Proton Production by Electron Collisions in Molecular Hydrogen

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The collision processes leading to the production of protons by single electron collisions with molecular hydrogen were investigated. A mass spectrometer was used for the analysis. The electron beam, along which ions were produced, was coaxial with a cylindrical conductor, and the radial field within this conductor due to the electron space charge was used as an energy selector for the ions. The ions measured were those moving initially at right angles to the electron beam. The "fast" protons (ions having several electron volts of energy) found by Bleakney were observed, and a rough measurement of the cross section for their production was made. The cross section was found to reach a maximum of about 0.015 cm^2/cm^3 for 110-volt electrons. No evidence was found for the slow protons observed by Bleakney. It is believed that these were formed by secondary collision processes. From the theory developed by Smith, it is possible to compute roughly the initial energy distribution of the ions. The distributions are in accord with the potential energy curves of the hydrogen molecule..

INTRODUCTION

THE mechanism of proton production by electron collisions in molecular hydrogen has been the subject of many investigations.[1–6] Of particular interest is the work of Bleakney.[4] Analyzing the results of electron collisions in hydrogen with a mass spectrometer, Bleakney found evidence for two groups of protons, one group having kinetic energies of the order of several electron volts and the other group having essentially thermal energies. The ion clearing field was used as an energy selector to separate these groups of ions.

The protons having relatively large energies ("fast" protons) were readily understandable in terms of an excitation of the molecule from the ground state to state *f* (see Fig. 1) in the electronic diagram. Upon application of the Franck-Condon principle[7] to this excitation, it is necessary that the dissociating atom and proton share from 10 to 15 electron volts between them. The collision process giving rise to the slow protons is not so clear, however. Bleakney attributed them to excitations to the electronic state for the molecular ion (state *e*, Fig. 1), indicating that a portion of the potential energy curve for this state, lying within the Franck-Condon region, was above the dissociation level. Curve *e* in Fig. 1, which was taken from the work of Burrau,[8] indicates that this process is not very probable.

The slower protons observed by Bleakney might arise from secondary collision processes. A possible process is the dissociation of the

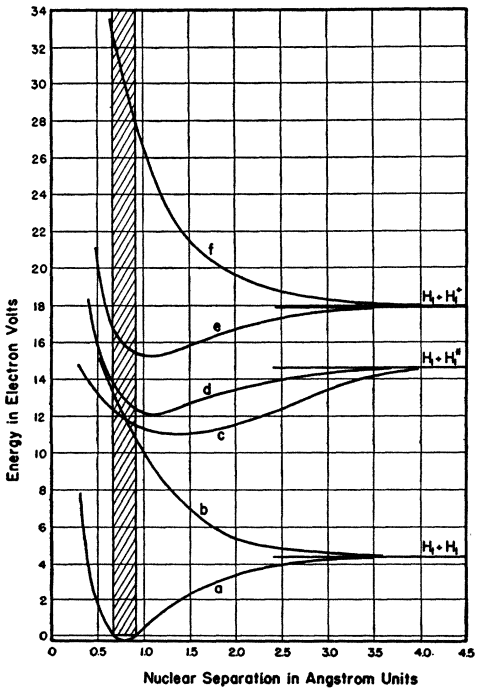

FIG. 1. Potential energy curves for the electronic states of the hydrogen molecule.

[1] A. J. Dempster, Phil. Mag. **31**, 438 (1916).
[2] H. D. Smyth, Phys. Rev. **25**, 452 (1925).
[3] H. D. Smyth and E. U. Condon, Proc. Nat. Acad. **14**, 871 (1928).
[4] W. Bleakney, Phys. Rev. **35**, 1180 (1930).
[5] W. Bleakney, Phys. Rev. **38**, 496 (1932).
[6] J. W. Hiby, Ann. d. Physik **34**, 5, 473 (1939).
[7] E. U. Condon, Phys. Rev. **32**, 858 (1928).
[8] Burrau, Kgl. Danske Vid. Selskal. Math-fys. Med. **7**, 14 (1927).

