A STUDY OF THE VELOCITIES OF H^+ IONS FORMED IN HYDROGEN BY DISSOCIATION FOLLOWING ELECTRON IMPACT

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Abstract

An apparatus is described which is suitable for a study of the velocity distribution of ions formed by single electron impact Electrons, confined to a narrow beam by a magnetic field, pass along the axis of two coaxial cylinders, ionize the gas, and are collected by a trap. The thick, inner cylinder, which is slotted, serves to allow only ions moving perpendicularly to the electron beam to pass to the outer collecting cylinder. A retarding voltage is applied between the cylinders. A study of the positive ion current collected as a function of the retarding voltage permits a determination of the velocity distribution of the ions. The above method is employed in a study of hydrogen.

Velocity distribution of H^+ ions formed by electron impact in H_2. Theory shows that when the H_2 molecule is ionized by electron impact, it may prove unstable and dissociate into $H^+ + H$ (or H′) or into $H^+ + H^+$ if two electrons have been removed. The H^+ ions thus formed possess kinetic energy. The H^+ ions coming from dissociation into $H^+ + H$ should occur at minimum electron velocities of about 27 to 40 volts, possessing roughly 5 to 11 volts velocity; while the H^+ ions resulting from removal of two electrons occur at minimum electron velocities of 46 to 56 volts, possessing 7.5 to 12.5 volts velocity. In agreement with the predictions of the theory it was found that the velocities of those ions resulting from dissociation into $H^+ + H$ and $H^+ + H^+$ together with the minimum velocities necessary to produce them satisfy linear relationships.

Introduction

As PREDICTED by Condon[1] and first experimentally verified by Bleakney and Tate[2] and Bleakney[3] the ions formed by electron impact in hydrogen will, in general, if molecular dissociation follows the ionization process, acquire kinetic energies corresponding to several electron-volts. The repulsive forces which are operative in the dissociation process and to which the ions owe their resultant kinetic energies are due, in case both electrons are removed from the H_2 molecule, to the ordinary classical repulsion of two protons. In the case of the removal of but one electron from the molecule, however, the repulsive forces between the proton and the neutral (or possibly excited) H atom are non-classical and find their interpretation in terms of the quantum mechanics.[4] For this reason a more precise experimental study of the energy distribution among the ions so formed than was

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

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

[3] W. Bleakney, Phys. Rev. **35**, 1180 (1930).

[4] Burrau, Kgl. Danske Vid. Selskal. Math-fys. Med. **7**, 14 (1927). P. M. Morse and E. C. G. Stueckelberg, Phys. Rev. **33**, 932 (1929).

possible with the experimental arrangement of Bleakney and Tate was deemed advisable and was undertaken at their suggestion.

Predictions of the Theory

The theoretical potential energy curves for the hydrogen molecule given by Bleakney from sources quoted in his article[3] are reproduced in Fig. 1. The ordinates of these curves represent the potential energies, in volts,

