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LABORATORY MEASUREMENT OF CHARGE TRANSFER CROSS-SECTIONS FOR PROTON + HYDROGEN AND PROTON + DEUTERON COLLISIONS AT LOW RELATIVE VELOCITIES

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LABORATORY MEASUREMENT OF CHARGE TRANSFER
CROSS SECTIONS FOR $H^+ + H$ AND $H^+ + D$
COLLISIONS AT LOW RELATIVE VELOCITIES

by

John D. Cogan

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

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HOUSTON, TEXAS
JULY 1980
Abstract

Laboratory Measurement of Charge Transfer

Cross Sections for $H^+ + H$ and $H^+ + D$

Collisions at Low Relative Velocities

by

John D. Cogan

Total charge transfer cross sections for the reaction $H^+ + H(1s) \rightarrow H(1s) + H^+$ and the isotopic reaction $H^+ + D(1s) \rightarrow H(1s) + D^+$ are presented for collisions at center of mass energies ranging from 0.05 eV to 150 eV. These data were experimentally determined by the technique of merged beams. This reaction is the most fundamental charge transfer reaction and is also one of the primary processes resulting in loss of hydrogen from the upper atmosphere. The apparatus is described and a number of experimental difficulties associated with laboratory study of the reaction are discussed. A summary of theoretical treatments is also presented. The results include the first cross sections measured at collision energies below 1 eV. Agreement with theory at energies above 10 eV is excellent. The results below 5 eV agree with the best quantum mechanical calculations only to within about 30%. Possible causes of the disagreement are discussed.
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Chapter 1

During the 1950's and 1960's a growing interest was developing in the field of aeronomy due, among other factors, to the increasing accessibility of the upper levels of the atmosphere by high altitude rockets and satellites. A better understanding of the basic chemical processes occurring in the atmosphere was sought through both theoretical computations and controlled experiments in the laboratory. Among the reactions of interest was resonant charge transfer between hydrogen atoms and protons

\[ H^+ + H(1s) \rightarrow H(1s) + H^+ \] (1-1)

which is important for the additional reason that it is the most fundamental charge transfer reaction. A number of theoretical and experimental studies have been carried out for reaction (1-1) over a wide range of collision energies. Atmospherically, the interesting energy range is below 1 eV and some of the theoretical work (including the best quantum mechanical calculations to date) has covered this range. However, due to a number of difficulties, no experimental studies have been carried out below a few electron volts.

The purpose of this thesis is to report experimentally measured cross sections for reaction (1-1) and the isotopic reaction

\[ H^+ + D(1s) \rightarrow H(1s) + D^+ \] (1-2)
over a broad energy range (0.05 eV-150 eV) which includes the range of atmospheric interest. The remaining five chapters of the thesis are divided as follows. Chapter 2 is a discussion of the motivation for conducting the experiment. Chapters 3 and 4 are descriptions of the apparatus and the experimental details. Chapter 5 is a theoretical discussion of reactions (1-1) and (1-2) and Chapter 6 is a report of the results.
Chapter 2
Atmospheric Interest

Before a discussion of the experimental details is presented, the motivation for performing this experiment will be provided. There are two primary reasons for measuring cross sections for the charge transfer reaction

\[ \text{H}^+ + \text{H}(1s) \rightarrow \text{H}(1s) + \text{H}^+ \]  

(2-1)

First, it is the most elementary such reaction and consequently lends itself more easily than any other to accurate semiclassical and quantum mechanical calculations. Second, this process occurs in the atmosphere and is a major contributing factor to the balance of atmospheric hydrogen.

Since reaction (2-1) is the simplest charge transfer reaction, a large body of theoretical work (which will be discussed in Chapter 5) has been done both at high and low energies. In addition, a large number of experimental investigations of this process have been carried out to complement the theories. However, due to the difficulty of performing collision experiments at very low energies, all experimental studies to date have been done at energies above a few eV. Moreover, the best theories have covered the energy range from .0001 eV to 10 eV. Due to the lack of experimental data with which to compare these theories, the present work was undertaken with the purpose of filling in part of the gap, specifically from .05 eV to 10 eV.
Determination of the cross sections in this range is also important because of the role of reaction (2-1) in the upper atmosphere. The remainder of this chapter will be devoted to a discussion of this role, beginning with a brief description of the atmosphere.

Figure 2-1 shows the basic structure of the earth's atmosphere. The major regions may be delineated in various ways: for example, in terms of the sign and magnitude of the temperature gradient. Other criteria include density, chemical composition, electron density, and the occurrence of specific reactions or processes.

The region closest to the earth's surface—the troposphere—is characterized by a negative temperature gradient. The temperature drops from about 300K at sea level to 200K at an altitude of 10-12 kilometers. The majority of weather activity takes place in this region, although there are effects from high altitude winds in the region above, the stratosphere.

The upper boundary of the troposphere is the tropopause, above which the temperature increases with altitude, reaching a maximum of slightly over 300K at the stratopause. This positive temperature gradient results from the presence of ozone (O_3) which absorbs ultraviolet radiation in the range of wavelengths between 2200Å and 3400Å. Radiation in this band is extremely harmful to plants and animals; consequently, the ozone layer is an important shield for
Figure 2-1. Regions of the atmosphere.
life on earth. In addition, the absorbed energy results in stratospheric heating, producing the observed temperature increase.

The stratosphere extends to about 50 km, above which lies the mesosphere. Here the temperature gradient is again negative since there is little or no absorption of radiation, and at the mesopause, 90 km above sea level, the temperature reaches a low of ~190K.

Collectively, the troposphere, stratosphere and mesosphere are called the homosphere because the chemical composition of this region is not altitude dependent (except for trace gases such as ozone). Above this region, the composition is very dependent on altitude and as a result, the regions above 90 km are collectively called the heterosphere.

Between 90 km and 500 km is the thermosphere. Here the temperature increases with altitude primarily as a result of absorption of hard ultraviolet radiation by N$_2$ and O$_2$. The temperature in the upper levels of the thermosphere varies between 600K and 2000K depending upon the time of day and the state of solar activity.

The level of 500 km is an important atmospheric boundary referred to as the critical height. Above this boundary lies the exosphere in which the density of particles is so low that collisions are infrequent and most of the particles move on satellite or ballistic trajectories. Since collisions are rare, any atom which acquires escape
velocity will probably escape if its velocity vector is directed radially outward. Consequently, the critical height may be viewed as the outer "surface" of the atmosphere.

There are two major regions which have not been discussed yet. The first of these is the ionosphere which spans portions of the stratosphere, the mesosphere, and the thermosphere. It contains ions (and electrons) produced by photoionization and collisional ionization. The second region is the plasmasphere, a toroidal-shaped region consisting of charged particles trapped on geomagnetic field lines at high altitudes. These particles are primarily $0^+$, $H^+$, $He^+$ and electrons.

Hydrogen

Hydrogen is only a minor atmospheric constituent in the homosphere and it exists almost exclusively in molecules of $H_2$, $H_2O$, $OH$, and $CH_4$. Conversely, in the exosphere atomic hydrogen is a major component. The high altitude distribution of hydrogen atoms has been widely studied in recent years by the use of satellites, rockets, and radio telescopes. The techniques used may be classified into four methods: direct and indirect Lyman $\alpha$ measurements and charge transfer equilibrium calculations based on satellite and radio telescope data.

The first technique is direct measurement of the intensity of Lyman $\alpha$ radiation scattered from hydrogen atoms
in the exosphere, and use of the results to calculate a hydrogen distribution based on a particular atmospheric model. This method was used by Meier et al.\textsuperscript{2} who obtained Lyman \(\alpha\) intensity data from a high altitude rocket. Meier and Mange\textsuperscript{3} obtained radiation data from the OGO-4 satellite. Similar measurements were made by Bertraux\textsuperscript{4} using the OGO-5 satellite and by Thomas and Anderson\textsuperscript{5} with the OGO-6 satellite. These and other investigators have fit their data to atmospheric models by Kockarts and Nicholet,\textsuperscript{6} Chamberlain,\textsuperscript{7} and Jacchia\textsuperscript{8,9}

The second technique is measurement of absorption in the center of the solar Lyman \(\alpha\) line by hydrogen atoms between the detector and the sun. Such observations were carried out on the OSO-5 satellite by Vidal Madjar et al.\textsuperscript{10} with results that agreed with the direct Lyman \(\alpha\) measurements. Figure 2-2 shows the results of some of these measurements at 500 km for varying temperature.

The other two methods of determining hydrogen densities are based on an equilibrium for the charge transfer reaction

\[
0^+ + H \rightleftharpoons 0 + H^+
\]  \hspace{1cm} (2-2)

Brinton and Mayr\textsuperscript{11,12} used measurements of \(0^+\) and \(H^+\) densities obtained with a mass spectrometer aboard the Explorer 32 satellite along with a density of 0 based on the Jacchia model to calculate \(n(H)\) from the relationship\textsuperscript{13}
Figure 2-2. Hydrogen density as a function of temperature at 500 km. From Thomas and Anderson (1976).
\[ n(\text{H}) = \frac{8}{9} n(\text{O}) \frac{n(\text{H}^+)}{n(\text{O}^+)} \]  

(2-3)

Ho and Moorcraft\textsuperscript{14} used equation (2-3) and the Jacchia model in conjunction with \(0^+\) and \(\text{H}^+\) densities obtained from incoherent scatter data taken at Arecibo. Results of all of these measurements (with emphasis on the diurnal variation of hydrogen density) are discussed by Tinsley et al.\textsuperscript{15}

These techniques have provided a fairly consistent set of data for the density of hydrogen atoms as a function of altitude and temperature in the upper atmosphere. To provide a complete picture of the role of hydrogen, however, it is necessary to know the rates at which the element enters and leaves the exosphere. Averaged over a period of time, these rates must be equal since the density of hydrogen is constant except for small diurnal variations.

Hydrogen enters the thermosphere from the lower atmosphere chiefly in the form of hydrogen compounds. Reactions between these molecules and other particles release hydrogen atoms, some of which diffuse upward to the base of the exosphere.

The chemistry of hydrogen below 150 km has recently been studied by Liu and Donahue\textsuperscript{16-18} and by Hunten and Strobel.\textsuperscript{19} These authors have outlined the various reactions involving hydrogen compounds and have used measured reaction rates to model the dynamics of hydrogen in the atmosphere. Some of these reactions release hydrogen in its atomic form:
\[ \text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H} \quad (2-4a) \]
\[ \text{H}_2 + \text{O}(^3\text{P}) \rightarrow \text{OH} + \text{H} \quad (2-4b) \]
\[ \text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{H} \quad (2-4c) \]
\[ \text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H} \quad (2-4d) \]
\[ \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \quad (2-4e) \]

Although the hydrogen atoms may undergo further reactions, some fraction of them will diffuse through the thermosphere into the exosphere. This depletion of atomic hydrogen in the thermosphere coupled with the continual influx of hydrogen compounds from the mesosphere causes the balance of reactions (2-4) to always favor production of more atomic hydrogen. The rate of hydrogen diffusion into the exosphere can be calculated from a knowledge of the densities of the compounds involved and the various reaction rates. This rate has been found to be approximately $2.0 \times 10^8$ particles/cm$^2$ sec$^{20}$ independent of temperature over the range that applies to the upper atmosphere. The rate of hydrogen loss from the exosphere must be equal to this rate.

