dissociation into two normal atoms each having several volts kinetic energy. This transition has no significance in the present experiment since only ions are measured. A jump to the state $c$ results in the ordinary $H_2^+$ ion which should, according to this scheme, occur at 15.25 to 17.9 volts with various amounts of vibrational energy. An inspection of the figure shows that there is a small chance of a transition to a point on this curve which lies above the dotted line and the molecule in this state would then dissociate. Hence a small number of $H^+$ ions should be predicted at potentials above 17.9 volts. From 27 to 40 volts should be required to raise the molecule from its normal state to that represented by curve $d$ where dissociation would occur into a normal H atom and a proton each having from 5 to 11 volts kinetic energy. Finally to strip both electrons from the $H_2$ molecule at a single blow should require from 46 to 56 volts and the two protons would then fly apart each with 7.5 to 12.5 volts kinetic energy. Between the last two stages there are many other transitions possible as a result of which the molecule would dissociate into a proton and an excited atom. Summarizing, then, the theory would predict the following primary reactions;

| | |
|---|---|
| 1. $H_2 \rightarrow H_2^+ + e$ | 15.4—17.9 volts |
| 2. $H_2 \rightarrow H^+ + H + e$ | 17.9—18.0 volts |
| 3. $H_2 \rightarrow H^+ + H + e +$ kinetic energy | 27 —40 volts |
| 4. $H_2 \rightarrow 2H^+ + 2e +$ kinetic energy | 46 —56 volts. |

## Apparatus and Procedure

The apparatus was the same as that used for the study of mercury ions[17] and the details will therefore not be given here. In the present experiment the

[13] R. T. Birge and C. R. Jeppesen, Nature **125**, 463 (1930).

[14] Burrau, Kgl. Danske Vid. Selskal. Math-fys. Med. **7**, 14 (1927).

[15] P. M. Morse and E. C. G. Stueckelberg, Phys. Rev. **33**, 932 (1929).

[16] For the details of this theory see E. U. Condon, Phys. Rev. **32**, 858 (1928).

[17] W. Bleakney, Phys. Rev. **34**, 157 (1929) and Phys. Rev. **35**, 139 (1930).

flow method was used, the hydrogen being admitted to the system through a palladium tube. This tube was surrounded on the outside with hydrogen at atmospheric pressure and its temperature was maintained at the required value by an electric heating element. The rate of flow of the gas into the apparatus could be regulated by adjusting the rheostat controlling the heating current. The pressure of the gas in the ionization chamber was not measured but it was estimated to be in all cases in the neighborhood of $10^{-3}$ mm Hg. A trace of mercury vapor was allowed to remain in the apparatus for calibration purposes.

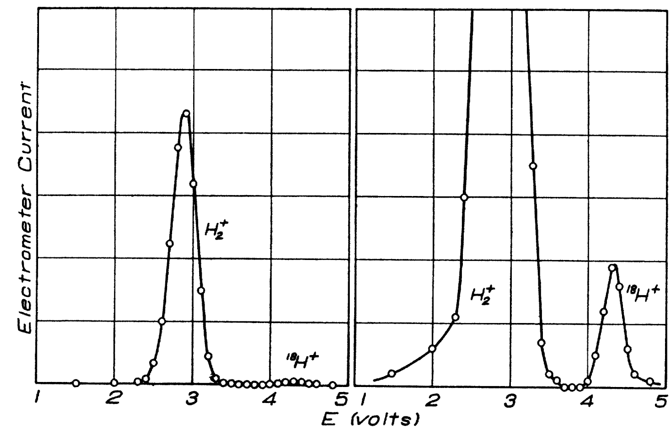


Fig. 2. A typical $e/m$ analysis curve. Electron velocity = 150 volts. The second curve is the first magnified 40 times.

## Experimental Results

*Primary ions in hydrogen.* Figure 2 illustrates an $e/m$ analysis curve for hydrogen ions produced by 150 volt electrons. The symbol $^{18}H^+$ is used to designate the atomic ion which begins to appear at 18 volts. The two curves represent the same data but in the second the ordinates have been expanded forty times. These two ions have at the instant of formation very little kinetic energy compared to that given them by the analyzing fields. In Fig. 3 is shown another peak obtained when the field $V_2$ ordinarily used to draw out the positive ions was made 1 volt per cm negative. In this case all the ordinary ions were prevented from reaching the analyzing chamber but those having high kinetic energy reached the collector. The number, however, was small and it was necessary to increase the sensitivity of the electrometer considerably in order to detect them at all. It will be noticed that the peak is very broad compared to those in Fig. 2. The second curve in Fig. 3 represents the maximum height of this peak as a function of the electron velocity. It is evident that weak ionization sets in at about 26 volts and becomes quite strong at 30 volts. This ion will be designated by the symbol $^{30}H^+$. These results can only be interpreted as *primary* processes. No trace of secondary reactions such as the formation of $H_3^+$ could be found.