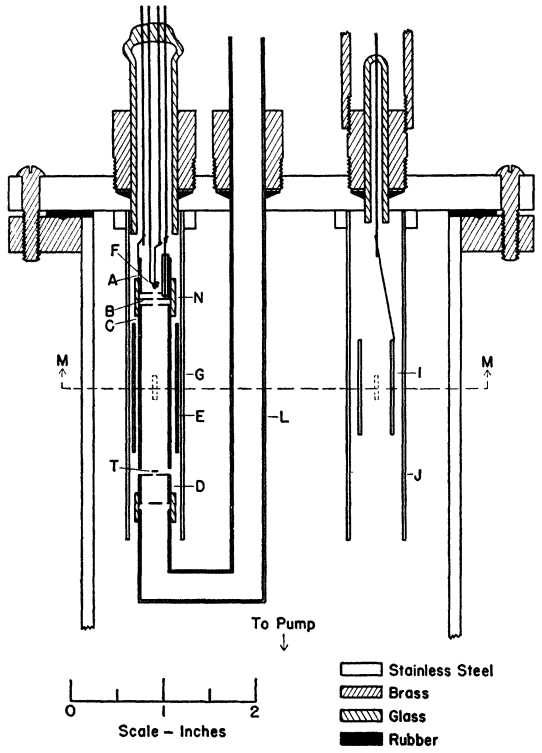

FIG. 2. Sectional view of the experimental apparatus.

molecule into two atoms, with subsequent ionization of one of the atoms, as indicated:

$$\begin{aligned} H_2+e &\rightarrow H_1+H_1+e \\ H_1+e &\rightarrow H_1^++2e. \end{aligned} \quad (1)$$

The collision cross section for the first step in this process has been computed by Massey and Mohr,[9] and they find it to be quite large for low electron energies (around 15 volts). However, the cross section decreases rapidly for higher energies. This dissociation process (excitation to state *b*, Fig. 1) gives the atoms a considerable amount of kinetic energy, and they would be expected to go to the walls of the apparatus. They may, however, return and form an appreciable atomic concentration, depending on the rate of recombination at the walls. Another process giving rise to slow atomic ions involves molecule-molecular ion collisions:

$$\begin{aligned} H_2+H_2^+ &\rightarrow H_3^++H_1 \\ H_3^+ &\rightarrow H_1^++H_2. \end{aligned} \quad (2)$$

[9] N. Massey and F. Mohr, Proc. Roy. Soc. **A135**, 258 (1932).

The unstable ion H_3^+ and the products resulting from it have been observed by several investigators.[2,10,11] In order for this process to occur, the molecular ion must acquire enough energy to dissociate the molecule.[12]

In view of the results of Bleakney, it seemed worthwhile to investigate again the collision processes in hydrogen, in order to see if the production of slow protons was the result of a direct collision process. Furthermore, it was thought worthwhile to attempt to make a rough measurement of the collision cross section for the production of the fast protons (excitation to state *f*, Fig. 1). This process is somewhat similar to the simple dissociation process (excitation to state *b*), and the two cross sections might be expected to be comparable and to vary similarly with electron energy.

EXPERIMENTAL METHOD

The experimental apparatus is shown in cross section in Fig. 2. Electrons are emitted by