Until recently only one process, thermal escape, was invoked to explain exospheric loss of H. This process (somewhat analogous to the evaporation of vapor from the surface of water) is the result of some atoms having the velocity required to escape the earth's gravitational field. The formula which describes thermal escape for an atmosphere with a Maxwellian velocity distribution was first derived
by J. H. Jeans $^{21}$ and the process is sometimes called Jeans escape. The flux is given by $^{22}$

$$
\xi_J = \frac{1}{2} n_c \left[ \frac{2kT}{\pi m} \left[ 1 + \frac{GMm}{kTR_C} \right] e^{-\frac{GMm}{kTR_C}} \right] \tag{2-5}
$$

where $n_c$ is the number density of hydrogen at the critical height, $R_C$ is the radial distance to the critical height, $m$ is the atomic mass of hydrogen and $M$ is the earth's mass. Recently it has been shown that the behavior of the atmosphere is not exactly Maxwellian and (2-5) is not strictly correct. The discrepancy is due to depletion of particles in the high energy tail of the velocity distribution. Chamberlain and Smith $^{23}$ and Brinkman $^{24}$ have shown that a more correct thermal escape rate is 0.73 times that given by equation (2-4).

The corrected calculated rate of Jeans escape is about 5.0x10$^7$ cm$^{-2}$ sec$^{-1}$ at 1100K, the average exobase temperature. This flux is not large enough to balance the influx of mesospheric hydrogen. The discrepancy had been attributed to inadequate data by some authors, $^{19}$ but the most recent data seem to confirm the disagreement. Liu and Donahue $^{17,18}$ have suggested two other processes which would account for the loss of some exospheric hydrogen: the polar wind and charge transfer between hydrogen atoms and fast protons.

Dessler and Michael $^{25}$ pointed out that the earth's magnetic field lines, which form closed loops at middle and
low latitudes, are open ended on the night side at high altitudes due to the "pressure" exerted by the solar wind (see Figure 2-3). Charged particles, which would be trapped along closed field lines, are propelled away from the polar regions and form the geomagnetic tail. The reaction

\[ 0^+ + H \rightarrow 0 + H^+ \quad (2-6) \]

provides a source of protons from hydrogen atoms in the upper thermosphere and lower exosphere. Some of these protons are lost to the polar wind, favoring the balance of equation (2-6) in the forward direction and a consequent loss of hydrogen atoms. The resulting imbalance of hydrogen as a function of latitude creates a lateral flow toward the poles, and an effective loss of hydrogen from the entire atmosphere. This process has been investigated and described by Banks and Holzer. The approximate rate of hydrogen loss at 1000K is \(2 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}\).

The second additional process is loss due to reaction (2-1). Cole was the first to suggest that charge transfer might account for a large percentage of the atomic hydrogen loss. Such escape occurs when a fast proton, trapped on a closed geomagnetic field line, undergoes charge transfer and becomes a fast hydrogen atom. If the atom is energetic enough (\(kT > 0.63 \text{ eV}\)) and is traveling radially outward, its momentum will carry it out of the earth's gravitational field.
Figure 2-3. The polar wind.
A number of authors have calculated the rate of hydrogen loss due to charge transfer with protons. Cole used a simple method based on the equation for attenuation of a beam in a gas:

$$\dot{\xi}_H = \dot{\xi}_H^+ n_H \sigma V$$  \hspace{1cm} (2-7)

where $\dot{\xi}_H$ is the outgoing flux of fast hydrogen atoms, $\dot{\xi}_H^+$ is the flux of protons, $n_H$ is the density of atomic hydrogen, $V$ is the volume in space in which the reaction occurs, and $\sigma$ is the reaction cross section. Cole obtained a result of $\dot{\xi}_H \approx 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$.

Tinsley used the formula

$$\dot{\xi}_H = \int \beta K \left( \frac{r}{r_c} \right)^2 n_H(r) n_H^+(r) \, dr$$  \hspace{1cm} (2-8)

where $K$ is the rate constant (based on a value of $\sigma = 50 \text{A}^2$ over the applicable temperature range), $\left( \frac{r}{r_c} \right)^2$ normalizes the result to the critical height, $n_H$ and $n_H^+$ are the densities of hydrogen atoms and protons, and $\beta$ is a geometric factor which takes into account the fact that the momentum vector of the resulting hydrogen atom must be directly radially outward for escape to occur. Tinsley inferred an escape flux of $4 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$. Using the same formula and slightly different parameters, Liu and Donahue obtained a value of $2.5 \times 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$.

Chamberlain has solved the general problem of hydrogen-proton charge transfer in a spherically symmetric
atmosphere based on the Boltzmann equation for planetary coronae:

\[
\frac{P_r^2}{M} \frac{\partial f(r, p_i)}{\partial r} \left[ \frac{P_x^2}{Mr^2} - \frac{GM}{r^2} \right] \frac{\partial f(r, p_i)}{\partial p_r} = \int \sigma(v_r) \left[ f^*(r, p_k) f(r, p_j) - f^*(r, p_k) f(r, p_i) \right] v_r^3 d^3 p_k
\]

(2-9)

where \( P_x \) is the angular momentum of the hydrogen atom, \( \sigma(v_r) \) is the charge transfer cross section, \( f^* \) is the density of \( H^+ \), \( f \) is the density of \( H \) and \( v_r \) is the relative velocity of the colliding particles. In his calculations, Chamberlain took \( \sigma \) to be constant over the velocity range at a value of \( 50 \AA^2 \). His results given in terms of the ratio of charge transfer flux to Jeans flux vary from \( \frac{\phi_{ct}}{\phi_J} = 1.0 \) to 16.4.

Two recent papers by Tinsley\(^{29}\) and by Maher and Tinsley\(^{30}\) have summarized the relationship of the charge transfer process with the Jeans flux and the polar wind flux. Table 2-1, taken from the first of these papers, gives an overall view of the various loss rates as a function of temperature.

The calculations for loss of hydrogen due to charge transfer summarized in this chapter were carried out using a value of \( 50 \AA^2 \) for the cross section. This value is based on theoretical work and involves the assumption that the cross section does not vary much with temperature.
### TABLE 2-1
Hydrogen Loss Rates

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(\phi_{\text{polar wind}})</th>
<th>(\phi_{\text{Jeans escape}})</th>
<th>(\phi_{\text{charge transfer}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low solar activity (\sim 800 \text{ K})</td>
<td>(\sim 6 \times 10^7)</td>
<td>(2.8 \times 10^7)</td>
<td>(\sim 11 \times 10^7)</td>
</tr>
<tr>
<td>Moderate solar activity (\sim 1000 \text{ K})</td>
<td>(\sim 1.5 \times 10^7)</td>
<td>(4.6 \times 10^7)</td>
<td>(\sim 15 \times 10^7)</td>
</tr>
<tr>
<td>High solar activity (\sim 1300 \text{ K})</td>
<td>(\sim 0.5 \times 10^7)</td>
<td>(10 \times 10^7)</td>
<td>(\sim 10 \times 10^7)</td>
</tr>
</tbody>
</table>

* From Tinsley (1978)\(^29\)
Confirmation of both of these points is a major motivation for the present experiment.
Chapter 3

Experimental Technique and Apparatus

The discussion of Chapter 2 has outlined the motivation for measuring $H^+ + H$ charge transfer cross sections at low relative velocities; the present chapter is devoted to a description of the experimental technique and apparatus used to make these measurements. This description is purposefully brief because both the method and the apparatus have been described elsewhere in detail.

Technique

The technique employed in this experiment is that of merged beams. First proposed in 1959 by Cook and Ablow,\textsuperscript{31} the method was implemented in 1966 by Belyev \textit{et al.}\textsuperscript{32} and Trujillo \textit{et al.}\textsuperscript{33} to study charge transfer reactions at low collision energies. A number of other groups have since adopted the technique.

A number of authors including Trujillo \textit{et al.}, Hasted,\textsuperscript{34} Smith,\textsuperscript{35} and Rundel \textit{et al.}\textsuperscript{36} have discussed this technique. The concept is straightforward: beams of the reactants are merged into the same axial path and travel parallel to each other for some specific distance. The energy with which the reactants collide is governed not by the difference in their laboratory energies but by the difference in their laboratory velocities. The collision
energy \( W \) is given by

\[
W = \frac{1}{2} \mu v_r^2 \tag{3-1}
\]

where \( v_r \) is the relative velocity of one particle with respect to the other and \( \mu \) is the reduced mass. This relation may be expressed in terms of the laboratory energies of the beams, \( E_1 \) and \( E_2 \), by

\[
W = \frac{1}{2} \mu \left( \sqrt{\frac{2E_1}{m_1}} - \sqrt{\frac{2E_2}{m_2}} \right)^2 \tag{3-2}
\]

where \( m_1 \) and \( m_2 \) are the particle masses. It is interesting to rewrite equation (3-2) in terms of \( \Delta E = |E_1 - E_2| \), ignoring higher order terms:

\[
W \approx \left[ \frac{\Delta E}{4E_1} \left( \frac{m_2}{m_1 + m_2} \right) \right] \Delta E \tag{3-3}
\]

The factor in brackets is much less than unity and consequently the collision energy \( W \) is much less than \( \Delta E \). This reduction in the collision energy from the laboratory energy difference is called the energy demplification effect and it is the primary reason that the merged beams technique can be used to study collisions at energies as low as 0.05 eV.

The demplification effect also applies to variations in the beam energies which result from the energy distributions in the ion sources. If these variations are given by \( \delta E_1 \) and \( \delta E_2 \), then the variation in the energy difference \( \delta (\Delta E) \) may be written as
\[ \delta (\Delta E) = \frac{m_2}{m_1} \delta E_1 + \delta E_2 \]  
(3-4)

The resulting variation in \( W \) is

\[ \delta W = \frac{1}{2m_1} \left( \frac{\Delta E}{E_1} \right) \delta (\Delta E) \]  
(3-5)

Finally, in an ideal merged beams experiment the angle \( \theta \) between the velocities of the beams is \( 0^\circ \). If in the actual case \( \theta \) is non-zero, the resulting error in the collision energy is

\[ \Delta W_\theta = \frac{m_2}{m_1 + m_2} \theta^2 E_1 \]  
(3-6)

The upper limits on \( \theta \) for the present experiment have been determined and the resulting values of \( \Delta W_\theta \) are given in Chapter 6.

The reason for studying collisions in the laboratory is to obtain some information on the likelihood of the process occurring. The parameter most suitable for measurement by the merged beams technique is the total collision cross section \( \sigma \). This quantity is given in terms of measurable parameters by

\[ \sigma = \frac{S}{F} \frac{v_1 v_2}{v_r} \]  
(3-7)

where \( S \) is the rate of signal ion production, \( v_1 \) and \( v_2 \) are the primary beam velocities and \( F \) is the overlap integral, a measure of the superposition of the beams in three dimensional space. This quantity is given by
\[ F = \int_{\text{all space}} j_1(x,y,z)j_2(x,y,z) \, dx \, dy \, dz \quad (3-8) \]

where \( j_1 \) and \( j_2 \) are the current densities of the beams. \( F \) is identically zero at any point where either \( j_1 \) or \( j_2 \) is zero.

The methods used to measure the parameters in equation (3-7) will be outlined in the next section and in Chapter 4.

Apparatus

The merged beams apparatus is shown schematically in Figure 3-1. Extensive descriptions of this apparatus are included in a number of places.\(^{35-40}\) Consequently, this discussion is limited to a general description.

There are four main sections: two beam formation systems, an interaction region and a detection region. The neutral beam originates as an ion beam extracted from a medium pressure magnetically confined arc ion source. The typical energy spread of the ions emerging from the source is \( \lesssim 2 \) eV. The ions are accelerated and formed into a parallel beam by a set of electrostatic cylindrical lenses.

Momentum analysis is accomplished with a pair of 60° sector magnets arranged so that the downstream focal point of the first magnet coincides with the upstream focal point of the second. Consequently, the magnet system has no ultimate effect on the beam geometry.
A fast neutral beam is produced from the momentum analyzed ion beam in a gas cell by charge transfer. The cell pressure is maintained at 0.4 to 1.0 mtorr which results in conversion of 20%-40% of the ions into neutral particles. The remaining ions are electrostatically removed farther down the beam line. There are a number of difficulties associated with this method of neutral beam production. The primary difficulty is that the relative ground state and excited state populations of the beam are unknown. In addition, space charge effects due to the slow ions produced in the gas cell can affect the energy spectrum of the neutral beam. The approach used to deal with these problems for the present experiment will be discussed in Chapter 4.

