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Collisions between electrons and H_2^+ ions
I. Measurements of cross sections for proton production

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Abstract. Cross sections have been measured for the production of protons by collisions between electrons and H_2^+ ions for interaction energies between 18·4 and 980 eV. An ion source was specially designed to produce the H_2^+ ions under clearly defined conditions. At energies greater than 250 eV the present cross sections merge with those calculated by Peek in the limit of Born's approximation. This asymptotic behaviour was not displayed by previous measurements.

1. Introduction

Although H_2^+ is frequently an important constituent of astrophysical and laboratory plasmas, the unique interest in this ion stems from the fact that it is the simplest of all molecules. A series of experiments is planned to investigate collisions between electrons and H_2^+; the present paper describes measurements of cross sections for proton production. Similar cross sections have already been measured by Dunn *et al.* (1965), Dunn and Van Zyl (1967) and by Dance *et al.* (1967), but at high energies their results do not merge with the results of a closure calculation which Peek (1967) performed in the limit of Born's approximation. The present results do agree with this calculation, but only when the interaction energy of the collidants (ie energy in centre of mass coordinates) is greater than about 250 eV.

Protons can be produced either by dissociative excitation,

$$\begin{aligned} &H_2^+(1s\sigma_g)+e \to H_2^+(2p\sigma_u)+e \to H+H^++e \\ &H_2^+(1s\sigma_g)+e \to H_2^+(2p\pi_u,\ 2s\sigma_g,\ 3d\pi_g,\ \text{etc.})+e \to H^*+H^++e \end{aligned} \tag{1}$$

or ionization,

$$H_2^+(1s\sigma_g)+e \to H^++H^++2e. \tag{2}$$

The more important states of H_2^+ are illustrated by the potential energy curves of figure 1. If cross sections for ionization and for all dissociative states of excitation are respectively denoted by σ_i and σ_e, it follows that a measurement of the total current of protons produced by the collisions will give a cross section, $\sigma_p = \sigma_e + 2\sigma_i$, because each ionization produces two protons. The present experiment differs from those previously reported in that the currents of protons were not measured, but they were detected by a particle multiplier and counted. Since ionization results in the simultaneous production of two protons, these were recorded as single events so that a cross section $\sigma_p' = \sigma_e + \sigma_i$ was obtained. The differences between σ_p and σ_p' are not, however, large because σ_i is usually an order of magnitude smaller than σ_e.

The following sections include some comments on the two previous experiments and a description of the present apparatus and method. The results are presented in § 4 where they are discussed and compared with theory.

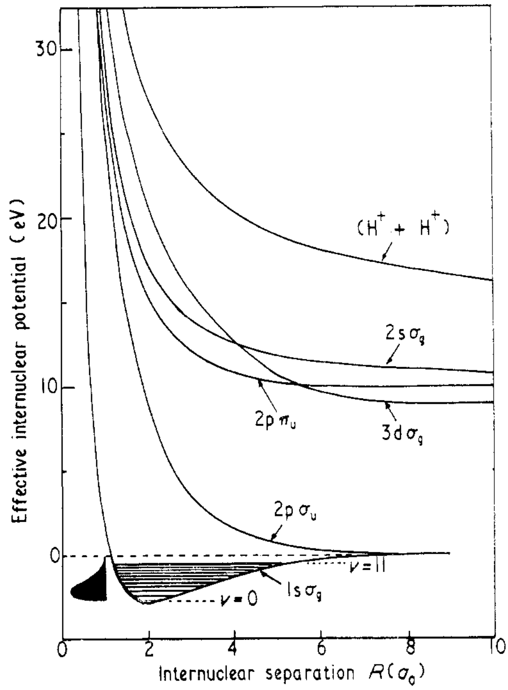

Figure 1. Potential energy curves of H_2^+. Vibrational levels of the $1s\sigma_g$ state are shown. The histogram indicates populations of these levels determined by Franck–Condon factors.