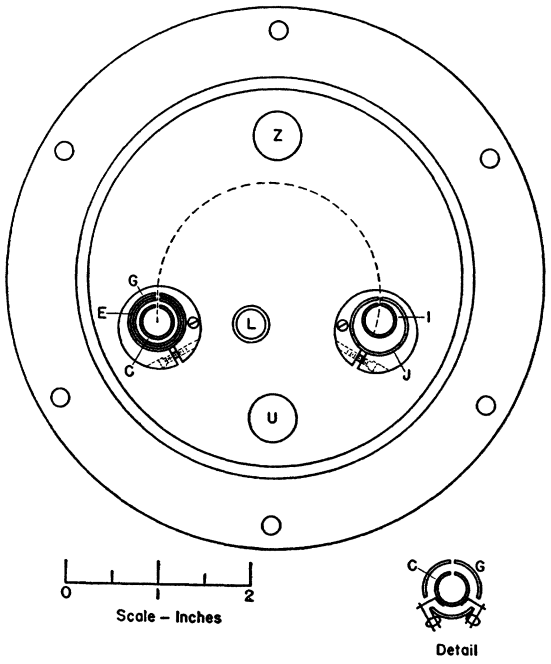

FIG. 3. Sectional view of the experimental apparatus (section through *MM* of Fig. 2). *U*, port for electrical connections. *Z*, port for ionization gauge.

[10] H. D. Smyth, J. Frank. Inst. **198**, 795 (1924).
[11] T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 44 (1925).
[12] K. E. Dorsch and H. Kallmann, Zeits. f. Physik **53**, 80 (1929).

the filament F and are accelerated and collimated by the electrodes A and B. The electron beam is coaxial with the cylindrical electrode C. The electron current is collected at the target T. The electrode D was used in adjusting the collimation and direction of the electron beam.

Hydrogen was introduced into the vacuum system through the tube L, and ions were formed by electron collision along the electron beam. Some of the ions go toward the slit in C (indicated by broken lines in Fig. 2). They are accelerated by the electrodes E and G, concentric with C. Under the action of the magnetic field parallel to the electron beam, the ions move in a circular path and are collected at the electrode I, which is surrounded by the guard J. The ion path is indicated by the broken line in Fig. 3, a sectional view through MM of Fig. 2. The magnetic field also serves to confine the electron beam.

The distinction between the collision processes leading to proton production is accomplished by the separation of the protons according to their kinetic energies. The field within the cylinder C due to the space charge of the electron beam is used as the energy selector. The radial variation of potential across the interior of a cylindrical conductor, in which there is an axial electron beam, has been computed by Smith.[13] The potential distribution is shown in Fig. 4, where V represents the potential (with respect to the electron source) at a point r from the axis of the cylinder. The space charge potential V_R will, of course, increase with increasing electron current and decrease with increasing electron energy. Ions produced by electron collisions in the beam will be able to reach the walls of the cylinder C (and the slit) only if they have at least an energy eV_R, where V_R is the potential difference between the center of the beam and the wall. The potential variation across the beam is neglected.

This experimental arrangement also serves to suppress proton production by molecule-molecular ion interactions. As was mentioned above, the molecular ion must acquire some energy to make this process possible. Molecular ions produced in the beam are effectively trapped there by the space charge field, unless their thermal energies are enough for them to reach the wall. In any case, they can acquire no energy from the radial field. There is, of course, a potential gradient along the beam, but this must be small.

As indicated in Fig. 2, the vacuum system was constructed almost entirely of stainless steel, U.S. 18–8 non-magnetic steel being used throughout. The electron gun was carried on

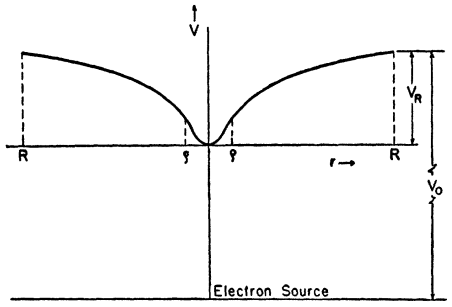

FIG. 4. Radial potential distribution across the cylinder C. V_0 = potential difference between electron source and cylinder C. V_R = potential difference between middle of electron beam and wall. R = inner radius of cylinder C. ρ = radius of electron beam.

one press seal, and it was centered with respect to C by the glass sleeve N. The filament was spiral of 5-mil tungsten wire. The aperture in B had a diameter of 1 mm and that in the cap on C a diameter of 2 mm. Electrodes B and C were held at fixed potentials, and the potential corresponding to the desired electron energy applied between the filament and C. Beam currents as large as 900 microamperes could be obtained with electron energies of 40 volts or more, though it was found desirable to limit the current to about 500 microamperes. From the size of the discolored spot found on the target T, it was concluded that the beam divergence was not appreciable.