The neutral beam is collimated by two 5 mm apertures separated by 60 cm limiting beam divergence to ≤.01 radian. The observed divergence is typically .003 radian.

The primary ion beam is produced in an arc ion source similar to the first and is focused into a parallel beam by a set of cylindrical lenses. An identical pair of sector magnets provide momentum analysis. The second of these merges the ion beam into the neutral beam. The beams then travel together through a one meter-long interaction chamber.

Inside this chamber is a mechanical device used to measure the overlap integral. It consists of a rotatable shaft on which are mounted four pie-shaped plates. Each of
these has nine small (.1 mm) apertures spaced at equal angles and increasing radial distance from the shaft. As the shaft turns, each hole moves through a different section of the superimposed beams. The sampled currents are individually monitored and then multiplied together and integrated by an analog calculator. The output is the two dimensional overlap integral at the plane of the scanner plate. The three dimensional integral is produced by integrating a second degree polynomial fit to the four points provided by the scanners.

The overlap device has a second purpose: to facilitate alignment of the beams prior to a cross section measurement. Figure 3-2 shows a set of plots made by recording neutral and ion currents as the shaft turns. By aligning the individual peaks of one beam with those of the other, the beams may be arranged in space for maximum overlap. Horizontal and vertical positioning of the beams is accomplished by sets of electrostatic deflection plates located near the lenses and between the sector magnets.

Adjacent to the interaction chamber is the detection chamber. An electrostatic field established by two parallel plates at the entrance to the detection region is used to separate the ions from the neutral beam. Product ions are deflected through an angle of 22.5° into a five grid retarding potential energy analyzer. Ions which pass through the analyzer are deflected 90° upward into a Johnston Laboratories MML electron multiplier.
Figure 3-2. Typical beam profiles made with the overlap scanners.
The energy analyzer, discussed in some detail by Geis\textsuperscript{41} and by Cogan\textsuperscript{42} is an assembly of five copper frames with 2 inch by 3 inch apertures. A uni-directional mesh of .001 in diameter tungsten wire is stretched across these frames in order that a uniform potential may be established at the plane of each. The outer grid on either side marks the electrostatic boundary of the analyzer; consequently these are operated at ground potential. The central grid is set to the desired retarding potential and the second and fourth grids are operated at 97\%-99\% of this value. The purpose of these inner grids is to reduce field penetration from the outer grids at the plane of the central grid.

The primary use of the energy analyzer is rejection of ions other than product ions. Included in this group are reactant ions and stripped neutral atoms. These latter particles are produced from the reaction

\[ H + X \rightarrow H^+ + X + \Delta E \]  
(3-9)

where the symbol X represents a background gas particle. $\Delta E$ represents the energy required to ionize the atom, 13.6 eV. This energy is lost from the kinetic energy of the projectile; hence, this proton is less energetic than a product proton by at least 13.6 eV, and the energy analyzer may be used to discriminate against such ions.

The 90° upward deflection is carried out by an electrostatic field established by two coaxial quarter cylinders.
This system, a modification to the original apparatus, was
designed by M. R. McGuire.43

In the present experiment, the signal is much smaller
than the background count rate, typically by a factor of 10
to 100. Although a portion of the background is due to
stripped atoms, most of it is due to secondary processes
occurring when the primary ion beam strikes metal surfaces
in the detection chamber. Measurement of the signal rate in
the presence of a much larger background presents a for-
midable problem. To circumvent this difficulty, a beam
modulation system is employed. Both beams are square wave
modulated at a frequency of one KHz, 90° out of phase with
each other. The scalers are gated to accept counts during
four distinct periods. In the first quarter cycle counts
result from the background due to one beam only. The second
quarter cycle contains background due to both beams plus
signal. The third has only background from the second beam.
During the fourth quarter cycle both beams are off. Sub-
traction of the count rates occurring during the first and
third intervals from the sum of those during the second and
fourth yields the signal.

The detection chamber contains four other particle
detectors: three Faraday cups for measurement of charged
particle currents, and a neutral beam detector. The neutral
beam detector is a lead zirconate titanate (PZT) disk
silvered on both faces. The neutral beam flux is determined
by measuring its secondary electron current and dividing by \( \gamma^o \), the secondary electron coefficient for the surface. \( \gamma^o \) is measured by using the pyroelectric property of the PZT disk. The impact of a beam striking the surface causes the crystal to heat up, producing an electric field between the front and back faces. The magnitude of this field, which is proportional to the beam intensity, is measured with a phase sensitive detector tuned to the beam modulation frequency (typically 5-10 Hz for this procedure). The ratio of electric field magnitude to beam intensity is established with an ion beam of known current. The flux of a neutral beam of the same energy may then be determined. \( \gamma^o \) follows from measurement of the number of secondary electrons produced by the neutral beam.

Measurement of absolute cross sections requires measured values for all of the variables on the right hand side of equation (3-7). Of particular importance is accurate signal measurement which makes it essential to know the signal detection efficiency. In this experiment one must ensure that the fraction of product ions which produce pulses is known and that the detector has a uniform efficiency over the product collection area. This latter requirement was checked by sweeping a .03 in diameter probe ion beam across the entrance to the detection chamber while monitoring the count rate. This test indicated the collection efficiency was uniform for a beam 1.0 inch in
diameter centered on the beam axis. The detection efficiency was measured by directing a low intensity ion beam at the detector, recording the count rate and then measuring the current of the same beam in a Faraday cup. Detection efficiencies for this experiment were found to be \(0.37 \pm 0.03\) for 1500 eV H\(^+\) and \(0.32 \pm 0.02\) for 1500 eV D\(^+\).

The beam velocities are measured with the energy analyzer. The ion beam energy measurement is straightforward: current transmitted through the analyzer is recorded as a function of the retarding potential. The resulting graph, an example of which is shown in Figure 4–2, is an integral of the energy spectrum of the beam. The mean particle velocity can be determined from this curve. The procedure used to determine the neutral beam energy will be discussed in Chapter 4.

The experimental apparatus is contained in twelve vacuum chambers, each pumped by an oil diffusion pump. The interaction and detection chamber pumps are liquid nitrogen trapped and these chambers are periodically baked at 120°C for 6-10 hours. The ultimate pressure attained is \(\sim 1 \times 10^{-9}\) torr with operating pressures ranging from 2-7 \(\times 10^{-9}\) torr.

In the course of performing the present experiment, a number of unforeseen difficulties were encountered. A discussion of these problems and apparatus modifications required to solve them is included in the next chapter.
Chapter 4

Experimental Details

The merged beams apparatus has been successfully used in the measurement of \( \text{He}^+ + \text{He} \) charge transfer cross sections at collision energies ranging from 0.1 eV to 187 ev.\textsuperscript{36} and it might be anticipated that such measurements for similar reactions would be straightforward. However, the case of \( \text{H}^+ + \text{H} \) presents a number of problems which are either peculiar to this reaction or were not as critical in the helium experiment. A discussion of these difficulties and actions taken to solve or circumvent them is the purpose of this chapter.

Product Ion Detection

As was mentioned in Chapter 3, the energy analyzer functions to discriminate against ions which are not products of the reaction under study. Included in this group are protons in the primary reactant beam, protons resulting from collisional ionization of fast \( \text{H} \) atoms by the background gas in the chamber, and protons formed in charge transfer reactions from hydrogen atoms in excited states.

Measurement of the cross sections requires measurement of the flux of protons resulting from the charge transfer reaction. However, some arrangement must be made to prevent the protons of the reactant beam from being collected. This may be accomplished by using a proton beam that is less energetic than the neutral beam.
Since the product beam has the same energy as the neutral beam, the energy analyzer may be used to discriminate between reactant protons and product protons. At a very low collision energy of 0.05 eV, the reactant proton beam is 25 eV less energetic than a 1500 eV neutral beam. Discrimination of this energy difference by means of the energy analyzer is easily accomplished.

A more difficult problem is encountered in an attempt to discriminate between protons produced by charge transfer and those produced in stripping collisions:

\[ H + M \rightarrow H^+ + M + e^- - \Delta E \]  \hspace{1cm} (4-1)
\[ \Delta E \geq 13.6 \text{ eV} \]

where M represents a background gas particle. These two groups of protons differ in energy by only 13.6 eV and resolution of this difference by the energy analyzer is slightly more complicated. The energy analyzer is aided in discrimination against protons produced by reaction (4-1) by the beam modulation scheme, since counts from these ions constitute part of the background associated with the neutral beam. However, their rejection by the energy analyzer diminishes the total count rate and decreased the amount of time required to accumulate good counting statistics.

Finally, the reaction under study is between protons and ground state (1s) hydrogen atoms. However, not all
of the atoms produced in the neutralization process are in the ground state. Consequently, to insure a cross section measurement representing only ground state reactions, some means must be devised to discriminate against those products which originate from excited state atoms. A suitable means of doing so results from energy considerations of excited state formation.

Consider the reaction by which neutralization occurs in the gas cell:

\[ \text{H}^+ + \text{Kr}(4p^6) - \text{H}(n) + \text{Kr}^+(4p^5) + \Delta E \quad (4-2) \]

where \( \Delta E \) is the difference between the ionization potentials of Kr and H(n). For instance, if the final state of the hydrogen atom is the 1s state, \( \Delta E = 0.4 \) eV. For this experiment, excited H atoms with \( n \leq 9 \) (except for the 2s state) are too short lived to travel as far as the interaction chamber. (Any 2s state atoms are quenched by an electric field of \( \sim 5000 \) V/cm.) Consequently, any excited state atoms that survive into the interaction region will have principal quantum numbers \( n \geq 10 \) and will be less energetic than ground state atoms by at least 13.4 eV. The energy analyzer is thus required to discriminate between protons that differ in kinetic energy by this amount in order to insure that all collected signal ions result from ground state atoms.
In fact, this requirement was in doubt for the energy analyzer described by Rundel et al.\textsuperscript{36} Geis,\textsuperscript{41} Nitz,\textsuperscript{44} and Cogan\textsuperscript{42} (Figure 3-3). Consequently, it was modified to improve its resolution. This improvement was accomplished by making two changes. First, the grid wire spacings in the second and third grids were changed from 1/40 inch and 1/56 inch respectively to 1/240 inch for both, creating a more uniform potential in the plane of these grids. The spacing of the fourth grid was changed to 1/140 inch. In addition, the distance between the first and second grids was increased by a factor of three to reduce the value of the potential gradient in this region. This action was taken to lessen the focusing effect that occurs around grid wires of the 2nd grid, this effect being inversely proportional to the difference in magnitudes of the electric fields to either side.\textsuperscript{45} Tests conducted to compare the energy analyzer resolution before and after it was modified indicated improvement by a factor of three to five.

A test of the new analyzer was conducted to determine whether or not the refinement was sufficient to solve the excited state problem. Signal from the charge transfer reaction was measured at a collision energy of 2 eV with the energy analyzer set to reject protons resulting from highly excited atoms. A large electric field ($\sim 6700 \text{ V/cm}$) was periodically applied to a pair of parallel plates located between the charge transfer cell and the interaction
region. A field of this magnitude is sufficient to ionize excited atoms with principal quantum numbers greater than about \( n = 20 \). The signal rate measured when the plates were on was compared with that measured when the plates were off. This rate was unchanged by application of the field, indicating the absence of signal from states of \( n > 20 \). Since the kinetic energy of atoms with \( n = 10 \) is only 0.1 eV larger, it is assumed that product ions from states where \( 10 \leq n < 20 \) are also rejected by the energy analyzer. The results of the test are given in Table 4-1.