2. Considerations which influence experimental design

The methods used to measure the production of protons from H_2^+ are broadly similar to those used to study the ionization of atomic ions by electrons. These techniques have been extensively reviewed by Harrison (1968), Dolder (1969, to be called I) and Dunn (1969). However, when the target is a molecular ion, two further complications arise. One must take particular care to collect the ionic fragments, because these can be produced with considerable initial velocities, and it is also necessary to specify the initial state of vibrational excitation of the ion, because this influences the dissociative cross sections very considerably (Peek 1965, Oksyuk 1967, Peek and Green 1969).

Both previous experiments were designed to collect energetic molecular fragments, but only in the experiments of Dunn *et al.* was a source designed in an attempt to produce H_2^+ with a calculable distribution of vibrational states. In this source (which was simply a modified ionization gauge) hydrogen, at pressures of order 10^{-3} torr, was ionized by electrons which had much more energy than was needed to form H_2^+. At room temperature molecular hydrogen is predominantly in the $v = 0$ state, so it was argued that when hydrogen is ionized by fast electrons, the H_2^+ ions should be formed with a distribution of vibrational states defined by the appropriate Franck–Condon factors. This distribution should be preserved if the ions are removed quickly from the source without further collisions. Subsequently, von Busch and Dunn (in preparation, private communication) studied the photodissociation of beams from this source and found that there was less vibrational excitation than these simple arguments predict. They pointed out that either of two mechanisms can account quantitatively for this discrepancy. First, the matrix element for electronic transitions cannot be assumed to be independent of nuclear separation, and second, there may be a significant production of H_2^+ by autoionization. Nevertheless, the measured populations and those deduced by Franck–Condon factors gave calculated values of σ_p which did not differ by more than 4% at high interaction energies.

As it is not yet practicable to obtain an adequate beam of H_2^+ ions in a single vibrational state, it was decided, in the present experiments, to prepare H_2^+ by ionizing cold tenuous molecular beams of hydrogen with fast electrons. A special source was developed which is described in § 3. The conditions under which the ions were formed are therefore well defined and it was demonstrated that the results are remarkably insensitive to the source conditions, even at low interaction energies. When the present results are compared with theory it would be preferable to assume that the initial vibrational populations are given by the measurements of von Busch and Dunn, rather than by Franck–Condon factors. The existing theory, however, assumes large interaction energies and, under these conditions, the two population distributions lead to values of σ_p' which differ by less than the experimental error.

3. Apparatus and method

Figure 2 is a schematic scale plan of the apparatus. The source (S) produced H_2^+ ions which were accelerated to 20 keV and selected by deflection through 10° in the field

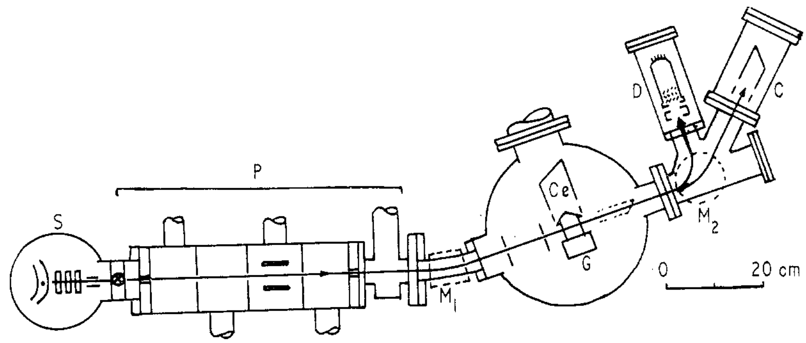

Figure 2. Scale plan of the apparatus. This shows the ion source (S), selector and analyser magnets (M_1 and M_2), electron gun (G), particle detector (D), electron and ion collectors (Ce and C), and differential pumping system (P).

of a magnet M_1. The magnetically shielded slits selected a collimated beam of H_2^+ which was bombarded by an electron beam which passed between the gun (G) and collector (Ce). Protons formed by these collisions were deflected through 90° by the field of magnet M_2 so that they struck the particle detector D (EMI type 9642), whilst the parent beam of H_2^+ was collected at C. The interior height of the tank between the poles of M_2 was 2·3 cm and the H_2^+ ions had 20 keV energy, consequently, protons formed at the electron beam with vertical components of energy less than 10 eV reached the proton detector. Dunn and Van Zyl calculated the energy distribution of protons formed by collisions between H_2^+ and fast electrons whilst Zare (1967) has predicted their angular distribution. If one assumes that H_2^+ ions were initially moving parallel to their beam axis, and discounts the convergence of protons by the field of M_2, it follows that, in these experiments, more than 98% of the protons formed by electron impacts reached the detector.