*Critical potentials for ionization.* The ionization potentials for $H_2^+$ and $^{18}H^+$ obtained by plotting the heights of the peaks as functions of the electron velocity in volts are shown in Fig, 4, The $Hg^+$ ion is included in order to determine one point on the voltage scale assuming its ionization potential to be 10.4 volts. In this figure the curve for $^{30}H^+$ was obtained by measuring with a galvanometer the positive current reaching the plate, to which the

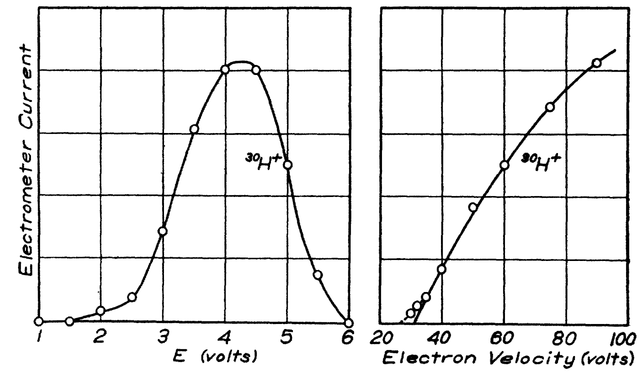


Fig. 3. A broad peak due to the initial high velocity of the ions. The second curve shows the ionization potential.

total positive ion current is ordinarily measured, against a small retarding field. This curve checks closely the one shown in Fig. 3 which was obtained in a different way. It would indicate that the critical potential for the forma-

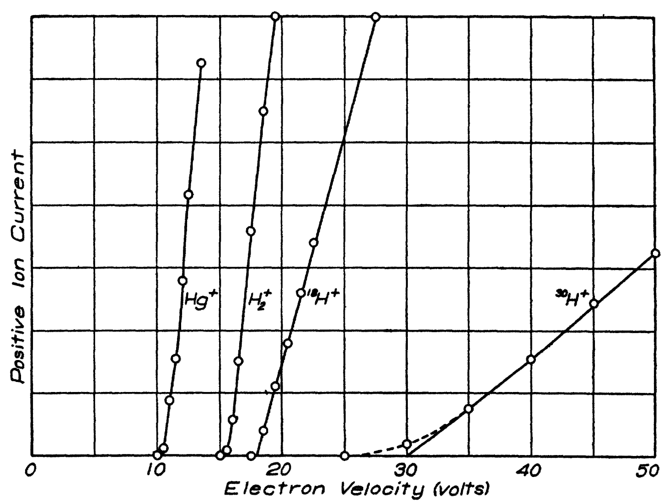


Fig. 4. Ionization potentials.

tion of this ion is about 26 volts while strong ionization of this type sets in from 30 to 35 volts. A summary of these results may be expressed in the following way.

| Process | Predicted | Observed |
|---|---|---|
| 1. $H_2 \rightarrow H_2^+ + e$ | 15.25 volts | $15.4 \pm 0.1$ volts |
| 2. $H_2 \rightarrow H + H^+ + e$ | 17.9 | $18.0 \pm 0.2$ |
| 3. $H_2 \rightarrow H + H^+ + e +$ kin. energy | 27. | $26 \pm 1.$ |

These conclusions constitute a striking confirmation of the theory.

*Relative numbers of the different ions.* The number of $^{18}H^+$ ions relative to the number of $H_2^+$ ions was determined by finding the relative areas[18] under the peaks in the $e/m$ analysis curves. Such a procedure was unsuitable, however, for determining the relative number of those ions having kinetic energy

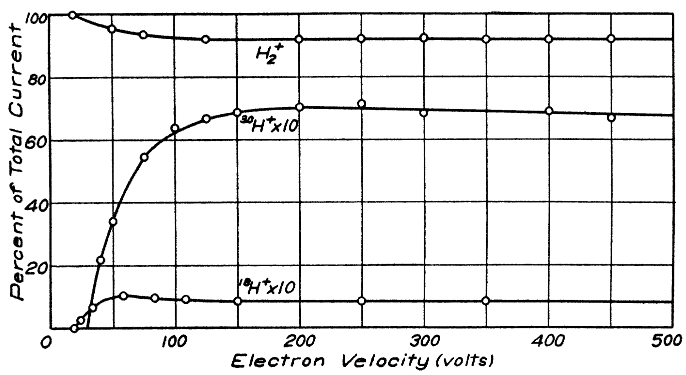


Fig. 5. Relative intensity of the different types of ions.