Table 4-1
Test for Rejection of Signal from Highly Excited Atoms

<table>
<thead>
<tr>
<th>Field Ionizing Plate</th>
<th>Total Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>6700 V/cm</td>
<td>1078 ± 90</td>
</tr>
<tr>
<td>0 V/cm</td>
<td>1070 ± 92</td>
</tr>
</tbody>
</table>

No mention has yet been made of one important quantity, the energy (actually the energy distribution) of the product ion beam. It is necessary to know this quantity in order for the retarding potential of the energy analyzer to be set to transmit product ions and reject unwanted ions, and it must be known to a high degree of accuracy since the total spread in energy of a beam (99% of all beam particles) approaches 12 eV in some cases. The margin of error must be small, consequently, on the order of 2 eV or less.
As discussed in Chapter 3, the energy distribution of a beam of charged particles may be determined by measuring the transmitted current as a function of the retarding potential. Such a curve is shown in Figure 4-1. As discussed by Cogan, the functional form of this curve is a convolution of the energy analyzer transmission function and the beam energy distribution. The transmission function of the present energy analyzer is sharply peaked (fwhm ≈ 1 eV) so the shape of the energy analyzer curve in Figure 4-1 is due primarily to the energy distribution of the beam.

This procedure could be applied to the product proton beam in order to determine the optimum operating voltage for the analyzer. However, long signal accumulation times due to the low signal-to-noise ratio make this procedure time consuming and impossible to implement on a regular basis as would be required for cross section measurements. Consequently, other methods of determining the product ion beam energy have been sought.

Since the reaction being studied is resonant (that is, no internal energy is lost or gained by either reactant), the product beam will have the identical energy spectrum of the neutral beam from which it is formed. (Appendix A discusses the kinematics of this reaction with regard to conservation of energy and momentum.) Determination of
Figure 4-1. Energy analysis of 1506 eV H\(^+\) beam.
the neutral beam energy spectrum therefore determines that of the product ions.

Measurement of the energy of the hydrogen beam is not as straightforward as it is for an ion beam since the absence of charge precludes the direct use of the electrostatic energy analyzer. Moreover, time of flight techniques do not easily lend themselves to measurement with the required resolution. In addition, a fairly quick procedure is desired.

A first approximation to the hydrogen beam energy is provided by the energy of its parent ion beam. The protons in this beam are neutralized by reaction (4-2) and in this process they might be expected to suffer an energy loss of only 0.4 eV if a ground state atom results. However, a number of factors which alter the beam energy by considerably more than this amount have been uncovered, making use of the parent proton beam's energy an unreliable indication of the neutral beam energy.

The energy of any particle which undergoes a change in the value of its charge is determined by the electric potential of the region in which the change occurs. Hence, if the protons in a 1500 eV beam are neutralized in a region at a potential other than ground, the final energy of the resulting hydrogen atoms will be different than that of the protons. Such a situation occurs during the neutralization process. When reaction (4-2) takes place,
thermal Kr\(^+\) ions are produced in the vicinity of the beam.
Due to their relatively low velocity (compared with the beam velocity), an accumulation of these ions occurs along the beam line resulting in a positive space charge potential. Protons in the parent beam are thus decelerated as they enter the charge transfer cell and, if neutralized, the resulting atoms will have less kinetic energy than the unneutralized protons which leave the gas cell. The magnitude of the space charge potential has been determined to be as large as 1.0 eV for a typical hydrogen beam. It is a function of a number of factors including ion beam intensity, density of gas in the cell, and mobility of the thermal ions.

Another factor worthy of note is that reaction (4-2) has a number of possible channels as shown by Benoit et al.\(^{46}\)

\[
\begin{align*}
H^+ + \text{Kr}(4p^6) &\rightarrow H(1s) + \text{Kr}^+(4p^5^2P_{3/2}) - 0.4 \text{ eV} \quad (4-3a) \\
&\rightarrow H(1s) + \text{Kr}^+(4p^5^2P_{1/2}) - 1.06 \text{ eV} \quad (4-3b) \\
&\rightarrow H(n=3) + \text{Kr}^+(4p^5^2P_{3/2}^{1/2}) - 12.5-13.2 \text{ eV} \quad (4-3c) \\
&\rightarrow H(1s) + \text{Kr}^+(4s4p^6 ^2S_{1/2}) - 13.9 \text{ eV} \quad (4-3d) \\
&\rightarrow H(n=4) + \text{Kr}^+(4p^5^2P_{3/2}^{1/2}) - 13.2-13.9 \text{ eV} \quad (4-3e)
\end{align*}
\]

Each channel results in a loss of kinetic energy of the hydrogen atom ranging from 0.4 eV to 13.9 eV, causing a
spread in hydrogen atom energies larger than the spread in energy of the parent proton beam. The result is a complication of any attempt to infer the neutral beam energy from that of the proton beam.

Finally, the gas in the charge transfer cell is maintained at a pressure for which the neutral beam intensity is maximized. At such a pressure some of the atoms formed near the front of the cell undergo second collisions with krypton atoms. If in this collision, either the hydrogen atom or the krypton atom is left in an excited state, the hydrogen atom will lose the excitation energy from its kinetic energy. The occurrence of such additional collisions further complicates the energy spectrum of the hydrogen beam compared to that of its parent proton beam.

Another indication of the neutral beam energy distribution might be derived from analysis of the energy of the protons formed by stripping via reaction (4-1). However, this beam, although reflecting the energy spectrum of the neutral beam, suffers additional energy losses due to excitation of the target and due to the released electron carrying away some variable amount of kinetic energy.

A successful procedure for determining the energy of the hydrogen beam has been initiated based on work done by J. Appell et al.\textsuperscript{47} in which negative hydrogen ions were produced in single and double collision processes:

\[ \text{H}^+ + \text{M} \rightarrow \text{H}^- + \text{M}^{++} \]  

(4-4a)
and
\[ \begin{align*}
H^+ + M \rightarrow H + M^+ & \\
H + M \rightarrow H^- + M^+ & 
\end{align*} \tag{4-4b} \]

The second part of the two step process (4-4b) may be used to produce a charged beam from a neutral hydrogen beam. Such a procedure has been tested and is now used in this experiment. Krypton is admitted to the interaction chamber at a rate which produces a pressure of about 2x10^{-7} torr. The neutral hydrogen beam is allowed to pass through, resulting in some collisions in which H^- ions are formed by charge transfer. The very low pressure in the chamber precludes the possibility of complicating second collisions or the production of a space charge potential, so that the only additional energy loss is due to the difference in ionization potentials occurring along the possible channels.

\[ \begin{align*}
H(1s) + Kr(4p^6) \rightarrow H^- + Kr^+(4p^5,^2P_{3/2}) & - 13.2 \text{ eV} & \tag{4-5a} \\
& \rightarrow H^- + Kr^+(4p^5,^2P_{1/2}) & - 13.86 \text{ eV} & \tag{4-5b} \\
& \rightarrow H^- + Kr^{++}(4s4p^6,^2S_{1/2}) & - 27.4 \text{ eV} & \tag{4-5c}
\end{align*} \]

The first two channels are energetically much more likely and for the purpose of this experiment, the energy difference between them (.66 \text{ eV}) is not very important. The energy spectrum of an H^- beam is shown in Figure 4-2. Also shown is the same curve shifted higher in energy by 13.2 eV. The energy distribution of the parent proton beam is included for comparison. This method of neutral beam
Figure 4-2. Energy analysis of an H\(^{-}\) beam produced by the reaction H + Kr → H\(^{-}\) + Kr\(^{+}\) = 13.2 eV. This curve is replotted at an energy 13.2 eV higher to show the energy spectrum of the incident H beam. The energy analysis of the H\(^{+}\) parent ion beam is shown for comparison.
energy determination provides a quick technique which is easily used on a daily basis.

To check the validity of the assumptions associated with this procedure, the energy of the product ion beam was measured on a number of occasions, each time at five points along the energy curve. (The number of points is limited by the amount of time required for this procedure.) Figure 4-3 shows a composite plot of these measurements compared with the neutral beam energy inferred from an $\text{H}^-$ beam energy spectrum. This latter curve fits the points fairly well along most of the energy range of concern, the chief exception being the existence of an increase in the slope of the product ion beam energy spectrum at about 1490 eV. This increase in the number of product ions collected is due to protons produced from excited state atoms. Cross sections for this process

\[ \text{H}^+ + \text{H}^*(n) \rightarrow \text{H}^*(n) + \text{H}^+ \]  

(4-6)

have been measured by Koch et al.\textsuperscript{48} for a number of $n$ values. These cross sections are as much as five orders of magnitude larger than that for the ground state reaction. Consequently, the existence of as little as 0.001% of the beam in such excited states could account for the shape of the product ion energy analysis.

Examination of Figure 4-3 indicates that if the energy analyzer is set to reject all of the signal from
Figure 4-3. Comparison of neutral H beam energy distribution and product ion beam energy distribution. The H beam energy distribution was made by energy analyzing an H⁻ beam.
excited state charge transfer, then only about 85–90% of the product ion beam will be energetic enough to pass through the energy analyzer. Consequently, the measured cross section must be corrected due to the loss of this small portion of the signal. Determination of the percentage of the signal which is collected is made for each cross section measurement as shown in Figure 4-4.

Reaction Kinematics of $\text{H}^+ + \text{H}$ and $\text{H}^+ + \text{D}$ Collisions

During a collision which results in charge transfer, the ion and atom produced may not continue along their initial trajectories, but may be scattered off the beam axis. This scattering is important from an experimental standpoint because the product ion may move on a final trajectory which takes it out of the solid angle subtended by the electron multiplier or which reduces the axial component of its velocity such that it no longer has the momentum required to carry it through the energy analyzer. Both of these problems must be considered with regard to the likelihood of their occurring in the present experiment.

Figures 4-5(a), (b) and (c) illustrate the laboratory and center of mass velocities of the $\text{H}^+ + \text{H}$ collision and the $\text{H}^+ + \text{D}$ collision along with the relationship of the center of mass scattering angles to the laboratory scattering angles. A product particle scattered through an angle $\theta$ in the center of mass frame of reference will have a laboratory scattering angle of $\beta$. In Figure 4-5a either
Figure 4-4. Determination of the energy analyzer operating voltage and percentage of signal which is detectable.
Figure 4-5(a). Collision kinematics of $H^+ + H$ collision in the laboratory and center of mass reference frames.
Figure 4-5(b). Collision kinematics of $H^+$ + D collision where $V_D > V_{H^+}$. 

\[
\begin{align*}
V_D & \quad 2V/3 \\
V_{H^+} & \quad V_H \\
V_{H^+} & \quad V_{H^+} \\
V_{H^+} & \quad V_{H^+}
\end{align*}
\]
Figure 4-5(c). Collision kinematics of $H^+ + D$ collision where $V_{H^+} > V_D$. 
particle may be taken as the proton since the masses are equal; however, in the case of an $H^+ + D$ collision two diagrams are required, one for the case of the proton initially having a velocity greater than that of the $D$ atom (4-5(c)) and one for the case of its velocity being lower (4-5(b)).

If the ion beam is initially slower than the neutral beam (particle 1 in Figure 4-5(a) is the atom, or Figure 4-5(b)), any scattering of the product ion off the beam axis will result in the $z$ component of its final laboratory velocity $V_{1z}'$ or $V_{D^+Z}^-$ being reduced from its initial value. If the energy corresponding to this velocity (given by $E_z' = \frac{1}{2} m_0 (V_{1z}')^2$ or $E_{D^+Z}^- = \frac{1}{2} m_0 (V_{D^+Z}^-)^2$) is less than required for transmission through the energy analyzer, the ion will not be counted. The result will be a measured cross section smaller than the real value.