Details of experimental techniques, the electron gun, detector, and other components of the apparatus have already been given by Peart *et al.* (1970, to be called II), Peart *et al.* (1971) and Dolder (1969). The ion source, which is illustrated by figure 3

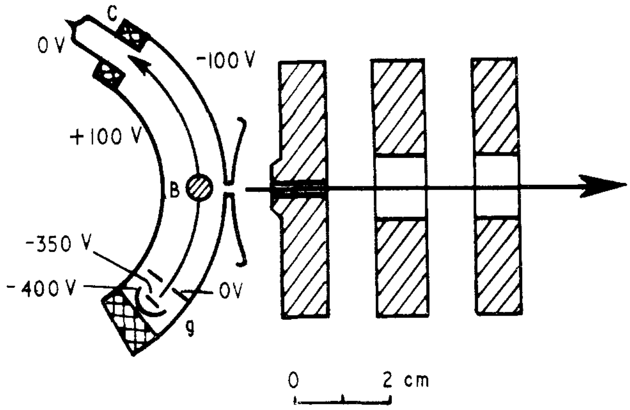

Figure 3. Scale plan of the ion source and einzel lens. Electrons from the gun (g) ionized a cold molecular beam of hydrogen (B) and were collected at C.

is, however, new. The gun (g) produced a beam of electrons, typically with energy 350 eV and a current 10^{-3} A, which was deflected into the collector C by an electric field of 150 V cm^{-1} between the two cylindrical electrodes. The electrons passed perpendicularly through a molecular beam of hydrogen (B) ($\simeq 10^{13}$ molecules cm^{-3}) which was obtained by expansion from a long thin tube. The H_2^+ ions formed were immediately propelled towards the exit aperture of the source by the electric field which curved the electron beam. It is estimated that only about 1% of the H_2^+ ions collided with a gas molecule after formation, so that the beam had a vibrational population corresponding to the ionization of cold hydrogen by fast electrons. It will be noted that, unlike most other sources, none of the hydrogen could be heated by collisions with the filament or vacuum envelope before it was ionized. To accelerate the ions, the whole source was held at potentials up to 20 kV so that the electrode potentials indicated in figure 3 are relative to the anode of the electric gun in the source. An electrostatic einzel lens focused the ion beam.

The cross section σ_p' is related to measurable quantities by,

$$\sigma_p' = \frac{R_s}{IJ} \frac{vV}{(v^2+V^2)^{1/2}} \frac{e^2F'}{\Omega} \tag{3}$$

where v and V are the electron and ion velocities in laboratory coordinates, I and J are the currents of the H_2^+ and electron beams, and R_s is the measured rate of signals due to electron–ion collisions. The factor F' (defined in I) takes account of non-uniformities in the current densities of the colliding beams and it is calculated from measured current density distributions. The detector efficiency Ω was measured as described by Peart *et al.* (1970). The interaction energy can be expressed in terms by the electron and ion masses and laboratory energies (m, M, E_e' and E_i', respectively) by,

$$E = \frac{M}{m+M}\left(E_e' + \frac{m}{M}E_i'\right). \tag{4}$$

The flux of protons formed by electron impacts was obscured by a large background, which was primarily due to protons formed by collisions between H_2^+ ions and residual gas. A beam modulation technique (illustrated by figure 5.2.8 of I) was therefore used to separate these signals and backgrounds. In this technique it is necessary to modulate both beams and gate two scalers at precisely related intervals. The scalers then respectively record the background and the sum of signal and background. Molyneux *et al.* (1971) have recently described a control unit employing integrated circuit logic which was used to provide these pulses.