The electrodes C, E, and D were mounted from the cylinder G by the Pyrex bead construction shown in the detail drawing in Fig. 3. The slits in C, E, and G were 1 mm wide and 6 mm long. A small fixed ion accelerating potential was applied between C and E, and the rest of the accelerating potential between E and G. The ion collector I was mounted from J by the same method used for C. The ion current

[13] L. P. Smith and P. L. Hartman, J. App. Phys. **11**, 220 (1940).

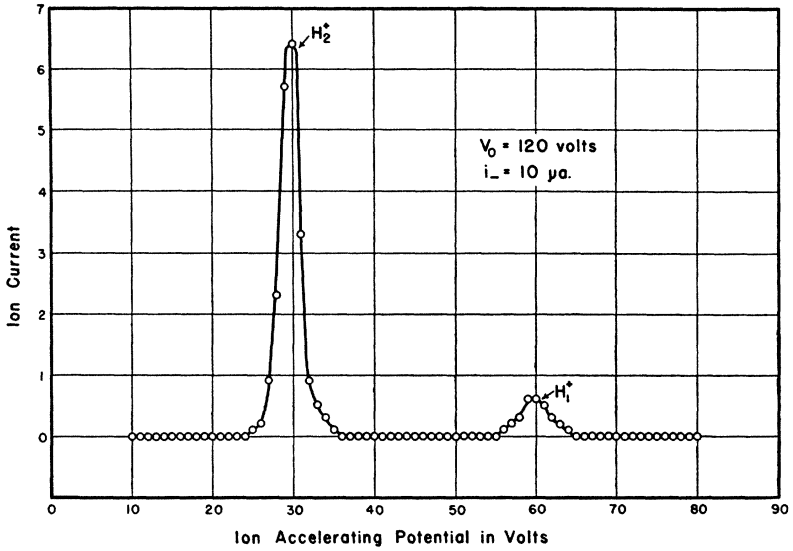

FIG. 5. Mass spectrum of hydrogen ions.

was measured with an electrometer tube circuit of the modified Barth type,[14,15] with the Western Electric D96475 tube. A maximum sensitivity of about 10,000 mm per volt was available, when a grid resistance of about 10^{10} ohms was used.

The system was evacuated by an oil diffusion pump of the type described by Malter and Marcuvitz.[16] A Cenco Megavac provided the fore vacuum. The hydrogen gas leaked into the system through a Hoke high vacuum valve. Commercial tank hydrogen was regarded as sufficiently pure for this work, as a mass-spectrometric analysis was being made. The operating pressure was about 5×10^{-5} mm Hg.

The magnetic field for the mass analysis was provided by a pair of Helmholtz coils. These coils gave a field of about 370 gauss at their center, with 7 amperes in the coils. The coils were mounted so their axis could be aligned with the desired direction of the electron beam.

EXPERIMENTAL RESULTS

A representative mass spectrum of the hydrogen ions is shown in Fig. 5. The magnetic field is held constant during such a series of measurements. The identification of the ion peaks is indicated in Fig. 5. At relatively high gas pressures, there was some background in the mass spectrum. This was attributed to the results of ion-molecule collisions in the ion-accelerating or in the analyzing region.

In order to observe the energy selection effect of the electron space charge, it is desirable to measure the variation in ion current with electron current, for a fixed value of the electron energy (V_0 in Fig. 4). By setting the apparatus to record the peak value of the ion current (for the atomic ions, say), this variation can be measured directly. Such a curve for protons at $V_0=60$ volts is shown in Fig. 6. It is seen that, for small electron currents, the ion current

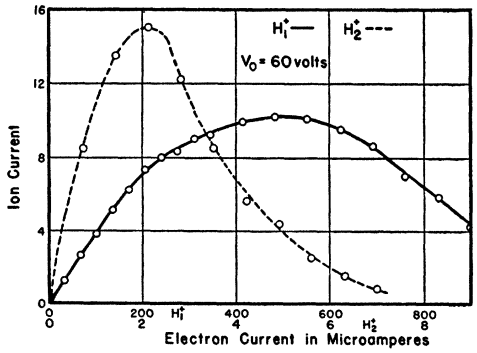

FIG. 6. Proton current and molecular ion current *vs.* electron beam current for 60-volt electrons.

