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Measurements of Chemiionization Cross Sections For
He(\(^1S,\(^3S\))−H\(_2\) and He(\(^1S,\(^3S\))−H Collisions

by

John Stephen Howard

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ABSTRACT

Measurements of Chemiionization Cross Sections
For He(2\(^1\)S, 2\(^3\)S)-H\(_2\) and He(2\(^1\)S, 2\(^3\)S)-H Collisions

by

John Stephen Howard

Chemiionization cross sections for He(2\(^1\)S, 2\(^3\)S)-H\(_2\) and He(2\(^1\)S, 2\(^3\)S)-H collisions have been experimentally determined using a high vacuum crossed-beam apparatus. The experimental procedure and resulting cross section values for (1) total ion production and (2) production of particular ion species are presented, and a detailed analysis of the possible sources of error associated with the measurements is presented. Values obtained with the crossed-beam apparatus are compared with previous experimental results and with recent theoretical calculations.
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CHAPTER I: INTRODUCTION

(A) Purpose of Chemiionization Experiments

The collision between a metastable atom \( R^* \) and a neutral atom or molecule \( AB \) whose ionization potential is less than the excitation energy of \( R^* \) may lead to one of the following chemiionization reactions:

\[
R^* + AB \rightarrow R + AB^+ + e^- \quad (a)
\]

\[
RAB^+ + e^- \quad (b)
\]

\[
RA^+ + B + e^- \quad (c)
\]

\[
R + A^+ + B + e^- \quad (d)
\]

Reaction (a) is generally known as Penning ionization and reaction (b) is termed associative ionization. Reactions (c) and (d) are called rearrangement ionization and dissociative Penning ionization, respectively.

Chemiionization is known to occur in planetary atmospheres (Ferguson and Schluter, 1962; McElroy, 1965; Patterson, 1967) and in laboratory environments, e.g. flowing afterglows (Fehsenfeld et al., 1965). To properly analyze the effects of chemiionization in these and other areas of physics, it is desirable to measure (1) total
absolute ionization cross sections and (2) the cross sections for production of particular ion species. In addition, measurements of such cross sections are extremely useful in evaluating theoretical descriptions of chemiionization (Ferguson, 1962; Bell, 1970; Bell et al., 1968; Fujii et al., 1970; Miller, 1970; Cohen and Lane, 1971).

It was therefore decided to conduct experiments on chemiionizing collisions involving He\(^{1}\,{}_{1}\,{}_{S},{}_{2}{}_{S}\) metastable atoms with both H\(_2\) and H. Helium and hydrogen were selected as the two colliding particles since both species are abundant not only in the earth's atmosphere but in the entire observable universe. Furthermore, because of the relative simplicity of the colliding particles, a considerable amount of theoretical work has recently been carried out on the cross section for ionization in He\(^*\)-H collisions (Cohen and Lane, 1971; Miller et al., 1972; Miller and Schaefer, 1970; Fujii et al., 1970), and a quantitative comparison between theory and experiment would be of great interest.
(B) Description of Apparatus

Details of the experimental apparatus have been presented elsewhere (Howard, 1971). Therefore only a brief description of the apparatus will be given here.

The basic differentially pumped crossed-beam apparatus is shown schematically in Figures (1) and (2). A helium beam, formed by flowing helium gas through a Bendix multi-channel glass capillary array, is exposed to a beam of electrons ($\sim$34eV.) constrained to travel colinearly with the atom beam due to the application of an axial magnetic field. A large number of excited helium atoms are produced, but most of the excited particles quickly decay back to the ground state, typically in times less than $10^{-8}$ seconds. However, a fraction of the helium beam is excited to the $2^1S$ and $2^3S$ states, both of which have lifetimes sufficiently long ($2.0 \times 10^{-2}$ seconds for singlets and $\sim 10^5$ seconds for triplets†) to enable them to arrive at the interaction region and thus cause chemionization. It is also possible to excite helium atoms to high-lying Rydberg levels whose lifetimes may be long enough for them to intersect the target beam, but evidence will be given

†Rundel and Stebbings, 1972
in Chapter III indicating that few highly excited atoms are
in fact present. All charged particles formed from
e-He collisions are removed from the beam either by the
solenoidal magnetic field or by an electrostatic field
applied across the beam between the excitation region and
interaction region.