4. Results and discussion

In figure 4 the present measurements of σ_p' are plotted against the interaction energy; the vertical bars represent 90% confidence limits of random error which were

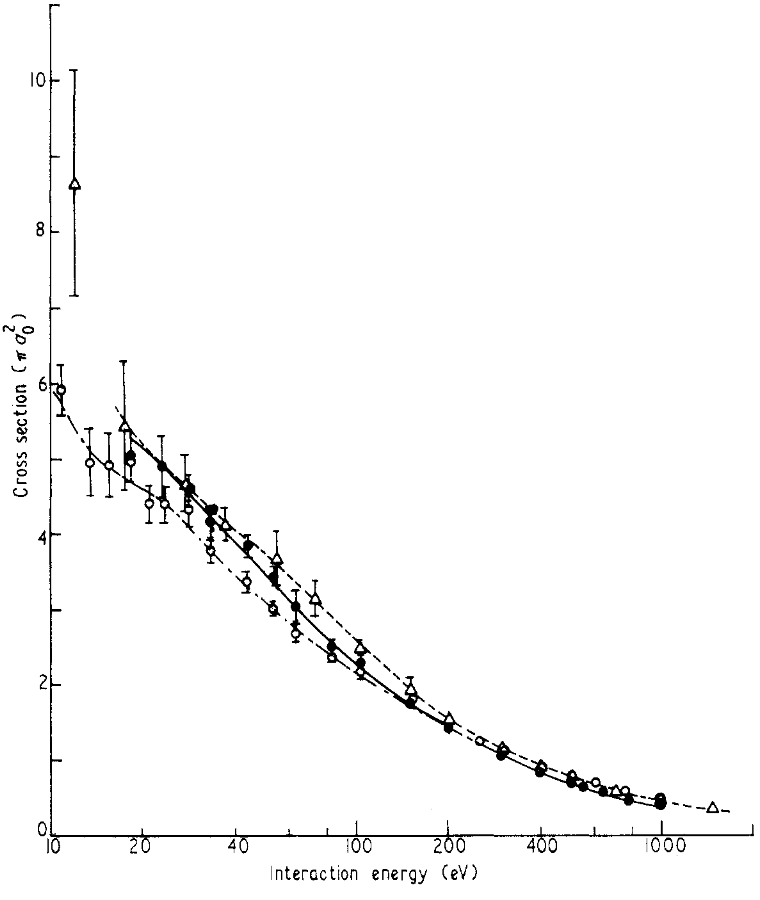

Figure 4. Measured cross sections for proton production, σ_p and σ_p' (see text) plotted against the interaction energy. ● present results of σ_p', △ Dunn and Van Zyl, ○ Dance *et al.* measurements of σ_p. The brackets show the various authors' estimates of random error.

assessed as described in II. The results and estimates of random and systematic errors are also presented in table 1. Included in the figure are the measurements of σ_p by Dance *et al.* and by Dunn and Van Zyl. It will be remembered that σ_p exceeds σ_p' by the dissociative ionization cross section σ_i.

Table 1

Interaction energy (eV)	Cross section (πa_0^2)	Random errors† (±%)	Maximum systematic error (±%)
18·4	5·05	7	12
23·4	4·90	9	9
28·4	4·65	4	8
33·4	4·18	6	8
43·4	3·85	4	7
53·4	3·44	4	7
63·4	3·05	7	7
88·4	2·51	4	7
103·4	2·30	3	7
153·4	1·77	4	7
203·4	1·45	4	7
300	1·06	5	7
400	0·86	7	7
500	0·69	4	7
550	0·64	5	7
640	0·57	5	7
785	0·46	4	7
980	0·40	8	7

† 90% confidence limits at each energy.

There is excellent consistency between the present results and those of Dunn and Van Zyl which lie above our measurements by an amount very close to the value of σ_i calculated by Alsmiller (1962) whilst, below the ionization threshold ($\simeq$25 eV), the two results almost merge.