The velocity $V_{1z}'$ is easily found as a function of center of mass scattering angle:

$$V_{1z}' = V_{CM} + \frac{V_0}{2} \cos \theta$$  \hspace{1cm} (4-7)

where $V_{CM} = \frac{V_1 + V_2}{2}$. In Figure 4-5(b) $V_{D^+Z}^-$ is given by

$$V_{D^+Z}^- = V_{CM} + \frac{V_0}{3} \cos \theta$$  \hspace{1cm} (4-8)

where $m_D = 2m_H$ (accurate to 4 decimal places), and $V_{CM} = (2V_{D^+} + V_{H^+}) / 3$. By calculating the minimum $z$-axis component of the velocity required for transmission through
the energy analyzer, the largest center of mass scattering angle \( \theta_{\text{max}} \) for which the product ion is detectable may be calculated. This angle is given for various collision energies in Table 4-2.

Whether this effect presents a problem or not in the present experiment depends on the differential scattering cross section \( \sigma(\theta) \). For the case of \( \text{H}^+ + \text{H} \), a number of differential cross sections have been computed and plotted by Kuriyan \(^{49} \) (see Figures 5-4 in the next chapter). These plots indicate that a problem only exists for energies below a few eV since the amount of off axis scattering at very large angles decreases with increasing energy, as might be expected.

Solution of this problem could be provided by operating the reactant proton beam at a higher velocity than the neutral beam. In Figure 4-5a particle 2 would be the initial neutral particle and for \( \text{H}^+ + \text{D} \) Figure 4-5c would apply. In this case the \( z \) component of the product ion velocity in the laboratory will increase if the ion is scattered off axis. This solution cannot be applied in the experiment for \( \text{H}^+ + \text{H} \), however, since the reactant proton beam would be energetic enough to pass through the energy analyzer and would totally obscure the signal. In the case of an \( \text{H}^+ + \text{D} \) collision, this is no problem. A proton beam of slightly greater velocity than the neutral deuterium beam will have only about half of the energy
TABLE 4-2
(a) Energy Analyzer Limited Scattering Angles (Center of mass)

<table>
<thead>
<tr>
<th>$W \ (H^+ + H)$ (eV)</th>
<th>$H^+ + H$ (degrees)</th>
<th>$H^+ + D \ (v_H^+ - v_D^+)$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>48</td>
<td>49</td>
</tr>
<tr>
<td>0.10</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>0.20</td>
<td>33</td>
<td>34</td>
</tr>
<tr>
<td>0.35</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>0.50</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>1.0</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>2.0</td>
<td>19</td>
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</tr>
<tr>
<td>3.5</td>
<td>16</td>
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</tr>
<tr>
<td>5.0</td>
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<td>15</td>
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<td>10.0</td>
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<td>13</td>
</tr>
<tr>
<td>20.0</td>
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<td>11</td>
</tr>
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<td>35.0</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>50.0</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>100.0</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>
### TABLE 4-2

(b) Geometry Limited Scattering Angles (center of mass)

<table>
<thead>
<tr>
<th>$W$ ($H^+ + H$) (eV)</th>
<th>$H^+ + H$ (degrees)</th>
<th>$H^+ + D$ ($v_D &gt; v_{H^+}$) (degrees)</th>
<th>$H^+ + D$ ($v_{H^+} &gt; v_D$) (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>77</td>
<td>-</td>
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<td>100</td>
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since deuterium has twice the mass of hydrogen. Since the scattering problem is critical at low collision energies, all of the cross sections reported in this thesis at low energies are for H\(^+\) + D reactions.

A related problem is the possibility of signal ions being scattered outside of the acceptance cone of the detector. This problem may be analyzed by examining the relationship between laboratory scattering angles and center of mass scattering angles. For the case of H\(^+\) + H, the relationship between these angles is given by

\[
\tan \beta = \frac{\sin \phi}{\frac{V_1 + V_2}{V_1 - V_2} + \cos \phi} \quad (4-9)
\]

For Figure 4-5b, H\(^+\) + D it is

\[
\tan \beta = \frac{\sin \phi}{\frac{V_{H} + 2V_{D}}{V_{D} - V_{H}} + \cos \phi} \quad (4-10)
\]

and for Figure 4-5c, H\(^+\) + D it is

\[
\tan \beta = \frac{\sin \phi}{\frac{V_{H} + 2V_{D}}{V_{H} - V_{D}} - \cos \phi} \quad (4-11)
\]

Table 4-2 also gives the maximum angle \(\phi\) for which products will be detectable assuming the detector subtends a laboratory angle of .017 radian.

Although the differential scattering cross sections of Kuriyan indicate the amount of large angle scattering
increases with decreasing energy, the value of $\beta$ as a function of $\Theta$ diminishes since $V_{1}-V_{2}$ (or $V_{H^+-V_{D}}$) decreases. For the $H^+ + D$ cross sections there are no collision energies where a significant fraction of the signal might be lost.

Signal From Merging and Demerging Regions

The concept of merging beams is of a reaction occurring between two beams of particles traveling along parallel coaxial paths. The beams have a relative velocity $v_{r}$ and travel a distance $l_{r}$ with respect to each other during the time period of the collision. $l_{r}$ is referred to as the effective interaction length. This situation applies to the interaction region of this apparatus with the exception of the merging and demerging regions. In these regions where the ion beam trajectory is changing with respect to the neutral beam trajectory, an additional component of the relative velocity $v_{r_{1}}$ exists in the direction perpendicular to the beam axis. The ion beam moves through the neutral beam, not only along the beam axis, but also perpendicular to it by an amount $\Delta l_{r}$. This effect can be seen in Figure 4-6 which is a diagram of the merging region showing the beam trajectories for the $H^+ + D$ collision. The dotted line represents the point past which signal ions will not be deflected outside the acceptance cone of the detector by the fringe field of the merging magnet. At this position the beams do not quite have parallel trajectories and as they move farther into the interaction region, the ion beam
moves in relation to the neutral beam by about $\Delta \lambda_r = 1.5$ mm. Although this distance is extremely small in comparison to the overall interaction chamber length ($\sim 90$ cm), it becomes significant in comparison to the effective interaction length $\lambda_r$ at low relative velocities. Table 4-3 gives $\lambda_r$ as a function of collision energy for the present experiment. At the lowest energy $\Delta \lambda_r$ is about 15% of $\lambda_r$. Compounding the problem is the value of the two dimensional overlap integral $f(x,y)$ which has its largest value in this region since the beams are the most dense at the front of the interaction chamber. This value of $f(x,y)$ may be 2 to 3 times larger than its average value $\bar{f}$ over the remaining part of the interaction region, meaning that a 15% additional interaction path length here could possibly produce an additional signal of 30-45%. The effect becomes less pronounced as the relative velocity increases till at a collision energy of 1 eV the maximum possible effect would be less than a 10% increase in signal.

To overcome this spurious signal effect, a small cylinder (Figure 4-7) was constructed and mounted in the front of the interaction chamber so that the beams would merge inside of it. The cylinder is electrically isolated from the remainder of the system and during a cross section measurement it is floated at $-17$ volts so that any product ions formed inside will be decelerated at the exit by 17 eV. This loss of energy prevents these ions from passing
TABLE 4-3

Effective Interaction Length

<table>
<thead>
<tr>
<th>$W$ (H$^+$ + H) (eV)</th>
<th>$\lambda_R$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.050</td>
<td>1.01</td>
</tr>
<tr>
<td>.089</td>
<td>1.37</td>
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<td>1.44</td>
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<td>.184</td>
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<td>.246</td>
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<td>.68</td>
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<td>7.44</td>
</tr>
<tr>
<td>4.16</td>
<td>8.58</td>
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</tbody>
</table>
Figure 4-7. Merging region cylinder. The grids define the electrostatic potential boundaries.
through the energy analyzer and consequently the detected signal does not include any of that produced inside the merging region. The exit end of the cylinder may be regarded as the beginning of the interaction region.

The same sort of problem exists at the demerging end of the interaction region. However, the two dimensional overlap integral in this region is less than the average \( \overline{F} \) by a factor of 2 to 3 and consequently a \( \Delta S_r \) of 15% to 20% creates a spurious signal of less than 10%.

Background Reduction

In Chapter 3 the problem of low signal-to-noise ratios was discussed. At the time work was begun on the present experiment, this difficulty was so acute, that, in order to achieve a reasonable standard deviation for signal rates, counting times well in excess of a day were required in some cases. This problem has been effectively addressed since that time.

The majority of the background is due to secondary processes occurring when the reactant ion beam strikes metal surfaces in the detection chamber. Since the detection system is operated to collect protons (or deuterons) of 1500 eV energy, the exact position the ion beam strikes is a function of its particular energy. (The ion beam energies corresponding to the various collision energies are listed in Table 6-1.) Figure 4-8 shows a top view of the detection region with the shaded region representing
Figure 4-8. View of the detection region from above.
The shaded area represents the possible trajectories for a reactant ion beam which is less energetic than the product ion beam.
the possible range of reactant ion trajectories. One or two bounces of one of these ions (or a secondary particle) could take it to the electron multiplier. Although the chances of such an occurrence are slim (~1 in $10^7$ to $10^9$), nevertheless, the primary ion beam flux is large enough that sizeable background rates may result. A means of reducing this rate has been implemented.

The major part of the problem was perceived to result from exposure of the electron multiplier to surfaces which might intercept reflected ions or secondary particles. These surfaces include portions of the 90° deflector, energy analyzer, and chamber floor. As a solution, a stainless steel barrier has been constructed around the perimeter of this portion of the chamber so that the only access to the multiplier is through the energy analyzer. This barrier increases the number of bounces required for a particle to hit the multiplier. Figure 4-9 is a graph of measured background rates for proton beams as a function of beam energy before and after the barrier was introduced. The success of this modification allowed the measurement of charge transfer cross sections to be completed within reasonable time periods. These periods ranged from a few hours to a few minutes.

Other Tests

A number of other tests have been conducted at various times to insure that the apparatus is working properly.
Figure 4-9. Background rates due to the reactant proton beam before and after a barrier was mounted around the detection assembly.
These include checks of signal dependence on the beam modulation system as a result of cross modulation or other inadequacies of the counting system, dependence of the signal rate on beam modulation frequency, and dependence of the measured cross sections on overlap integral. Details have been discussed by Nitz$^{44}$ and Geis.$^{41}$ All of these results were negative.

When the tests and modifications to the apparatus had been completed, the charge transfer cross sections were measured at energies between 0.05 eV and 100 eV. The results of these are reported in Chapter 6. The discussion of the theoretical results reported for this reaction are presented in Chapter 5.
Chapter 5

Theory

This chapter is devoted to a discussion of theoretical methods used for calculating $H^+ + H$ (and $H^+ + D$) charge transfer cross sections and the results obtained from application of these methods. The discussion is limited to energies below 100 eV since this is the range of interest in the present experiment. A similar discussion was presented by Nitz$^{44}$ although he also considered the charge transfer collision between $He^+ + He$.

Theoretical Techniques for Low Energy Calculations

If, during the collision of a proton and a hydrogen atom, the impact velocity is much smaller than the electronic velocity ($\ll 10^8$ cm/sec), molecular states of the $H_2^+$ molecule form during the collision (the Born-Oppenheimer Approximation). The relative motion of the nuclei may be considered as a perturbation of the electronic states in order to calculate the cross sections for charge transfer or elastic scattering. Such a treatment, referred to as perturbed stationary state theory, may be applied semiclassically or in the context of formal quantum mechanics by a partial wave analysis. The use of the quantum mechanical method is more exact; nevertheless, for collision energies where the particles may be considered to move on classical trajectories, the semiclassical formulation is a very good approximation. These two
techniques will be briefly outlined and compared. The presentation for both is limited to the lowest two electronic states, the gerade and ungerade states, since the asymptotic forms of these are linear combinations of the atomic ground state of hydrogen.