Downstream from the excitation region, the helium
beam may be irradiated with light from a helium discharge.
If sufficient radiation of the proper wavelength is
supplied, greater than 99% of the He($2^1S$) atoms may be
removed from the beam, i.e. quenched, by transitions of
the type $2^1S$ - $n^1P$ - $1^1S$. The He($2^3S$) atoms may also be
excited to higher states, but subsequent decay quickly
returns them to the $2^3S$ state, which is the ground state
of the helium triplet system.

Measurement of the metastable atom flux is carried
out utilizing secondary electron ejection from a stainless
steel surface, whose secondary electron ejection coefficient
$\gamma_*$ is known from an auxiliary experiment (see Chapter II).
The $2^3S$ flux $i_{2^3S}$ (number/second) may be found by turning
on the helium discharge lamp, thereby removing all $2^1S$
atoms:

\[ i_t = \frac{i'_t}{\gamma_t} \quad (1) \]

where \( i'_t \) is the number of electrons per second leaving the stainless steel surface. If the discharge lamp is extinguished a flux \( i'_t \) due to both metastable states is measured:

\[ i'_t = \gamma_s i_s + \gamma_t i_t \quad (2) \]

Combining equations (1) and (2) then gives the singlet flux:

\[ i_s = \frac{i'_t - i'_t}{\gamma_s} \quad (3) \]

The hydrogen beam source is shown in Figure (3). Hydrogen gas from a high pressure tank of \( \text{H}_2 \) is passed through a needle valve and into one end of a hollow tungsten tube, which was constructed by rolling tungsten foil (.001" thick) into a cylindrical tube approximately six layers thick. A target beam is then formed by effusion
from a small (.040" diameter) hole drilled into the side of the tungsten tube, the position of which may be adjusted both horizontally and vertically by manual drives located outside the vacuum chamber. High current leads are attached to the ends of the tungsten tube. When an H\textsubscript{2} beam is desired, no current is passed through the tube, which remains at room temperature (300°K). However, when an H beam is desired, a current of approximately 260 amp. is passed through the tube (hereafter called the hydrogen furnace) which causes a fraction D of the molecules to be thermally dissociated into H atoms. The effusing beam then contains a mixture of H and H\textsubscript{2}.

Ions formed by the intersection of the helium and hydrogen beams may be analyzed by two methods. If the total ionization cross section is being determined, an electrostatic field maintained across the interaction region extracts all product ions, and subsequent electrostatic fields accelerate them onto the first dynode of a Johnston Labs. MM-1 particle multiplier. If the cross section for production of a particular ion is being determined, the total ion collector (TIC) described above may be raised on a bellows drive assembly enabling a separate
set of extraction electrodes to be positioned around the interaction region. As before, an electrostatic field extracts the product ions, and a focusing system composed of an einzel lens and an electrostatic quadrupole lens pair directs the ions into a magnetic sector (60°) mass spectrometer. By varying the field strength of the magnet, ions of one particular mass may be focused into a second particle multiplier.

It is necessary to distinguish ions formed by He*-target gas collisions from those formed by He*-background gas collisions. Therefore, the target beam is modulated at 100Hz by a four-bladed chopper wheel whose rotation is monitored by a light-photocell combination. When the target beam encounters one of the blades of the wheel, helium metastables intersect only background gas at the interaction region. When the target beam encounters an opening on the wheel, metastables intersect both background and target beam particles. One scaler, gated by the photocell, accepts output pulses from the particle multiplier when the target beam is on, while another scaler accepts multiplier pulses when the target beam is off. Subtraction of the two scaler readings then gives
the ion contribution due to ionization of the target beam.