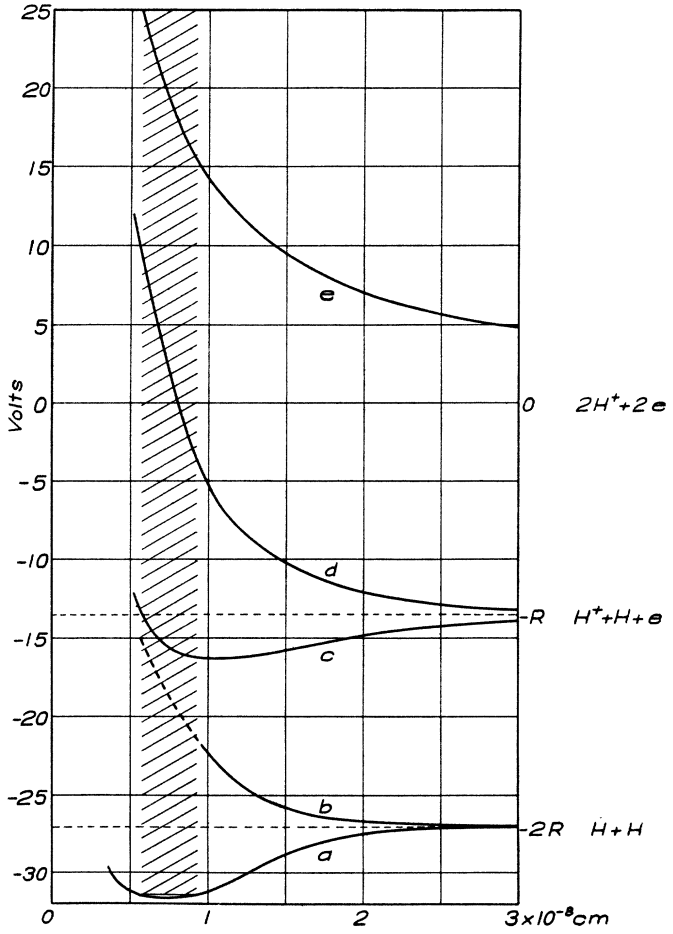

Fig. 1. Potential energy curves for the H_2 molecule.

of the various modes of bringing together the constituents of the hydrogen molecule as a function of the nuclear separation in Angstrom units. The zero of energy is taken with all of the constituents an infinite distance apart.

Curves *a* and *b* represent the two modes of bringing together two normal H atoms to form an H_2 molecule. The state *b* is unstable, while the state *a* represents the stable H_2 molecule. Curves *c* and *d* represent the two modes of bringing together a proton and a normal H atom to form the H_2^+ molecular ion. Curve *e* represents the one mode of bringing together two protons

to form an unstable H_2^{++} ion. The shaded area on the diagram represents approximately the range of separation of the two H atoms in the lowest vibration state of the H_2 molecule. It must be pointed out that this region is not entirely definite. The relative probability of finding the normal molecule with a given separation is greatest for the position of minimum potential energy and diminishes for separations greater or less than this. There is, however, some slight probability of finding the molecule with separations lying outside the shaded area.

The Franck-Condon principle states that transitions caused by electron impact, from the normal state to the states represented by the upper curves will be undergone without appreciable change in the nuclear separation. The molecule can be raised to the various states by an impacting electron possessing sufficient energy. Transitions to the state *b* would result in the dissociation of two normal atoms having from 3 to 6 volts kinetic energy. These have no significance for the present experiment, for the products would be uncharged. Transitions to state *c* would result in two possibilities. If the molecule be raised to any potential below -13.5 volts there would be formed stable H_2^+. However, for transitions to slightly higher potentials dissociation could result, giving H^+ and H possessing small amounts of kinetic energy. Only slight evidence for this transition was observed in the present experiment, however it has been observed by Bleakney[3] and has been suspected by others.[5] At minimum electron velocities of 27 to 40 volts, transitions to state *d* should be effected, resulting in dissociation into H^+ and H, each having velocities of 5 to 11 volts. With minimum electron velocities of 46 to 56 volts transitions to *e* should be possible, resulting in two H^+ ions having from 7.5 to 12.5 volts velocity. These are the transitions with which these experiments are concerned. The values given assume the transitions to take place within the shaded area. Since there is some probability of finding the molecule with separations beyond this region we would not expect the velocity distribution of the ions to terminate abruptly at the given values, but quite rapidly decrease beyond these.

In addition to these potential energy curves, there are a number of similar ones, not shown, corresponding to the removal of one electron from the H_2 molecule followed by dissociation into H^+ and H in its various excited states. In these experiments there was observed no evidence of transitions leading to dissociation into $H^+ + H'$. This leads one to suspect a relatively low probability for these processes.