Semiclassical Formulation

The semiclassical approach requires one to consider the possible classical trajectories and calculate the probability of charge transfer as a function of the impact parameter b (Figure 5-1). Consequently, this method is often referred to as the impact parameter technique. A general description of it, applied to the case of resonant charge transfer, was first presented by Bates et al.\textsuperscript{50} in 1952. Modifications have been suggested by Bates and McCarrol,\textsuperscript{51} Gurnee and Magee,\textsuperscript{52} and Rapp and Ortenburger.\textsuperscript{53} The following discussion parallels that of Bates et al.\textsuperscript{50}

Consider $\chi^\pm$ to be the eigenfunctions representing the lowest symmetric and antisymmetric states of a singly charged homonuclear molecule such as $\text{H}_2^+$. In the limit of $R$ (the internuclear separation) going to infinity, these functions become a linear sum of the atomic ground state wavefunctions

$$\chi^\pm_{R \to \infty} \phi_1 \pm \phi_2$$

(5-1)

where the subscripts 1 and 2 refer to the nuclei. The time dependent wave function of the colliding nuclei may be written
Figure 5-1. Collision Geometry.
\[ \psi(t) = \left[ c^+(t) \chi^+ \exp(-\frac{i}{\hbar} \int^t \epsilon^+(R(t)) \, dt) \right. \\
+ c^-(t) \chi^- \exp(-\frac{i}{\hbar} \int^t \epsilon^-(R(t)) \, dt) \left. \right] \]  
(5-2)

where \( \epsilon^\pm(R(t)) \) are the molecular state eigenvalues. If the electron is initially in the ground state of atom 1, then the initial wave function is

\[ \psi(-\infty) = \varnothing_1 = \frac{1}{\sqrt{2}} (\chi^+ + \chi^-) e^{\frac{-iE_0 t}{\hbar}} \]  
(5-3)

where \( E_0 \) is the atomic state eigenvalue. The desired final condition is for the electron to be bound to nucleus 2, described by

\[ \psi(t) = \frac{1}{\sqrt{2}} (\chi^+ - \chi^-) e^{\frac{-iE_0 t}{\hbar}} \varnothing_2 \]  
(5-4)

The probability for this situation to occur is given by

\[ P = |<\varnothing_2|\psi(\infty)>|^2 \]  
(5-5a)

The first order the coefficients \( C^\pm \) may be taken to be equal to \( \frac{1}{\sqrt{2}} \). Thus

\[ P = \frac{1}{4} \left| \int (\chi^+ - \chi^-) e^{-i \frac{E_0 t}{\hbar}} \right|^2 \]

\[ \times \left[ \chi^+ \exp\left(-\frac{i}{\hbar} \int^{-\infty} (\epsilon^+ - E_0) \, dt \right) \right. \\
+ \chi^- \exp\left(-\frac{i}{\hbar} \int^{-\infty} (\epsilon^- - E_0) \, dt \right] \]  
(5-5b)

Since \( \chi^\pm \) are normalized and orthogonal, (5-5b) reduces to
\[ P = \sin^2 \left[ \frac{1}{\hbar} \int_{-\infty}^{\infty} (\epsilon^+(t) - \epsilon^-(t)) \, dt \right] \]  (5-6)

Since \( \epsilon^\pm \) are more readily determined as a function of \( R \) rather than of \( t \), (5-6) may be made a function of \( R \) by noting that for a constant velocity \( v = \frac{dz}{dt} \),

\[ dt = \frac{1}{v} \frac{R}{\sqrt{R^2 - b^2}} \, dR \]  (5-7)

where the \( Z \) axis is along the direction of the initial trajectory. (5-6) becomes

\[ P(b) = \sin^2 \left[ \frac{1}{2\hbar v} \int_{-\infty}^{\infty} \left( \frac{\epsilon^+(R) - \epsilon^-(R)}{\sqrt{R^2 - b^2}} \right) \, RdR \right] \]  (5-8)

The total cross section for charge transfer may be found by integration of \( P(b) \) over all impact parameters.

\[ \sigma_{tr} = 2\pi \int_{0}^{\infty} b \sin^2 \xi \, db \]  (5-9)

where \( \xi \) is the argument of \( \sin^2 \) in (5-8).

For large impact velocities the assumption of constant \( v \) is a good approximation. However, the internuclear interaction becomes important at lower velocities and the velocity is more accurately given as a function of \( R \). Equation (5-7) becomes

\[ dt = \frac{R}{v(R)} \left( R^2 - \frac{v(w)^2 b^2}{v(R)^2} \right)^{-\frac{1}{2}} \, dR \]  (5-10)
due to conservation of angular momentum. Equations (5-8) and (5-9) are modified accordingly. Results obtained for the case of constant \( v \) and the case of \( v \) as a function of internuclear separation will be considered in a later section.

A number of other contributions have been made to the impact parameter formulation. Bates and Williams\(^{54}\) expanded the two state approximation to include coupling to the 2p\( ^{\pm} \) state of the \( \text{H}_2^{+} \) molecule. Bates and Sprevak\(^{55}\) further expanded it for inclusion of the 3d\( ^{\pm} \) state. Coupling to these higher states becomes more important at higher collision velocities where more kinetic energy is available for excitation of either atom into a state above the ground state. Below the excitation energy of the 2s state of hydrogen, 10.2 eV, the two state approximation is very accurate.

Quantum Mechanical Wave Treatment

A formal quantum mechanical treatment of resonant charge transfer was first presented by Massey and Smith.\(^{56}\) Contributions have since been made by Bates \textit{et al.},\(^{50}\) Knudson and Thorson,\(^{57}\) and Hunter and Kuriyan.\(^{58}\) The following discussion is similar to that given by Mott and Massey.\(^{59}\)

Figure 5-2 is a diagram of the coordinate system referred to in this section. The nuclei are labeled 1 and 2 with the electronic coordinate \( \mathbf{r} \) referred to the center
Figure 5-2. Coordinate system.
of mass of the nuclei. The Hamiltonian for this system is given by

\[ \mathcal{H} = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla_r^2 + V_1(r_1) + V_2(r_2) + U(R) \quad (5-11) \]

where \( M \) is the reduced mass for the nuclei, \( U(R) \) is the internuclear potential energy and \( V_1 \) and \( V_2 \) are the potential energy terms of the electron with respect to each nucleus. The 2-state approximation is employed; \( \chi^\pm \) satisfy the electronic part of the Hamiltonian

\[ \left[ -\frac{\hbar^2}{2m} \nabla_r^2 + \epsilon^\pm(R) - V_1(r_1) - V_2(r_2) \right] \chi^\pm(\vec{r}, R) = 0 \quad (5-12) \]

and for large \( R \) are equivalent to the ground state atomic eigenfunction

\[ \frac{1}{\sqrt{2}}(\chi^+ + \chi^-) \sim \phi_1(r_1) \quad \text{as} \quad R \to \infty \quad (5-13) \]

\[ \frac{1}{\sqrt{2}}(\chi^+ - \chi^-) \sim \phi_2(r_2) \]

The eigenfunctions of the full Hamiltonian (5-11) may be expanded over this basis set

\[ \psi = F^+(\vec{R}) \chi^+(\vec{r}, R) + F^-(\vec{R}) \chi^-(\vec{r}, R) \quad (5-14a) \]

\[ = (F^+ + F^-) (\chi^+ + \chi^-) + (F^+ - F^-) (\chi^+ - \chi^-) \quad (5-14b) \]

\( F \) must have the asymptotic form

\[ F^\pm \sim_R \frac{1}{\sqrt{2}} \left\{ e^{ikZ} + e^{i\kappa R} f^\pm(\theta, \phi) \right\} \quad (5-15) \]

where \( Z \) is the axial component of \( R \) and \( k \) is the momentum vector given by

\[ k = \frac{M}{\hbar} \nu(-\infty) \quad (5-16) \]
The asymptotic form of $\psi$ becomes

$$\psi_{R^\infty} \equiv \frac{e^{ikZ}\varphi_1(r_1)}{\sqrt{2}} \frac{e^{ikR}}{R} \left[ \varphi_1(r_1)(f^+f^-) + \varphi_2(r_2)(f^+f^-) \right]$$

(5-17)

where the coefficients of the atomic wave functions are the scattering amplitudes. Since the initial state of the system was given by $\varphi_1(r_1)$, the squared scattering amplitude $|f^+-f^-|^2$ represents the differential cross section for charge transfer $\sigma_{tr}(\theta)$.

To determine $f^\pm(\theta, \varphi)$, (5-14) is substituted into the Hamiltonian equation (5-12). Use of (5-12) and the fact that $F$ is dependent only on $\vec{R}$ allows simplification of the resulting equation to

$$\chi^+ \left\{ \tilde{v}_R^2 + k^2 - \frac{2M}{\hbar^2} [U(R) + \varepsilon^+(R)] \right\} F^+ + 2\tilde{v}_R F^+ \chi^+ + F^+ \chi^+ = 0$$

$$\chi^- \left\{ \tilde{v}_R^2 + k^2 - \frac{2M}{\hbar^2} [U(R) + \varepsilon^-(R)] \right\} F^- + 2\tilde{v}_R F^- \chi^- + F^- \chi^- = 0$$

(5-18)

where $k^2 = \frac{2M}{\hbar^2} E$. This equation may be separately multiplied by $\chi^+$ and $\chi^-$ on the left and the two resulting equations integrated over the electronic coordinates. Since $\chi^\pm$ are orthogonal,

$$\int \chi^+ \chi^+ d\vec{r} = \int \chi^+ \tilde{v}_R \chi^+ d\vec{r} = \int \chi \tilde{v}_R^2 \chi^+ d\vec{r} = 0$$

(5-19)

The result is two uncoupled differential equations

$$\left[ \tilde{v}_R^2 + k^2 - \frac{2M}{\hbar^2} (U^\pm) \right] F^\pm + 2\tilde{v}_R F^\pm \int \chi^\pm \tilde{v}_R \chi^\pm d\vec{r} + F^\pm \int \chi^\pm \tilde{v}_R^2 \chi^\pm d\vec{r} = 0$$

(5-20)
The last two terms represent corrections to the internuclear potential due to the relative motion of the nuclei. These terms are small and may be dropped (although Hunter and Kuriyan have retained them) yielding

\[ \left[ \nabla_R^2 + k^2 - \frac{2M}{\hbar} (U + \epsilon^\pm) \right] F^\pm = 0 \]  

(5-21)

The functions \( F^\pm(R) \) are products of radial and angular components. The angular part may be expanded in Legendre polynomials (due to symmetry, the azimuthal dependency drops out), leaving the radial equation to be solved.

\[ \left[ \frac{d^2}{dr^2} + k^2 - \frac{2M}{\hbar^2} \frac{U(R)}{R} - \frac{\lambda (\lambda + 1)}{R^2} - \frac{2M \epsilon^\pm}{\hbar^2} \frac{G^\pm(\lambda)}{R} \right] G^\pm(\lambda) = 0 \]  

(5-22)

The solutions \( G^\pm(\lambda) \) which vanish at \( R = 0 \) have the asymptotic form

\[ G^\pm(\lambda) \sim_k R^{-\infty} \sin(kR - \frac{\lambda}{2} \pi \pm \eta^\pm) \]  

(5-23)

The scattering amplitudes \( f^\pm(\theta) \) are given in terms of the phase shifts \( \eta^\pm(\lambda) \) by

\[ f^\pm = \frac{1}{k} \sum_{\lambda} (2\lambda + 1) e^{\i \eta^\pm(\lambda)} \sin \eta^\pm(\lambda) P^\lambda(\cos \theta) \]  

(5-24)

and the total charge transfer cross section is

\[ \sigma_{tr} = \frac{\pi}{k^2} \sum_{\lambda} (2\lambda + 1) \sin^2(\eta^+(\lambda) - \eta^-(\lambda)) \]  

(5-25)

If the masses of the nuclei are not equal (e.g., as in the case for \( \text{H}^+ + \text{D} \) charge transfer) then the coupling
between states does not drop out and (5-20) does not hold. The coupled equations must then be solved.