(See Howard, 1971 for details).
CHAPTER II: Experimental Procedure

(A) Total Ionization Cross Sections

(1) Molecular Hydrogen

The total cross section for ionization of molecular hydrogen by metastable helium is given by

\[ S_* = \varepsilon_* \sigma_*(2)n_2 \lambda i_* \]  \hspace{1cm} (4)

where \( S_* \) is the total ion signal at the interaction region (number of ions per second), \( \varepsilon_* \) is the efficiency with which ions are detected, \( n_2 \) is the number density of the \( H_2 \) beam (number of molecules per cubic centimeter), \( \lambda \) (centimeters) is the effective path length of metastables through the target beam, and \( i_* \) is the metastable flux (number of metastables per second) for either \( \text{He}(2^3S) \) or \( \text{He}(2^1S) \) atoms. In this equation \( \sigma_*(2) \) is an average cross section appropriate to the relative speed distribution \( f(v_r) \) of the colliding beams:

\[ \sigma_*(2) = \int q(v_*,v_T)(1+v_T^2/v_*^2)^{-1/2} \frac{2}{\pi} f(v_*) f(v_T) dv_* dv_T \]

where \( v_r \) has been written in terms of \( v_* \) and \( v_T \).
It was stated in Chapter I that the true metastable flux $i_*$ is related to the number of secondary electrons per second ejected from a metal surface by

$$ i_* = i'_*/\gamma_* $$

(5)

A schematic drawing of the detector used for measuring $i'_*$ and $\gamma_*$ is shown in Figure (4). $i'_*$ may be continuously monitored by connecting the back plate to a Carey vibrating reed electrometer and biasing all other electrodes positive with respect to the back plate.

The determination of $\gamma_*$ can be made in a subsidiary experiment and is described in detail by Rundel et al. (1972). Briefly the procedure is as follows. A beam of metastable helium atoms is allowed to strike the back plate of the gas cell, and the current of secondary electrons $i_e = \gamma_* i_*$ is measured. Argon gas is then introduced into the gas cell so that the metastable beam is attenuated by Penning ionization to a value $j_*$. A smaller secondary electron current will therefore be measured at the back plate, $j_e = \gamma_* j_*$. The difference of the initial and final secondary electron currents is
\[ i_e - j_e = \gamma_*(i_* - j_*) \] (6)

But the difference between initial and final metastable fluxes is equal to the ion current \( i_+ \) resulting from Penning ionization, which may be measured by appropriate biasing conditions on the gas cell electrodes. \( \gamma_* \) may therefore be found:

\[ \gamma_* = \frac{(i_e - j_e)}{i_+} \] (7)

(For a detailed discussion of the problems associated with the gas cell method of determining \( \gamma_* \), see Rundel et al., 1972)

The value of \( \ell \) is not simply the geometrical path length of a metastable atom through the \( H_2 \) beam because the target particles possess a non-zero average speed \( \bar{v}_2 \), so that the average relative speed of the two beams is \( \bar{v}_r = (\bar{v}_*^2 + \bar{v}_2^2)^{1/2} \). The effective path length is therefore

\[ \ell = \bar{v}_r t \] (8)
where \( t \) is the time that a metastable atom is exposed to the target beam, which is equal to the geometrical path length \( \ell_{\text{geo}} \) divided by \( \bar{v}_* \). Equation (8) may then be written as

\[
\ell = \frac{\ell_{\text{geo}}}{\bar{v}_*} \bar{v}_r = \ell_{\text{geo}} \left( 1 + \frac{\bar{v}_0^2}{\bar{v}_*^2} \right)^{\frac{1}{2}}
\]  

(9)

The average beam speed can be calculated if the speed distribution functions for the beams are known. (See Chapter III for a discussion of these distribution functions).