[14] G. Barth, Zeits. f. Physik **87**, 399 (1934).
[15] D. B. Penick, Rev. Sci. Inst. **6**, 115 (1935).
[16] L. Malter and N. Marcuvitz, Rev. Sci. Inst. **9**, 92 (1938).

increases linearly with electron current. For larger electron currents, the energy selection effect becomes important, and, finally, the ion current decreases with increasing electron current. The corresponding curve for the molecular ions at $V_0=60$ volts is also shown in Fig. 6. It is important to notice that the electron current ranges are very different in the two cases. For the atomic ions, the ion current reaches a maximum for about 500-microamperes beam current, whereas the molecular ion current is a maximum for only two-microamperes beam current. Since the molecular ions acquire very little kinetic energy in the electron collision, the energy distribution of these ions should be essentially a Maxwellian one, corresponding to the gas temperature. The average energy of the molecular ions is therefore of the order of hundredths of electron volts with the gas at room temperature, and an electron current of only two microamperes is sufficient to produce a value of the space charge potential V_R in this range. In the case of the protons, however, an electron current of about 500 microamperes is necessary to increase V_R to the average energy of the ions. These protons clearly have much more than thermal energies, and it is reasonable to conclude that they arise from the excitation of the molecule from the ground state to state f (see Fig. 1).

Curves of proton current *vs.* electron current for various values of V_0 are shown in Fig. 7. The experimental points have been omitted from these graphs, for clarity. The fit for all the curves is about as good as in Fig. 6. The electron current for these data was limited to about 400 microamperes, because of difficulties with filament failure at higher currents. There is a regular variation in the slope of the linear portion of these curves with changing V_0, showing a variation of the cross section with electron energy (see below). The departure from linearity occurs at smaller electron currents for smaller values of V_0. This is reasonable, inasmuch as the electron current necessary to produce a given space charge potential V_R is smaller for smaller values of V_0. In the curves for large values of V_0, there seems to be a slight upward curvature, though this effect does not seem large enough to be significant.

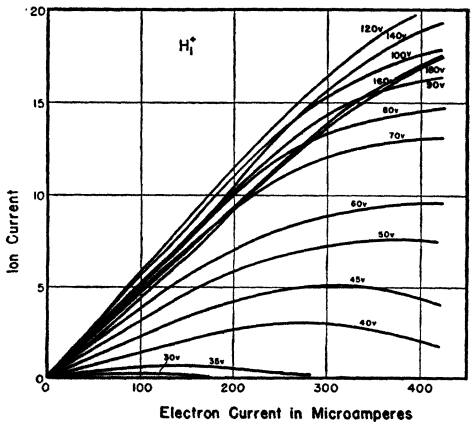

FIG. 7. Proton current *vs.* electron beam current for various electron energies.

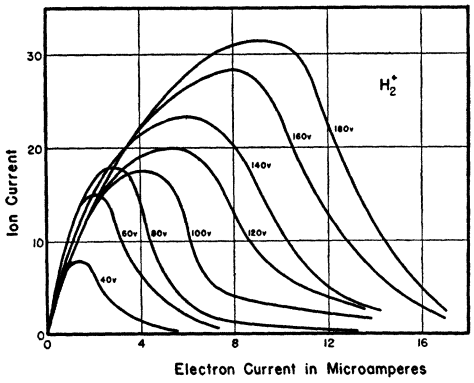

FIG. 8. Molecular ion current *vs.* electron beam current for various electron energies.