The Problem of Indistinguishable Particles

In the above analysis the nuclei are treated as if they were distinguishable protons. In fact they are not (unless one of them is part of a polarized beam) and hence quantum mechanics gives no assurance that a proton scattered from a collision is an elastically scattered proton from the reactant proton beam or one resulting from a hydrogen atom which has lost its electron in a charge transfer reaction. Parcell and May and Smith have discussed this problem and have pointed out that the scattered part of (5-17) should be rewritten

$$\gamma_{\text{scat}}(\theta) \sim \frac{e}{2\sqrt{2R}} \left[ \phi_1 \left[ f^+(\theta) \mp f^+(\pi-\theta) + f^-(-\theta) \mp f^-(-\theta) \right] 
+ \phi_2 \left[ f^+(\theta) \mp f^+(\pi-\theta) - f^-(-\theta) \mp f^-(-\theta) \right] \right] \quad (5-26)$$

the sign depending on whether the spatial wave function is symmetric or antisymmetric. The total differential cross section (including charge transfer and elastic scattering) is given by

$$\sigma_t(\theta) = \frac{1}{4} \left[ 2 |f^+_3(\theta)|^2 \right] + \frac{3}{4} \left[ 2 |f^-_3(\theta)|^2 \right] \quad (5-27)$$

where $f^+_3(\theta)$ is the coefficient of $\phi_1$ in equation (5-26).

The impact of this problem may be observed in an experiment designed to measure the charge transfer cross
Figure 5-3. Different views of $H^+ + H$ scattering.
section in that some of the product protons supposed to be due to charge transfer may be elastically scattered protons. The result will be a measured cross section which is larger than the cross section given by (5-23) for the case of distinguishable particles. The cross sections which would be measured in a laboratory situation have been calculated by Crothers, Kennedy, and Smith. According to them, the error decreases with increasing energy and is negligible above a few electron volts. The reason for this decrease is that the cross section for elastic scattering of a proton at an angle \( \pi \) (in the center of mass) with respect to its initial direction rapidly diminishes with energy. Consequently, most of the protons exiting at an angle of \( \pi \) at higher collision energies are due to charge transfer. Recent calculations of total differential cross sections and charge transfer cross sections by Kuriyan\(^4\) demonstrate the effect graphically.

Figures 5-4a, c, e show the total differential cross section for energies of 2.7 eV, 1.0 eV and 0.1 eV. At the highest energies, \( \sigma_t(\theta) \) is strongly peaked in the directions 0 and \( \pi \), these peaks interpreted as being due to elastic scattering and charge transfer respectively. This reasoning is confirmed by Figure 5-4b which is a plot of just the charge transfer cross section at 2.7 eV. It is nearly identical with the portion of Figure 5-4a in the region of \( \pi/2 < \theta < \pi \). At lower energies (compare Figures
Figure 5-4(a). Angular distribution of scattered protons at 2.7 eV. (Kuriyan)
Figure 5-4(b). Angular distribution of protons resulting from charge transfer at 2.7 eV. (Kuriyan)
Figure 5-4(c). Angular distribution of scattered protons at 1.0 eV. (Kuriyan)
Figure 5.4(d). Angular distribution of protons resulting from charge transfer at 1.0 eV. (Kuriyan)
Figure 5-4(e). Angular distribution of scattered protons at 0.1 eV. (Kuriyan49)
Figure 5.4(f). Angular distribution of protons resulting from charge transfer at 0.1 eV. (Kuriyan)
5-4c and 5-4d and 5-4e and 5-4f) one's ability to distinguish the cutoff between the forward and backscattered peaks is diminished. It is evident, for instance, that at a collision energy of 0.1 eV, an experiment designed to collect ions scattered at any angle $\theta$ measured from $\pi$ would include a large contribution from elastically scattered ions and would not include all of the charge transfer ions. Consequently, from a quantum mechanical viewpoint, it does not make sense to measure "charge transfer" cross sections at energies below a few eV's for collisions of identical particles. In the present experiment this problem was circumvented by using distinguishable particles: at low collision energies charge transfer cross sections were measured between protons and deuterium atoms.

Equivalence of Impact Parameter and Wave Treatments

The two methods previously discussed for calculating cross sections may be shown to be equivalent if the quantum mechanical wave treatment is applied to the case where the particle trajectories are classical. In this case, the largest contribution from the phase shifts will result from large values of $\lambda$, and the series (5-25) may be replaced by an integral over $\lambda$:

$$\sigma_{tr} \sim \frac{2\pi}{k^2} \int_{0}^{\infty} (\lambda + \frac{1}{2}) \sin^2 (\eta_+^- - \eta_+^-) \, d\lambda \quad (5-28)$$

where $\lambda$ is related to the classical impact parameter $b$ by
\[ b = (l + \frac{3}{2}) / k \quad (5-29) \]

Jeffries (JWKB) approximation gives the phase shifts as

\[ \eta_{l}^{\pm} = -\frac{M}{\sqrt{\hbar}} \int_{0}^{\infty} \{ U(R) + \epsilon_{l}^{\pm}(R) \} dZ \quad (5-30) \]

Since \( dZ = (R/\sqrt{R^2 - b^2}) dR \), substitution of (5-30) and (5-29) into (5-28) yields (5-9), the impact parameter cross section. It is noteworthy that (5-30) may also be used to approximate the phase shifts for substitution into the series (5-25).

**Summary of Theoretical Results for \( H^+ + H \) and \( H^+ + D \)**

**Charge Transfer at Collision Energies below \( \sim 100 \text{ eV} \)**

In 1953 Dalgarno and Yadav published the first theoretical cross sections for charge transfer between protons and hydrogen atoms. They calculated these cross sections by partial wave analysis (eq. 5-25) using phase shifts calculated by the JWKB approximation. At the higher energies where large numbers of partial waves were involved, they divided (5-25) into two parts, summing the partial waves at low \( l \) and using the integral form (5-28) for large \( l \). The values used for the molecular eigenvalues were determined by the Heitler-London approximation modified by second order terms provided by Coulson.

Rapp and Francis reported cross sections for \( H^+ + H \) charge transfer in 1962 using the impact parameter formulation (5-4). They simplified the probability function by
assuming it had a value of \( \frac{1}{2} \) out to some value of the impact parameter \( b \), and integrating over the resulting step function to obtain the total cross section (see Figure 5-5). The calculated cross section was given as a function of the initial velocity \( v \) by

\[
\sigma = -k_1 \ln v + k_2 \tag{5-31}
\]

They used molecular wave functions due to Bates, Ledsham, and Stewart.\(^{68}\)

Rapp and Francis made note of the failure of the simplified form of the impact parameter to take into account the change in the relative velocity of the nuclei due to their interaction as discussed in connection with equation (5-10). In particular, they showed that the long-range potential between an atom and an ion due to the polarization of the atom (given by \( V(R) = -\frac{e^2d}{2R^4} \)) will result in some of the classical trajectories producing orbiting collisions. These collisions have been discussed by Gioumousis and Stevenson.\(^{69}\) The charge transfer cross sections will increase at low velocities as a result of such collisions because the nuclei will stay in a common vicinity for a longer time. Cross sections at higher energies will not be affected.

In a similar manner, Bates and Boyd\(^{70}\) considered the effect on the classical trajectory of the change in relative velocity due to the internuclear coulomb repulsion. Their results give slightly larger cross sections
Figure 5-5. The approximation to $P(b)$ used by Rapp and Francis is a step function of value 0.5 for $0 < b < b_1$. For $b > b_1$ it is 0.
for this case as compared with the straight line trajectory case.

Other calculations using the impact parameter method were carried out by Murakhver\textsuperscript{71} and by Smirnov\textsuperscript{72} both using values for the molecular states which they approximated themselves. Smith\textsuperscript{61,73} investigated the effect of nuclear symmetry on the cross sections and noted the existence of oscillations in the cross sections at very low energies due to the interference of the phase shifts. Crothers et al.\textsuperscript{63} reported cross sections for H\textsuperscript{+}+H as well as for H\textsuperscript{+}+D.

Hunter and Kuriyan\textsuperscript{58,75,76} have carried out quantum mechanical calculations of the charge transfer cross sections for H\textsuperscript{+}+H and H\textsuperscript{+}+D as well as D\textsuperscript{+}+H using phase shifts determined by numerically solving the coupled differential equations. This treatment was applied to cases where the collision energy was less than 10.2 eV, the energy required to excite the n = 2 level of the hydrogen atom, so that the two state solution is almost exact. The electronic eigenvalues they used for the H\textsubscript{2}\textsuperscript{+} molecule are due to Hunter, Gray, and Pritchard.\textsuperscript{77} Their stated error limits are ±0.1%.

The results of most of these calculations are shown in Figures 5-6, 5-7, and 5-8. The cross sections obtained in the present experiment will be compared with these in the next chapter.
Figure 5-6. Theoretical $H^+ + H$ charge transfer cross sections between 1 eV and 100 eV.
Figure 5-7. Theoretical $\text{H}^+ + \text{H}$ charge transfer cross sections between 0.001 eV and 10 eV.
Figure 5-8. Theoretical $H^+ + H$ and $H^+ + D$ cross sections of Hunter and Kuriyan and theoretical $H^+ + D$ cross sections of Crothers et al and Murakhver.
Chapter 6

Experimental Results

Table 6-1 contains a list of the cross sections measured for H\(^+\)+H and H\(^+\)+D charge transfer using the merged beams apparatus. The laboratory energies of the primary beams are given along with the relative velocities. Center of mass collision energies are listed, and for the H\(^+\)+D collisions, the corresponding energy of an H\(^+\)+H collision of the same relative velocity is also given. This format is used because the reaction cross sections for H\(^+\)+D and H\(^+\)+H are more accurately compared as a function of relative velocity rather than collision energy, but discussion of such reactions is often in terms of energy.

Contained in Table 6-2 are the major contributions to uncertainty in the measured cross sections. The range of values for each source of uncertainty is given separately for the H\(^+\)+H reactions, the H\(^+\)+D reactions (D beam with greater lab velocity) and the H\(^+\)+D reactions (H\(^+\) beam with greater lab velocity).