The \( H_2 \) number density may be obtained in the following manner. An electron gun, mounted on a bellows drive assembly and normally positioned above the helium beam axis (see Figure 1a), is lowered onto the beam axis. The helium beam is thus replaced by an electron beam of 960eV., which passes through approximately the same portion of the target beam as did the metastables. An equation similar to equation (4) then relates the TIC ion signal \( S_e \) to the experimental parameters:

\[
S_e = \epsilon_e \sigma_e (2)n_2 \ell_i
\]
or

\[ n_2 = \frac{S_e}{\epsilon_e \sigma_e (2)} I_e \]

(10)

In the equation \( i_e \) is the electron beam current measured with the same electrometer as was \( i'_e \). \( \epsilon_e \) is the efficiency with which ions from e-H\(_2\) collisions are detected by the TIC, which is assumed to be equal to \( \epsilon_* \). \( \lambda_e \) may be replaced by \( \lambda_{geo} \) since \( \tilde{v}_2 \ll v_e \). In addition, the total ionization cross section \( \sigma_e^{tot} (2) \) is known from the literature (Kieffer and Dunn, 1966) as well as the cross section \( \sigma_e^{diss} (2) \) for production of ions having kinetic energies \( \geq 2.5 \text{eV} \).

Ideally, the best procedure for obtaining \( n_2 \) would be to measure total ion production with the TIC and use \( \sigma_e^{tot} (2) \) in equation (10). However, total ion collection would require a relatively strong TIC extraction field (15-20 volt/cm) across the interaction region which would deflect the electron beam, causing it to miss either the target beam or the Faraday cup detector. As an alternative it was decided to measure the thermal energy ion contribution to the TIC signal and use
\[
\sigma_{e}^{th}(2) = \sigma_{e}^{tot}(2) - \sigma_{e}^{diss}(2) \tag{11}
\]
as the appropriate cross section. A plot of \( S_{e} \) versus extraction field, similar to the one in Figure (5), is constructed. It is evident from this figure that as zero extraction field is approached from the left, a sharp increase in ion signal occurs, signifying that thermal energy ions are being collected. The slow increase of signal on either side of zero field is attributed to energetic ion collection. If straight line least-squares fits are performed on the two high field portions of the curve and extrapolations to zero field are made, a reasonable value for the thermal ion signal \( S_{e}^{th} \) results, leading to

\[
n_{2} = \frac{S_{e}^{th}}{\varepsilon_{e} \left[ \sigma_{e}^{tot}(2) - \sigma_{e}^{diss}(2) \right] \varepsilon_{i}} \tag{12}
\]

Combining this equation with equation (4) gives the proper expression for \( \gamma_{e} \):

\[
\sigma_{*} = \left[ \sigma_{e}^{tot}(2) - \sigma_{e}^{diss}(2) \right] \frac{S_{e}^{*}}{i_{e}} \frac{\varepsilon_{e}^{th}}{S_{e}^{*}} \frac{\varepsilon_{e}}{\varepsilon_{i}} \gamma_{*} \tag{13}
\]
(2) Atomic Hydrogen

The procedure for determining the total ionization cross section $\sigma_*(1)$ due to $\text{He}^* - \text{H}$ collisions is similar to the procedure for obtaining $\sigma_*(2)$ but is complicated by the fact that in general not all of the hydrogen molecules have been thermally dissociated in the furnace. The target beam is therefore a mixture of $\text{H}$ and $\text{H}_2$ and, as a result, the TIC signal due to metastable atom-target gas collisions has two components:

$$S_* = \epsilon_* \sigma_*(1) n_1 \frac{\lambda_1 i^*}{\gamma_*} + \epsilon_* \sigma_*(2) n_2 \frac{\lambda_2 i^*}{\gamma_*}$$

where $\lambda_1$ is the effective path length of metastables through atomic hydrogen and $\lambda_2$ is the corresponding path length through molecular hydrogen. Solving for the desired cross section leads to

$$\sigma_*(1) = \frac{S_*}{\epsilon_* n_1 \lambda_1 i^* \gamma_*} - \sigma_*(2) \frac{n_2}{n_1} \frac{\lambda_2}{\lambda_1}$$

(14)

It is convenient to find an expression for $n_2$ in terms of $n_1$ and $D$, the fraction of molecular hydrogen that has been dissociated.
Mathematically $D$ may be defined as

$$D = \frac{I_C^2 - I_2}{I_C^2} \quad (15)$$

where $I_2$ is the beam intensity (number/cm$^2$-sec) for molecular hydrogen. A superscript $c$ will be placed on intensity $I_2$ when referring to the intensity of a "cold" furnace, i.e. one at a temperature where no dissociation occurs.