since only a small fraction is shot out in the direction of the analyzer. A rough estimate of their intensity was made in the following manner. The total positive ion current was measured with the galvanometer in the usual way and then the field $V_2$ was reversed so that only ions having kinetic energy

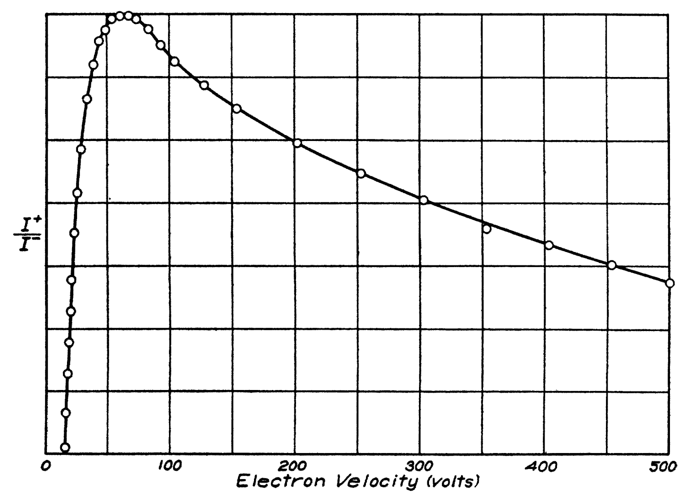


Fig. 6. Efficiency curve for hydrogen.

could reach the plate. This number reaching the plate was plotted as a function of the retarding field and the curve so obtained extrapolated to zero field. Knowing the solid angle subtended at the electron beam by the plate and assuming cylindrical symmetry the fraction of the total current due to those ions having kinetic energy was calculated. The results are shown in Fig.

[18] For a discussion of the assumption that the numbers are proportional to the areas see the second paper of reference 17.

5 where the ordinates for $^{18}H^+$ and $^{30}H^+$ have each been multiplied by ten. The curve for $^{30}H^+$ may include ions having kinetic energy as a result of some transition other than the 30 volt variety but it is believed that these are relatively very small in number.

*Efficiency of ionization.* Since in this experiment the pressure of the gas was not measured the efficiency of ionization could only be determined within an arbitrary constant factor. The result is given by the ratio of the electron current to the total positive ion current plotted as a function of the electron velocity. The curve, Fig. 6, shows a well-defined maximum at 60 volts. From the previous data it may be concluded that over ninety percent of the total number is made up of $H_2^+$ ions.

There is a marked difference between the shape of this curve and that reported by Compton and Van Voorhis[19] in that the maximum appears at a much lower electron velocity and the curve falls off more rapidly beyond this point. Qualitatively the agreement with the data of Hughes and Klein[20] is good.

## Discussion

It is believed that the results of this experiment yield, at present, the most direct evidence for the existence of those repulsive forces represented by the potential energy curves for the $H_2^+$ ion. It will be recalled that such an energy state is contrary to the concepts of the classical theory which predicts only a force of attraction. Indirectly these results also lend support to the reality of the other repulsive curves predicted by the quantum theory.

The determinations of the critical potential for the formation of $H_2^+$ as made by a large number of observers[21] cluster about a mean value of about 16.0 volts. That found in this experiment, 15.4 volts, is lower than any experimentally determined value known to the writer but it is believed that the method lends itself to greater accuracy than any of the previous methods. The close agreement with the theory lends support to this view. As Condon[9] has pointed out, it is now impossible in the light of the theory and these experiments to interpret the critical potential near 30 volts which has been reported by Krüger,[22] Horton and Davies,[23] and Vencov[24] as double ionization accompanied by dissociation. In the present work a search was made for the 50 volt transition resulting in $H_2^{++}$ but only slight evidence for its existence could be found. An effort is being extended in this laboratory to throw more light on this question with an apparatus designed to measure the velocity distribution of high velocity ions.

The author is greatly indebted to Professors E. U. Condon and John T. Tate for their many helpful suggestions.

[19] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26**, 436 (1925) and Phys. Rev. **27**, 724 (1926).

[20] A. L. Hughes and E. Klein, Phys. Rev. **23**, 450 (1924).

[21] For a compilation of these values see the paper by Hogness and Lunn, Phys. Rev. **26**, 44 (1925).

[22] T. Krüger, Ann. d. Physik **64**, 288 (1921).

[23] F. Horton and A. C. Davies, Phil. Mag. **46**, 872 (1923).

[24] S. Vençov, Comtes Rendus **189**, 27 (1929).