The corresponding curves for the molecular ions for various values of V_0 are shown in Fig. 8. Here again the experimental points are omitted, the fit being as good as that in Fig. 6. There is some variation in the slope of these curves near the origin, indicating a change in the ionization cross section with energy (see below). The variation of the beam current required to produce a given value of V_R as V_0 is changed, is shown more strikingly in these curves, as the maxima occur at smaller electron currents for smaller values of V_0.

If there are any slow protons (i.e., having energies in the thermal range) produced by single electron collisions, these protons should appear as a deviation from linearity in the curves of Fig. 7 for small electron currents. To

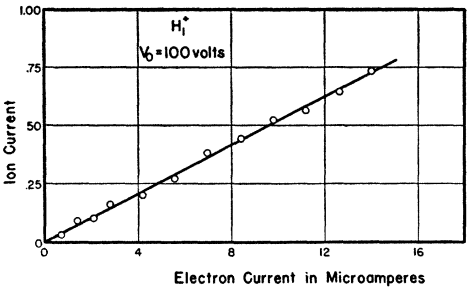

FIG. 9. Proton current *vs.* electron beam current for 100-volt electrons (small electron currents).

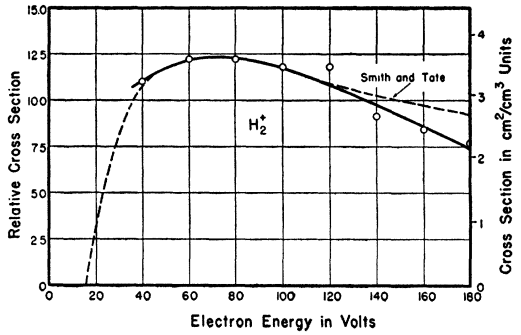

FIG. 10. Ionization cross section for molecular ions.

investigate this, the proton current was measured for the electron current range of Fig. 8, for various values of V_0. A typical curve for $V_0=100$ volts is shown in Fig. 9. There seems no reason to describe the variation as anything but linear. Similar curves were obtained for other values of V_0 in the range investigated.

INTERPRETATION

A. Cross Section for Molecular Ions

The slopes of the linear portions of the ion current *vs.* electron current curves are a measure of the collision cross section for the process involved. The relative molecular ionization cross section, as measured this way, is shown by the solid curve in Fig. 10. This result is not very accurate, since the curves of Fig. 8 depart from linearity for very small values of the electron current. The ionization cross section for hydrogen molecular ions has been measured absolutely by Smith and Tate,[17] and their result is shown by the broken line in Fig. 10. The two curves were matched at the maximum at 70 volts. The scale on the right is the ionization cross section for Smith and Tate's curve in cm^2/cm^3 units. When the uncertainty in the present results is considered, the agreement in trend is satisfactory.

B. Cross Section for Atomic Ions

The cross-section curve for the atomic ions (Fig. 11) was obtained in the same way as that for the molecular ions. The right-hand scale in Fig. 11 (in cm^2/cm^3 units) was obtained from the correspondence between the two scales in Fig. 10. The cross section for fast proton production is seen to be roughly 1/200 that for molecular ions, for the electron energy range investigated. This result does not agree with the work of Bleakney,[4] who found the ratio to be about 1/15. It was mentioned above that Bleakney measured the fast ions by reversing the ion collecting field across the collision region. In order to make the measurements on fast ions comparable with those on slow ions, Bleakney measured the fast ion current as this retarding field was reduced. By extrapolating to zero field, he obtained a value for the fast ion current which was presumably comparable with the slow ion currents measured. However, Hagstrum and Tate[18] have shown that the efficiency of collection of ions under such circumstances is a sensitive function of the ion energy. It is not certain, therefore, that the comparison is accurate.

C. Energy Distribution of the Ions

Since the ion current *vs.* electron current curves represent the result of an energy selection process, it is possible to derive the initial energy distribution of the ions from them. In order to compute the distribution, it is necessary to obtain an analytic expression connecting V_R, V_0 and the electron current i_-. From the theory developed by Smith,[13] it can be shown that, if V_R is not too large compared to V_0, the following relation holds:

$$V_R=\{1.52\times10^4 i_-(1+2\log R/\rho)\}/V_0^{\frac{1}{2}}. \quad (3)$$

In this expression, i_- is measured in amperes

[17] P. T. Smith and J. T. Tate, Phys. Rev. **39**, 270 (1932).