By contrast the measurements of Dance *et al.* are smaller at lower energies. This is not surprising because they used an oscillating electron ion source in which the plasma could easily destroy the highly excited states of H_2^+ so that the vibrational populations in their beams would be weighted towards the lower states which have smaller cross sections.

It is interesting to plot $\sigma_p'E$ and $\sigma_p E$ against $\lg E$ to compare the results with linear relations predicted by theory. Peek (1967) has calculated cross sections at high energies for dissociative excitation to the $2p\sigma_u$ and $2p\pi_u$ states and also for the sum of all states excluding $2p\sigma_u$, but including ionization. The latter result was represented by $\sigma(\Sigma'')$. The cross sections were expressed in the form $\sigma E = A \lg E + B$ and values of the constants A and B were given for each of the three processes. Dunn and Van Zyl assumed that,

$$\sigma(\Sigma'') = \sigma(2p\pi_u) + \sigma_i \tag{5}$$

which implies that only the $2p\sigma_u$ and $2p\pi_u$ states contribute to dissociative excitation. It follows that,

$$\sigma_p = \sigma(2p\sigma_u) + 2\sigma(\Sigma'') - \sigma(2p\pi_u) \tag{6}$$

so that σ_p can be deduced from Peek's results. One can obtain,

$$\sigma_p' = \sigma(2p\sigma_u) + \sigma(\Sigma'') \tag{7}$$

without neglecting the contribution to excitation of any state. In each case the various cross sections must be averaged over an assumed vibrational population.

These estimates of σ_p and σ_p' are respectively represented by the thick broken and continuous lines in figure 5 which assume the vibrational population given by Franck–Condon factors. The population measured by von Busch and Dunn leads to slightly smaller cross sections represented by the thinner broken and continuous lines. The

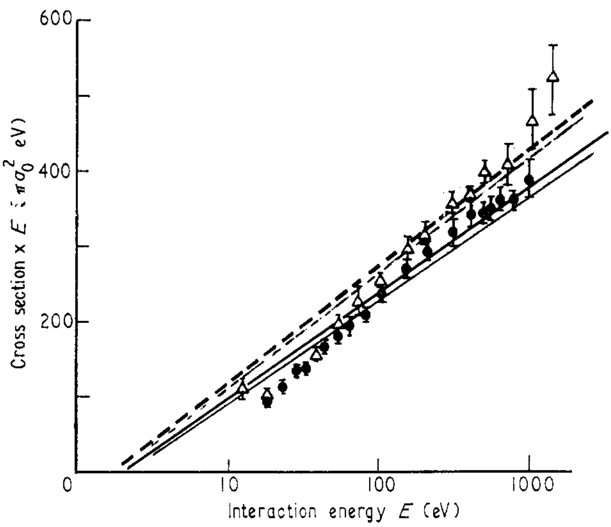

Figure 5. The present measurements (●) of σ_p', and those of Dunn and Van Zyl (△) for σ_p, expressed as a Bethe plot. The continuous and broken lines are the respective theoretical predictions by Peek. The thicker lines assume a vibrational population given by Franck–Condon factors, whilst the thinner lines are based on vibrational populations measured by von Busch and Dunn.

solid and hollow symbols in the figure respectively represent the present measurements of σ_p' and the results of Dunn and Van Zyl for σ_p. If the measurements of σ_p at the two highest energies are disregarded, the corresponding theoretical experimental results converge when $E \gtrsim 250$ eV. When the measurements of Dance *et al.* are plotted in this way they are more linear but their gradient is inconsistent with theory. Dance *et al.* noted that an accumulation of slow, secondary electrons in the region where the beams collide can cause the cross section to be overestimated. This effect will be discussed in § 5 and it is particularly significant at high interaction energies. It is suggested that it may not have been entirely eliminated from the previous experiments. Preliminary measurements by Dance *et al.* gave even larger cross sections at high energies and, although these erroneous results were not included in their paper, they have been published by Massey and Burhop (1969).