The measured cross sections are plotted in Figure 6-1 along with some of the theoretical results discussed in Chapter 5. Also, a comparison is made between the present data and other experimental results, all of which lie above 1 eV. Included are the crossed beams results of Pite,
Table 6-1

$H^+ + H$ and $H^+ + D$ Charge Transfer Cross Sections

(a) $H^+ + H$, H Beam Faster

<table>
<thead>
<tr>
<th>Beam Energies (eV)</th>
<th>$V_r$ (10^6 cm/sec)</th>
<th>$W$ (eV)</th>
<th>$\sigma_{tr}$ ($^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$H^+$</td>
<td></td>
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</tr>
<tr>
<td>1502</td>
<td>460</td>
<td>23.94</td>
<td>150</td>
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<tr>
<td>1501</td>
<td>500</td>
<td>23.51</td>
<td>134</td>
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<tr>
<td>1502</td>
<td>542</td>
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<td>607</td>
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<tr>
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<td>650</td>
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<tr>
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<tr>
<td>1501</td>
<td>800</td>
<td>14.48</td>
<td>54.8</td>
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</table>

(b) $H^+ + D$, D Beam Faster

<table>
<thead>
<tr>
<th>Beam Energies (eV)</th>
<th>$V_r$ (10^6 cm/sec)</th>
<th>$W$ (eV)</th>
<th>$\sigma_{tr}$ ($^2$)</th>
</tr>
</thead>
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<tr>
<td>D</td>
<td>$H^+$</td>
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<td></td>
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<tr>
<td>1502</td>
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<tr>
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<td>414</td>
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<tr>
<td>1500</td>
<td>443</td>
<td>8.79</td>
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<tr>
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<td>479</td>
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<td>15.4</td>
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<td>503</td>
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<td>516</td>
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<td>549</td>
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<td>1500</td>
<td>554</td>
<td>5.33</td>
<td>7.42</td>
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Table 6-1(b) Continued

<table>
<thead>
<tr>
<th>Beam Energies (eV)</th>
<th>( V_r ) (10^6 cm/sec)</th>
<th>W(eV)</th>
<th>( \sigma_{tr} ) A²</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H^+ + D )</td>
<td>( H^+ + H )</td>
<td>( H^+ + D )</td>
<td>( H^+ + D )</td>
</tr>
<tr>
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<tr>
<td>1504</td>
<td>630</td>
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</tbody>
</table>

*These values do not represent the total cross section (see text).

(c) \( H^+ + D, H^+ \) Beam Faster

<table>
<thead>
<tr>
<th>Beam Energies (eV)</th>
<th>( V_r ) (10^6 cm/sec)</th>
<th>W(eV)</th>
<th>( \sigma_{tr} ) A²</th>
</tr>
</thead>
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<tr>
<td>( H^+ + D )</td>
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<td>( H^+ + D )</td>
<td>( H^+ + D )</td>
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<td>4.16</td>
</tr>
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</tr>
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<tr>
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<td>.54</td>
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<tr>
<td>1501</td>
<td>804</td>
<td>1.29</td>
<td>.43</td>
</tr>
<tr>
<td>Beam Energies (eV)</td>
<td>$V_r$ (10^6 cm/sec)</td>
<td>$H^+ + H$</td>
<td>$H^+ + D$</td>
</tr>
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<td>-------------------</td>
<td>---------------------</td>
<td>-----------</td>
<td>-----------</td>
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<tr>
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<td>776</td>
<td>.62</td>
<td>.099</td>
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<tr>
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<td>774</td>
<td>.59</td>
<td>.089</td>
</tr>
<tr>
<td>1504</td>
<td>770</td>
<td>.43</td>
<td>.050</td>
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Table 6-2

Range of Uncertainties for $H^+H$ and $H^+D$

Cross Section Measurements

<table>
<thead>
<tr>
<th>Source</th>
<th>$H^+D$</th>
<th>$H^+D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D Faster</td>
<td>H Faster</td>
</tr>
<tr>
<td>Statistical Uncertainty in Signal (1 std. dev.)</td>
<td>2-8%</td>
<td>5-12%</td>
</tr>
<tr>
<td>Calibration of Multiplier</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td>Energy Analyzer Operating Voltage</td>
<td>5%</td>
<td>4-5%</td>
</tr>
<tr>
<td>$\gamma$ Measurement</td>
<td>7%</td>
<td>7%</td>
</tr>
<tr>
<td>Overlap Integral (except error due to $\gamma$)</td>
<td>9-10%</td>
<td>9-11%</td>
</tr>
<tr>
<td>Relative Velocity</td>
<td>&lt; 1%</td>
<td>1%-23%</td>
</tr>
<tr>
<td>Beam Divergence ($\Delta W_D$)</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
</tr>
</tbody>
</table>
Figure 6-1. Present experimental results compared with other experimental and theoretical results.
Smith, and Stebbings, and an early merged beams (technically, an "overtaking" beams) experiment carried out by Belyaev, Brezhnev, and Erastov. The primary similarity between this second experiment and the present one is that in both cases the collision occurred between particles in beams traveling parallel to each other. Unlike the present work however, Belyaev et al. performed a single beam experiment in which protons, remaining in the partly neutralized beam, were accelerated into the interaction region to produce a reaction between the two components of the beam. No account was taken of the contribution to the reaction of long-lived (n ≥ 10) excited states of H.

The results of the present experiment may be divided into three parts, each of which will be discussed separately. The first of these includes the high energy (55-100 eV) H⁺+H results. The second group consists of H⁺+D reaction measurements between 2.7 eV and 35 eV in which the deuterium beam had a larger laboratory velocity than the proton beam. The last group includes the H⁺+D results in which the proton beam was faster. These measurements extend from 4.6 eV to 0.05 eV.

The upper limit on the energy of the H⁺+H cross sections resulted from the difficulty of operating the reactant proton beam at an energy below ~400 eV. This problem could have been circumvented by scaling up both beams in energy, but since the multiplier had been
calibrated for a 1500 eV \( \text{H}^+ \) product ion beam and the neutral beam detector for 1500 eV H atoms, such a procedure would have required recalibrating both detectors. Furthermore, since the primary focus of this work has been on very low collision energies, 150 eV was considered an acceptable upper limit. The low energy limit for \( \text{H}^+ + \text{H} \) at \( \sim 55 \) eV is due to the presence of a large background from the reactant proton beam which makes data acquisition times prohibitively long at energies from 5 eV to 50 eV. Below 5 eV measurement of cross sections for \( \text{H}^+ + \text{H} \) charge transfer is not possible due to the problem of detecting scattered protons which have lost part of their axial component of velocity. This problem, which was discussed in Chapter 4, affected some of the cross section measurements for \( \text{H}^+ + \text{D} \) collisions in the medium energy range.

Figure 6-2 includes a plot of all of the cross section measurements attempted for the \( \text{H}^+ + \text{D} \) collision in which the deuterium beam had a larger initial laboratory velocity. These data agree with the theory of Dalgarno and Yadav\(^{65}\) at energies between 11 eV and 35 eV. Below 11 eV, however, they fall below the values expected from the theory, the difference increasing as the energy decreases. According to the results of Kuriyan,\(^{49}\) the differential cross sections (for \( \text{H}^+ + \text{H} \) collisions) become less strongly peaked in the forward direction as the energy decreases. Consequently, one expects a greater fraction of the product ions to be
Figure 6-2. Measurements of $H^+ + D$ charge transfer cross sections with $v_D > v_H$ showing loss of signal due to angular scattering.
scattered into angles large enough to render them undetectable. At 2.7 eV only those product ions scattered at center of mass angles less than 20° are detectable. Integration of the differential cross section (Kuriyan 49) at 2.7 eV indicates that only about 65% of the product ions fall into this group, in agreement with the measured value at this energy which is only about 69% as large as the theoretical value.

The data at the lower energies (0.05 eV to 46 eV) were measured under circumstances in which the proton beam velocity was greater than the neutral (deuterium) beam velocity. In this case, scattering of a product ion off the beam axis results in an increase of the axial component of its velocity. Consequently, all product ions are energetic enough to pass through the energy analyzer (see Figure 4-5c). The low energy limit for this set of measurements (0.05 eV) results from uncertainty in the relative velocity.

This lowest set of data lies above the theoretical H+D results of Hunter and Kuriyan 76 by 10-40%. The reasons for this discrepancy are not completely understood at this time. At least part of the disagreement is due to an effect of the merging region cylinder. As discussed in Chapter 4, this cylinder is floated at a potential of -17 volts so that product ions formed inside will not have enough kinetic energy to pass through the energy analyzer.
and be counted. However, some of the product ions which
are scattered off axis acquire enough additional velocity
along the beam axis to offset the effect of the negative
cylinder bias. Detection of these ions results in a
measured cross section which is larger than the real value.
A calculation of the limiting value of the error due to
this effect was carried out using the differential cross
sections of Kuriyan. (Implicit in this calculation is the
assumption that the $H^+D$ differential cross sections are
similar for equal relative velocities.) The results of
this computation are given in Table 6-3. The actual errors
are probably not as large as these limiting values; never-
theless, the disagreement between the present data and the
theoretical results of Hunter and Kuriyan may at least be
partially explained by this effect.

Another possible reason for the disagreement may be
an error in the measurement of the secondary electron
coefficient of the neutral beam detector. Such an error
would have affected the medium energy $H^+D$ results as well,
since all of the $H^+D$ measurements were made during the
same time period. The maximum error attributable to such
a miscalibration is no larger than 10%.

These results are obviously not in finished form.
Nevertheless, they represent the first cross sections
measured for this reaction at energies below 1 eV and they
qualitatively confirm the theoretical work carried out for
these energies.
<table>
<thead>
<tr>
<th>W(eV) [H^+ + H Collision]</th>
<th>Maximum Error (% Possible Increase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.050</td>
<td>33</td>
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<td>.089</td>
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<td>4.16</td>
<td>6</td>
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</table>
Appendix

Kinematics of Charge Transfer Collisions

Consider a charge transfer collision between an ion of mass \( m_1 \) and a neutral particle of mass \( m_2 + m_e \). The initial velocity of the ion is \( v_1 \) and the initial velocity of the neutral particle is \( v_2 \). The final velocities are \( v_1' \) and \( v_2' \). If a reference frame is selected such that \( v_2 = 0 \), then for the case where there is no angular scattering, conservation of momentum requires:

\[
\frac{m_1 v_1}{m_1 + m_e} = \frac{m_1}{m_2} v_1' + \frac{m_2}{m_2} v_2' \quad (A-1)
\]

From conservation of energy:

\[
\frac{m_1 v_1^2}{m_1 + m_e} = \left(\frac{m_1}{m_2} v_1'\right)^2 + \frac{m_2}{m_2} v_2'^2 + 2\Delta E \quad (A-2)
\]

where \( \Delta E \) is the difference in the ionization potentials of the particles. Solving (A-1) for \( v_2' \):

\[
v_2' = \frac{\frac{m_1 v_1}{m_2}}{m_1 + m_e} - \frac{\frac{m_1 + m_e}{m_2}}{m_2} v_1' \quad (A-3)
\]

Substituting (A-3) into (A-2):

\[
(m_2 + m_1 + m_e)\left(\frac{m_1 + m_e}{m_2}\right)v_1'^2 - 2m_1(m_1 + m_e)v_1v_1' \]

\[
+ m_1(m_1 - m_2)v_1^2 + 2m_2\Delta E = 0 \quad (A-4)
\]

Solving the quadratic equation:
\[ v_1' = \frac{m_1 v_1}{m_2 + m_1 + m_e} \]

\[ + \sqrt{\frac{m_2 v_1^2}{m_2 + m_1 + m_e} - \frac{m_2 + m_1 + m_e}{m_1 + m_e} m_1 (m_1 - m_2) v_1^2 + 2m_2 \Delta E} \]

(A-5)

For the reaction \( H^+ + H \rightarrow H + H^+ \), \( \Delta E = 0 \) and \( m_1 = m_2 \).

Thus:

\[ v_1' = \frac{2m_1}{2m_1 + m_e} v_1 \]  

(A-6)

\[ v_2' = \frac{-m_e}{2m_1 + m_e} v_1 \]  

(A-7)

For the present experiment, if a 1500 eV H beam undergoes charge transfer at a collision energy of 150 eV, the product protons will have a kinetic energy of 1499.6 eV. At a collision energy of 10 eV, the product protons will have a kinetic energy of 1499.9 eV.

Consider the case of \( H^+ + Kr \rightarrow H + Kr^+ \) - 0.4 eV which is the reaction by which the neutral beam is formed. If the proton beam has an initial kinetic energy of 1500.0 eV, the energy of the neutral hydrogen atoms (calculated via equation (A-5)) is 1499.6, the only energy loss being due to the difference in ionization potentials.
References

42. J. D. Cogan, Master's Thesis, Rice University (1978).
62. Ref. 59, page 646.
64. Ref. 59, page 433.