Relations between energy of ions and energy of impacting electron. The electron velocity necessary to produce a given velocity ion from one of the states may well be called the ionization potential for the formation of an ion of that velocity from the specified state. If the initial energy of the molecule be E_1, that after dissociation E_2, the ionization potential V_i, and the kinetic energy of the ions V_P, then for the states *d* and *e*, or any similar ones,

[5] H. D. Smyth, Proc. Roy. Soc. **A105**, 116 (1924) and Phys. Rev. **25**, 452 (1925). T. R. Hogness and E. G. Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924) and Phys. Rev. **26**, 44 (1925).

$$V_i = (E_2 - E_1) + 2V_F. \tag{1}$$

This assumes; the dissociating entities possess equal kinetic energies, and no radiation takes place during the process of dissociation. For transitions to the state d this becomes

$$V_F = \tfrac{1}{2}V_i - \tfrac{1}{2}(31.4 - 13.5) \text{ (volts)} \tag{2}$$

While for transitions to the state e

$$V_F = \tfrac{1}{2}V_i - \tfrac{1}{2}(31.4 - 0). \tag{3}$$

These are the equations of straight lines with the slope one-half. Regardless of the shape of the potential energy curve for either of these states, the velocities of the ions and their ionization potentials must satisfy the relations above. The shape of the potential energy curves would, however, have an effect upon the form and range of the velocity distribution curve of the ions.

The Apparatus

The apparatus, shown in Fig. 2, was constructed of copper and was sealed in a Pyrex glass tube, which was then evacuated and baked out

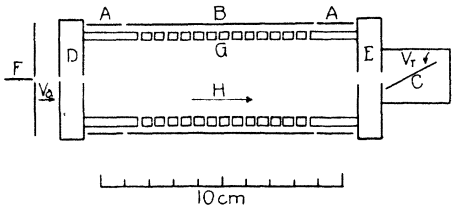

Fig. 2. Diagram of the apparatus.

several hours at 400° C. The source of electrons was a fine, sharply-pointed tungsten wire filament. An accelerating potential V_a was applied between the mid-point of the filament and the diaphragms D. The electrons passed through the holes in D and then through those in the diaphragms E and were finally collected at C. V_T was a potential of 175 volts holding the electrons to the plate C. A magnetic field H in the direction of the electron beam prevented any lateral spread. The electrons in traversing their path ionized the gas and ions were liberated, presumably in all directions. G was a circular cylinder with its axis along the electron beam. In it were cut a number of slots running around the circular boundary of the cylinder. These served to define the directions of the positive ions issuing from the electron beam and let pass only those ions having velocities very nearly perpendicular to the axis of the cylinder. These slots were of dimensions, 0.5 mm wide and 3 mm thick, requiring that the ions have 98 percent of their velocity or 96 percent of their volt-velocity perpendicular to the electron beam in order to pass through the slots. Parts A were cylindrical guard rings to B. Between A and G could be applied on the ions a retarding potential V_R. A Compton

electrometer with suitable carbon ink shunts was connected between A and B to measure currents to B.

The flow method was used to obtain a supply of hydrogen, which was admitted through a palladium tube surrounded by an electrical heating coil. The pressure used was estimated to be of the order of 2.0×10^{-4} mm Hg.

It was necessary to use electron currents of from 5 to 8 microamperes to obtain measureable positive ion currents.

For all of the data shown there was an initial velocity correction of 1.5 volts to be applied to the potential V_a. This was determined by noting the ionization potential of mercury vapor, which was not completely eliminated from the tube but was reduced to a very low pressure by liquid oxygen.

For such light ions as those of hydrogen the effect of the magnetic field upon the ions is not negligible. The effect was calculated. If ions be formed at the center of the cylinder with volt velocity V_F and pass out perpendicularly to the axis of the cylinder and are just able to reach B, in the presence of a retarding potential V_R and the magnetic field H, then

$$V_F = V_R + 300b^2eH^2/8mc^2 \text{ (volts)} \tag{4}$$

where b is the radius of the collector B in cm, e/m is the specific charge for the ion in e.s.u./gr., and H is the magnetic field in gauss. For H^+ ions, using the constants of the apparatus, this becomes

$$V_F = V_R + 0.63 \times 10^{-4}H^2 \text{ (volts)}. \tag{5}$$

For 100 and 150 gauss this correction becomes 0.63 and 1.42 volts, respectively.