5. Experimental checks

Several of the experimental checks are illustrated by figure 6. Figure 6(*a*) shows three examples of the linear relations between $R_s F'/I^+$ and the electron current J which were measured at each interaction energy. The cross sections were obtained from the gradients of these lines whilst the random errors are represented by the 90% confidence limits of the slope. In calculating these slopes, the origin is given equal weight to the points and the observed linear relations are regarded as valuable experimental checks. The points in figure 6(*b*) show how measurements of the cross section, taken for an interaction energy of 103 eV, tend to a constant value as the ion beam energy is increased. This must be partly due to the loss of energetic protons from the slower beams and partly to the lower detection efficiency for slow protons. The continuous curve of figure 6(*b*) shows the effect of correcting for the variation of detector efficiency with proton energy.

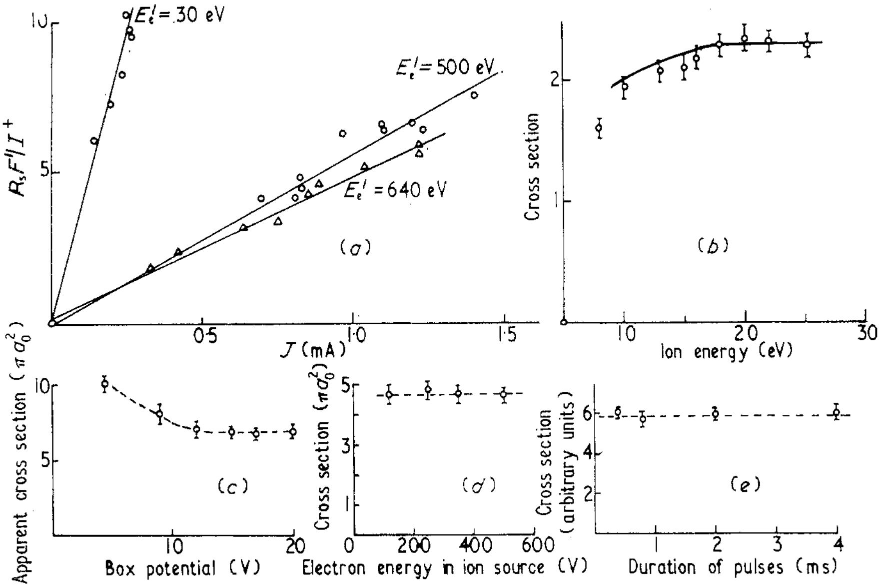

Figure 6. Some experimental checks; the interaction energy (E) or the electron laboratory energy (E_e') is shown in each case. (*a*) linear relations observed between R_sF'/I^+ and the electron current J. (*b*) Dependence of measured cross section upon H_2^+ beam energy, with $E = 103{\cdot}4$ eV. The variation is due to loss of energetic protons from slower beams and the lower detection efficiency for slower protons. The continuous curve shows the effect of correcting for loss of detection efficiency. (*c*) The effect upon the measurements of the negative potential used to eject slow electrons from the interaction region. $E_e' = 500$ eV. (*d*) Invariance of the measurements with energy of the electrons in the ion source. $E = 28$ eV. (*e*) Invariance of the results with the period of beam modulation. $E_e' = 100$ eV.

It has already been mentioned that an accumulation of slow secondary electrons in the interaction region gives spuriously large results. This arises because the excitation threshold of H_2^+ is low and σ_e is large even at small energies. Consequently, a fast ion can easily be dissociated by an almost stationary electron. Dance *et al.* tackled this problem by placing a negatively charged box around the interaction space to eject slow electrons, which were only troublesome in experiments at high interaction energies. The same remedy was adopted here and figure 6(*c*) shows apparent cross sections, measured with 500 eV electrons, as a function of box potential. Potentials of -20 V were used to obtain the results shown in table 1 at high energies and it was carefully verified (by obtaining several curves similar to figure 6(*c*)) that this potential was sufficient to eject all of the slow electrons.