[18] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

and V_R and V_0 in volts. R and ρ are the radii indicated in Fig. 4. In the computation of the energy distributions, it is assumed that the ions measured are those which start out initially at right angles to the electron beam. Since the angular aperture of the collector slit, as seen from the accelerating slits (around the ion path), is quite small, this assumption is reasonable. It is quite accurate in the case of the fast protons, since these ions must have a very small original velocity component parallel to the electron beam if they are to be collected. Since the magnetic field supplies no energy to the ions, its effect on the motion of the ions within the cylinder C is neglected.

Let $f(E)dE$ be the fraction of the total number of ions produced per unit electron current per unit gas pressure, which have an energy between E and $E+dE$. $f(E)$ is, then, the desired energy distribution function. Let n_+ be the rate at which ions reach the wall per unit beam length. It is assumed that the measured ion current is proportional to n_+. Ions will reach the wall only if they have an energy greater than eV_R. The total rate at which they reach the wall is

$$n_+ = i_- \sigma p \int_{eV_R}^{\infty} f(E)dE, \tag{4}$$

where σ is the collision cross section and p the gas pressure. V_R can be expressed in terms of i_-, by use of Eq. (3). For the apparatus used, R is 3.9 mm and ρ is estimated to be 0.5 mm. Equation (3) reduces to:

$$V_R = \{7.8\times 10^4 i_-\}/V_0^{\frac{1}{2}} = \lambda i_-. \tag{5}$$

Equation (4) then becomes:

$$n_+ = i_- \sigma p \int_{e\lambda i_-}^{\infty} f(E)dE. \tag{6}$$

Let δ be the ratio of n_+ to i_-.

$$\delta = \sigma p \int_{e\lambda i_-}^{\infty} f(E)dE. \tag{7}$$

Differentiating δ with respect to i_-, one obtains:

$$d\delta/di_- = -e\sigma\lambda p f(E), \tag{8}$$

where E is the energy corresponding to the potential difference $V_R = \lambda i_-$.

The energy distribution of the ions is found from the experimental curves for a particular value of V_0 by first dividing each ion current value by the corresponding electron current. This ratio (δ) is plotted as a function of the electron current and the slope measured for various values of the electron current. The slope is plotted against λi_-, where λ is evaluated for the value of V_0 involved. This analysis has been carried through for the fast protons for several values of V_0. Figure 12 shows the resulting energy distribution curves, with the computed points indicated. The ordinates of these curves have been corrected for the change in cross section with V_0. These computations have been carried through only for rather small values of V_0, since the location of the maximum of the energy distribution requires that the ion current *vs.* electron current curves be measured well beyond the maxima. The method is not very accurate for finding the shape of the energy

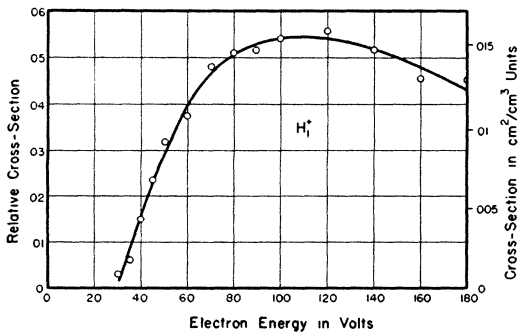

FIG. 11. Collision cross section for proton production.

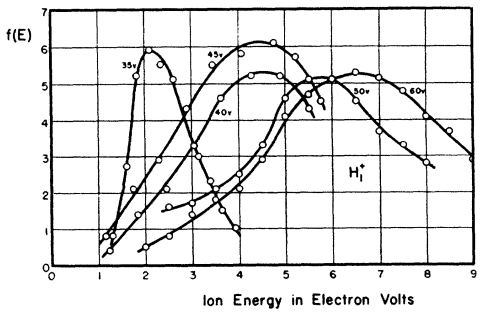

FIG. 12. Energy distributions of protons for various electron energies.