Equation (15) assumes that constant mass flow through the furnace applies at all temperatures. This assumption may be expressed as

$$I_C^2 = \frac{1}{2} I_1 + I_2 \quad (16)$$

where the factor of $\frac{1}{2}$ occurs in front of the atomic hydrogen intensity since two hydrogen atoms are formed from each dissociated molecule.

Combining equations (15) and (16) gives

$$I_2 = \frac{1-D}{2D} I_1$$
or, in terms of number densities \( n_1 \) and \( n_2 \),

\[
\frac{1}{2D} \frac{\bar{v}_1}{\bar{v}_2} n_1
\]

(17)

where \( \bar{v}_1 \) and \( \bar{v}_2 \) are the average speeds for the H and \( \text{H}_2 \) beam components, respectively.

If the gas effusing from the hydrogen furnace is in thermal equilibrium, the speed may be expressed by

(Reif, 1965)

\[
\bar{v}_i = \left( \frac{8kT_i}{\pi m_i} \right)^{\frac{1}{2}}
\]

(18)

However, \( T_1 = T_2 \) and \( m_1 = \frac{1}{2}m_2 \) so that the number density of molecular hydrogen becomes

\[
\frac{1}{\sqrt{2D}} n_1
\]

(19)

Substituting this expression in equation (14) gives

\[
\sigma\star(1) = \frac{S\star}{\epsilon\star n_1 \lambda_1 \star} \gamma\star - \sigma\star(2) \frac{1}{\sqrt{2D}} \frac{\lambda_2}{\lambda_1}
\]

(20)

The only remaining quantity to be determined is
n_1, which may be obtained by ionizing the target beam
with 960eV electrons in a manner similar to the deter-
mination of n_2. The resulting TIC ion signal is therefore
composed of ions formed from e-H collisions and ions from
e-H_2 collisions. Energetic protons will again arise
from this last type of collision but their contribution
is now small. A simple calculation shows that if typical
dissociation fractions \( \approx 0.75 \) are used in the experiment,
a maximum possible error of between 1 and 1.5% will arise
if only thermal ions are collected. The TIC ion signal
may therefore be written as

\[
S_e = \epsilon \sigma_e (1) n_1 \epsilon \epsilon \epsilon \epsilon + \epsilon \sigma_{\text{tot}} (2) n_2 \epsilon \epsilon \epsilon \epsilon \\
= n_1 \left[ \epsilon \sigma_e (1) \epsilon \epsilon \epsilon \epsilon + \epsilon \sigma_{\text{tot}} (2) \frac{n_2}{n_1} \epsilon \epsilon \epsilon \epsilon \right]
\]

Using equation (19) for \( n_2 \) and solving the above equation
for \( n_1 \) gives

\[
n_1 = \frac{S_e}{\left[ \sigma_e (1) + \sigma_{\text{tot}} (2) \frac{1 - D}{\sqrt{2D}} \right] \epsilon \epsilon \epsilon \epsilon \epsilon}
\]

(21)
Again \( \lambda_e \) is assumed to be equal to the geometrical path length of metastables through the target beam, \( \lambda_{geo} \).