It was also verified that the cross sections were insensitive to conditions in the ion source. These checks were deliberately performed with an interaction energy of only

28 eV because dissociative excitation is probably more sensitive to the vibrational population at lower energies. Figure 6(*d*) shows that no variations were observed when the energy of electrons in the ion source ranged from 100 to 500 eV. Measurements of pressure in the source tank confirmed that the particle density in the molecular beam was of order 10^{13} cm^{-3}, whilst the diameter of this beam was about 2 mm. It was therefore unlikely that more than about 1% of the ions suffered a collision before leaving the source.

Dance *et al.* suggested that pressure fluctuations, caused by outgassing of the electron collector in synchronism with the electron beam modulation, might also give spuriously large cross sections at the higher interaction energies. They avoided this problem by using a specially designed collector. This approach was carried further in the present measurements and figure 7 shows the electron collector used. It

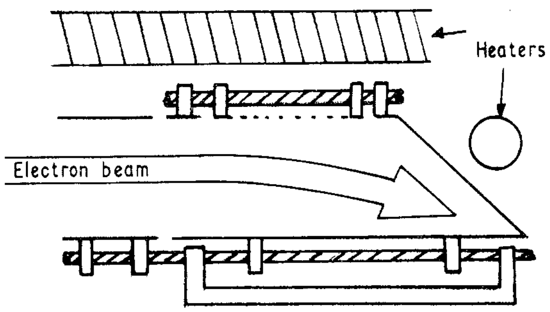

Figure 7. The electron collector designed to avoid pressure fluctuations synchronous with the electron beam modulation.

consisted of a stainless steel collecting plate which could be thoroughly outgassed by prolonged baking *in situ*. A negatively biased stainless steel gauze was used as a suppressor and this permitted gas to escape from the collector without entering the interaction region. To check that these precautions were effective σ_p' was measured for a wide range of modulation frequencies. Figure 6(*e*) shows the observed invariance of cross section with the duration of the electron and ion pulses for an electron energy of 100 eV.

6. A comparison of the present and previous experiments

Table 2 summarizes conditions which the various authors have stated to be typical of their experiments. Most of the symbols were defined in § 3 but P indicates the residual gas pressure and R_T is the background current. The ratio of R_s to R_T is

Table 2

Expt.	J (A)	I (A)	P (torr)	R_s	R_T	E (eV)	E_i' (keV)	sbr
DVZ	10^{-3}	2×10^{-8}	0.7–2×10^{-9}	10^{-15}A	10^{-12}A	10–1500	10	10^{-3}
DHRS	10^{-3}	10^{-6}	2×10^{-9}	10^{-14}A	10^{-12}A	5–1000	10–20	10^{-2}
Present	10^{-3}	7×10^{-10}	3×10^{-10}	50 s^{-1}	10^4 s^{-1}	18–1000	20	5×10^{-3}

denoted by sbr. It has already been mentioned that in the previous experiments protons were collected in a Faraday cup, whilst here, they were detected by a particle multiplier. A cup has the advantages that it can have a large aperture, so that it is easier to intercept all the protons, and the collection efficiency remains uniform over the whole entrance aperture. Figure 6(*b*) implies that the aperture of the multiplier used in these experiments was also sufficient to intercept all the protons, provided that the ion energy was large enough, and in none of the measurements was there any evidence of error due to variations of detection efficiency over the multiplier aperture. It must be remembered that the efficiency of a multiplier is very much more uniform over the entrance aperture when the multiplier is used in the pulse counting mode, rather than as a current amplifier.

Several valuable advantages accrue if the experiment is designed with a particle detector. Much smaller ion currents are adequate, so that it is easier to design an ion source in which the conditions are closely specified. A sophisticated beam modulation technique can be employed which makes the measurements insensitive to long term drifts in experimental conditions, or to spurious signals due solely to either the ion or the electron beam. Dance *et al.* used a much simpler modulation scheme which made it necessary to hold their beam currents and residual gas pressure almost constant over periods of hours so that very elaborate stabilization was required. The greatest attraction of a multiplier is, however, that its greater sensitivity points the way to more refined experiments employing inclined beams. Moreover, if two multipliers were used, one could in principle detect protons and hydrogen atoms produced by dissociation of H_2^+ in coincidence, so that cross sections could be obtained specifically for dissociative excitation.

Acknowledgments

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