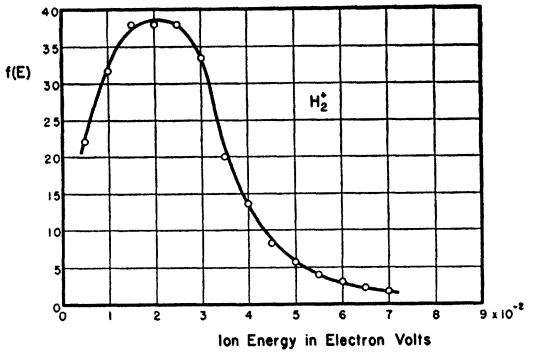

FIG. 13. Energy distribution of molecular ions for 60-volt electrons.

distribution curve, since it requires a measurement of the slope of the δ *vs.* i_- curves. However, the location of the maximum is probably accurate to half an electron volt. Most of the curves give average energies which are quite reasonable in terms of the potential energy curve for the state f (Fig. 1). There seems to be a significant shift of the maximum of the energy distributions toward lower energies, as the value of V_0 is reduced. This is in agreement with the work of Lozier.[19,20] The curve for $V_0=35$ volts is rather surprising as the maximum at about two electron volts is not compatible with the energy level diagram. However, the ion current for this value of V_0 is quite small, so the derived distribution is not reliable.

For comparison, the energy distribution for the molecular ions at $V_0=60$ volts has been computed. The result is shown in Fig. 13. As was mentioned above, the energy distribution should be Maxwellian. The derived distribution drops off a little too rapidly at high energies to be truly Maxwellian. However, the maximum occurs at about 2×10^{-2} electron volt, which is of the order $1/2kT$ for room temperature. It is not expected, however, that the analysis is as accurate for these ions as for the protons, since the molecular ions may have an appreciable fraction of their initial energy in a direction parallel to the electron beam and still be collected.

[19] W. W. Lozier, Phys. Rev. **36**, 1285 (1930).
[20] W. W. Lozier, Phys. Rev. **44**, 575 (1935).

CONCLUSIONS

From the measurements on the atomic ions, it may be concluded that, within the experimental error, there are no slow atomic ions formed by single electron collisions in molecular hydrogen. The slow ions observed by Bleakney may have come from either process (1) or from process (2). The fact that he observed these slow protons even at high electron energies (up to 500 volts), indicates that process (2), which involves ion-molecule collisions, is more likely.

The cross section for the production of protons was found to be about 1/200 that for molecular ions over the electron energy range investigated. This primary process for proton production cannot, therefore, account for the high proton yields obtained in several ion sources.[21–24] Presumably the secondary processes (1) or (2) are responsible for the majority of the protons obtained. In low voltage ion sources in which the walls have been treated to suppress recombination, process (1), involving dissociation and subsequent ionization, may be important.

It has been shown that the method used allows one to compute the energy distribution of the ions formed. It is possible that this method may be of value in analyses of the ions formed by electron collisions in more complex molecules. The thermochemical data relative to the molecules, as obtained from the appearance potentials of the various types of ions, are always in doubt because of the possible energy of formation of the ion measured.

In conclusion, the author wishes to acknowledge his indebtedness to Professor Lloyd P. Smith, both for suggesting this problem and also for many helpful discussions during the course of this research.

[21] E. S. Lamar, W. W. Buechner, and K. T. Compton, Phys. Rev. **51**, 936 (1937).
[22] G. W. Scott, Phys. Rev. **55**, 954 (1939).
[23] A. T. Finkelstein, Rev. Sci. Inst. **11**, 94 (1940).
[24] E. S. Lamar, W. W. Buechner, and R. J. Van de Graaff, J. App. Phys. **12**, 132 (1941).