Velocity Distribution of the Ions

The relative abundance of the positive ions at the various values of V_R was found by measuring the change in the electrometer current on varying V_R by a small amount ΔV, one-half of this on each side of the voltage V_R. Graphically, it was found that $\Delta V = 0.5$ volts was a small enough differentiating potential to give within the experimental error the form of the derivative curve of the total positive ion current-retarding potential curve for ions having velocities greater than 1.5 volts. The results are shown in Fig. 3. The magnetic field used was 100 gauss except in the 200 and 250 volt curves, for which it was 150 gauss. These curves were all taken at the same pressure and as shown have been reduced to equivalent electron current.

Curves of the ions without appreciable kinetic energy are not shown because the presence of mercury ions invalidated the results. It should be remarked, that, because of the magnetic field, theoretically there should be collected no H_2^+ ions having velocities of formation less than 0.3 volts. Actually a high peak is observed, coming in at about 15.5 volts electron velocity, with a velocity distribution maximum at about 1.0 volts. This is a much larger velocity than their expected temperature velocity at 25° C. It is to be remarked that the low velocity ions might be bent into small circles by the magnetic field, thereby creating an appreciable positive ion space charge which would impart to the ions some kinetic energy. Or, there

might exist an appreciable contact potential between the collecting cylinder and the defining cylinder G. Nevertheless, the corrections given by Eq. (5) were those applied.

For electron velocities up to 45 volts the maximum D of the velocity distribution curve shifts toward higher velocities as would be expected, for the electrons are acquiring sufficient velocities to produce the higher velocity ions. From 45 to 55 volts it remains approximately unchanged. Beginning

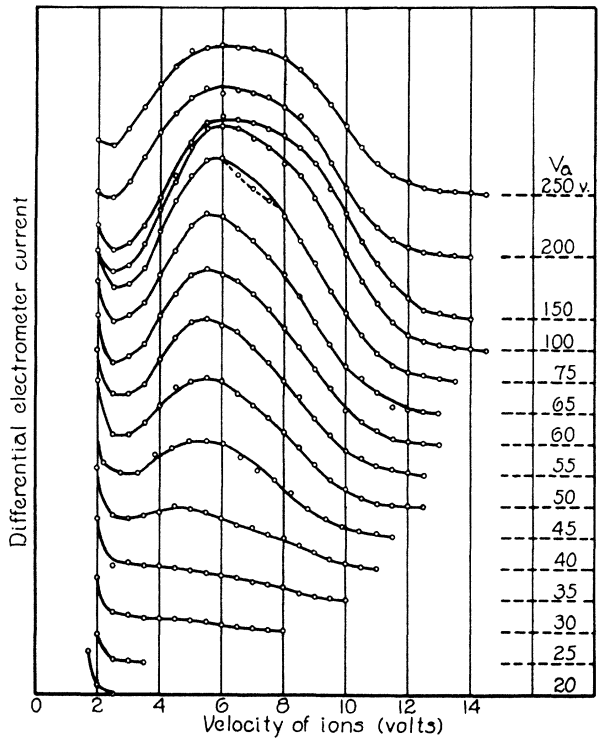

Fig. 3. Velocity distribution of the positive ions. An initial velocity correction of 1.5 volts should be applied to the values of V_a. The velocities of the ions have not been corrected for the effect of the magnetic field.

at about 60 volts the higher velocity ions increase noticeably in numbers, while the increase below the maximum is comparatively smaller. This is attributed to the yield of ions from the state e.

Ionization Potentials

Ionization potentials for those ions resulting from transitions to state d were determined by setting a certain retarding potential V_R and varying the potential V_a until positive ion current began to reach B.