The expression for \( \sigma_*(1) \) may then be written

\[
\sigma_*(1) = \left[ \sigma_e(1) + \sigma_{e\,tot}(2) \frac{1-D}{\sqrt{2D}} \right] \left[ \frac{\lambda_{e\,tot}(2)}{\lambda_1} \right] \frac{1-D}{\sqrt{2D}} \left( \frac{\lambda_e}{\lambda_1} \right) \gamma_*(2) (22)
\]

It is now appropriate to discuss the experimental method used in determining the dissociation fraction \( D \). \( D \) has already been defined by equation (15) as

\[
D = \frac{I_2^C - I_2}{I_2^C}
\]

under the assumption of constant mass flow. In order to determine \( I_2 \) at any furnace temperature \( T \), the 960eV electron beam is allowed to ionize the target beam mixture of \( H \) and \( H_2 \), and the mass spectrometer system is employed to monitor the \( H_2^+ \) signal, \( S_{H_2^+}(T) \). This signal is related to \( I_2(T) \) by

\[
S_{H_2^+}(T) = e^* [\sigma_{e\,tot}(2) - \sigma_{e\,diss}(2)] \frac{I_2(T)}{\varphi_2(T)} \frac{\lambda_e}{\lambda_1}
\]

or
\[ I_2(T) = \text{constant} \cdot S_{H_2}^+(T) \cdot \sqrt{\frac{T}{T}} \]

where \( \varepsilon_e' \) is the ion collection efficiency of the mass spectrometer system. If the gas in the furnace is in thermal equilibrium with the furnace walls, then equation (18) is applicable for \( \sqrt{\frac{T}{T}} \), giving

\[ I_2(T) = \text{constant} \cdot S_{H_2}^+(T) \cdot \sqrt{\frac{T}{T}} \] \hspace{1cm} (23)

Substituting this expression into equation (15),

\[ D = 1 - \frac{S_{H_2}^+ \sqrt{\frac{T}{T}}^h}{S_{H_2}^+ \sqrt{\frac{T}{T}}^c} \] \hspace{1cm} (24)

where superscript \( h \) refers to a high temperature furnace and \( c \) refers to a cold furnace. Thus, it is not necessary to know \( \varepsilon_e' \) as long as it is constant over the relevant temperature range. This assumption will be examined in further detail in the next chapter, as will the assumptions of constant mass flow and thermal equilibrium.

The furnace temperature \( T \) is monitored throughout the course of the experiment with an optical pyrometer positioned along the target beam axis so that the furnace
interior may be examined through the aperture in the tungsten tube.

(B) Mass Analysis of Ions Produced by He*-H Collisions

Collisions between metastable helium atoms and hydrogen atoms may produce H+ by Penning ionization or HeH+ by associative ionization. By using the mass spectrometer system it is possible to determine the probability for formation of H+ or HeH+ in an ionizing reaction. In addition, the total singlet-to-triplet ionization cross section ratio \( \sigma_s(1)/\sigma_*(1) \) may be determined with the mass spectrometer, thereby providing a systematic check on this ratio as determined by the TIC system.

The existing mass spectrometer system possesses high transmission properties. However, the present operating voltages have not been optimized to achieve 100% transmission for a particular ion mass at one magnetic field setting. Therefore, in order to obtain a signal which is representative of the total number of ions for a given mass, it is necessary to vary the magnetic field strength, record ion signal as a function of field setting, and then numerically sum the partial ion signals over the range of
magnetic fields appropriate for a particular ion.

When comparing signals for two ion masses, it is not sufficient merely to plot signal versus field strength and find the resulting area under the curve because ions with small masses are swept across the particle detector at a faster rate than heavier ions according to the equation (see Figure [6])

\[ \frac{\Delta y}{\Delta B} = \frac{\text{constant}}{B} \]  \hspace{1cm} (25)

To correct this problem it is necessary to plot ion signal versus some function of B such that

\[ \frac{\Delta y}{\Delta F(B)} = \text{constant} \]

for all ion masses. If both sides of equation (25) are multiplied by B,

\[ \frac{\Delta y}{\Delta B/B} = \text{constant} \]

results, which may be written
\[
\frac{\Delta y}{\Delta (\ln B)} = \text{constant}
\]

The proper function \( F(B) = \ln B \).