Ionization potentials for those ions formed by transitions to state e required a little different procedure. Theoretically those ions having velocities between 7.5 and 11.0 volts could also be obtained by transitions to state d.

Therefore for this range the ionization potentials must be detected as upward breaks in the positive ion current vs. electron velocity curves for the various values of V_R. These results are shown in Fig. 4. In these curves the

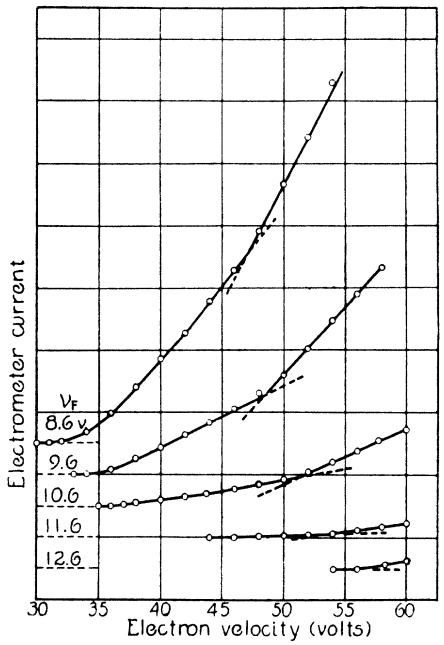

Fig. 4. Curves showing positive ion current reaching collecting cylinder against a definite retarding voltage, as a function of the electron velocity. The accelerating potential should be increased by 1.5 volts.

values of V_R have been corrected for the effect of the magnetic field. The electron velocities should however be increased by 1.5 volts, the initial velocity correction. The ionization potentials were determined and the results were plotted in Figs. 5 and 6. In Fig. 5 the straight line gives the theoretically predicted values for the state *d*, and Fig. 6 those for the state *e*.

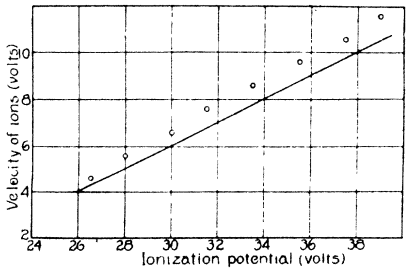

Fig. 5.

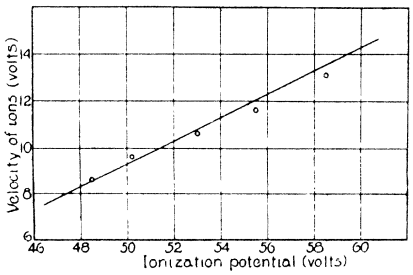

Fig. 6.

Relations between the velocities of the ions and their ionization potentials for transitions to states *d* (Fig. 5) and *e* (Fig. 6). The straight lines represent the theoretical relations and the circles represent the experimental values.

The circles give the experimental points. In these figures the above-mentioned corrections have been made.

Of the possible disturbing effects mentioned above, space charge would account for the direction of the discrepancy in Fig. 5. The effect of contact potential might cause a deviation in either direction. However, applying such a correction, the points in Fig. 6 would then lie below the straight line. But it is to be noticed that in Fig. 4 the breaks were taken at the intersections of the extrapolated straight lines, while it may be that they should have been taken at lower electron velocities, corresponding to the point where the smooth curve began to break away from the first straight line. In the last two curves of Fig. 4 the currents were quite small and the intersection with the zero axis is rather indefinite. This is to point out that the discrepancies are by no means serious.

Conclusions

The results of the present work constitute a striking confirmation of the essential correctness of the quantum mechanical theory of the hydrogen molecule. They provide a new method of attack on the general problem of molecular mechanics which will supplement the information gathered from the studies of band spectra by revealing the energy content of the unstable configurations of the molecule.

The experiments are now being extended to other gases. In conclusion, the writer wishes to express his gratitude to Professor John T. Tate and Dr. Walker Bleakney for their suggestion of the problem and for many practical aids throughout the investigation.