The numerically integrated ion signals for each mass may then be used to find the desired cross section ratios:

\[
\frac{\sigma_*(\text{HeH}^+)}{\sigma_*(1)} = \frac{S_*(\text{HeH}^+)}{S_*(\text{HeH}^+) + S_*(H^+)} ;\quad \frac{\sigma_*(H^+)}{\sigma_*(1)} = \frac{S_*(H^+)}{S_*(\text{HeH}^+) + S_*(H^+)}
\]

(27)

where \( \sigma_*(i^+) \) is the cross section for \( i^+ \) production and \( S_*(i^+) \) is the integrated mass spectrometer signal for \( i^+ \). \( \sigma_*(1) \) represents the total ionization cross section, as usual.

The singlet-to-triplet total ionization cross section ratio is

\[
\frac{\sigma_s(1)}{\sigma_t(1)} = \frac{S_s(\text{HeH}^+) + S_s(H^+)}{S_t(\text{HeH}^+) + S_t(H^+)} \frac{i_t'}{i_s'} \frac{\gamma_s}{\gamma_t}
\]

(28)

When the target beam is composed of a substantial fraction of \( H_2 \), the \( \text{HeH}^+ \) and \( H^+ \) mass spectrometer ion signals above may contain unwanted contributions from \( \text{He}^*-\text{H}_2 \) collisions. This effect must then be considered.
when ratios appropriate to He\textsuperscript{*}–H collisions are being determined. Further discussion concerning this effect will be delayed until Chapter III, Section B.
CHAPTER III: Results

(A) Cross Section Values

(1) Molecular Hydrogen

The experiment for determining the total ionization cross section for He*-H₂ collisions was conducted on four separate occasions over a period of several weeks. The results are shown in Table (1).

The pressure \( P_{H_2} \) in the \( H_2 \) source chamber, i.e. the chamber in which the furnace was mounted, was continuously monitored throughout each experimental run and provided a relative indication of the \( H_2 \) number density, \( n_2 \). Quantitatively the number density was determined from e-H₂ reactions in the manner discussed in Chapter II. On Runs 1 and 2 \( n_2 \) was measured at the start of the experiment. On the final two runs \( n_2 \) was measured both at the beginning and the end of the experiment to provide a systematic check on the constancy of \( n_2 \). Results for Run 3 showed that the number density measured at the end was within 5% of the value obtained at the start of the run. On Run 4 the two measurements agreed to within 3%, thereby giving indirect but convincing evidence that \( n_2 \)
was nearly constant during the course of the experiment.

Figure (7) shows a typical plot of TIC ion signal versus extraction field, from which the thermal ion contribution may be found. The change in slope, expected near zero extraction field, occurs at a slightly retarding extraction field placed between electrode Gl and the bottom plate electrode (see Figure 2a). It is believed that this shift is due to penetration of the high TIC accelerating fields (shown in Figure 2a) through the grid-ded aperture in electrode Gl. This field penetration would tend to accelerate product ions upward even though a small retarding potential difference existed across the interaction region electrodes.

The individual singlet and triplet cross sections are listed in Table (1). The error listed after each cross section represents the combined statistical error associated with the measurements of $S_*$ and $S_e$ for that particular run. A discussion of these errors will be deferred until Section B of this chapter.

Table (1) also contains the average total cross sections $\bar{\sigma}_s$ and $\bar{\sigma}_t$ which were found after weighting the cross section for each run according to its statistical
accuracy:

\[ \bar{\sigma}_* = \frac{\sum_i \sigma_i / \delta_i^2 (\sigma_i)}{\sum_i 1 / \delta_i^2 (\sigma_i)} \]

where \( \delta_i (\sigma_i) \) is the statistical error (standard deviation) for run \( i \). The uncertainties associated with the average values are again statistical in nature and are found by the equation

\[ \bar{\delta}_* = \left( \sum_i 1 / \delta_i^2 (\sigma_i) \right)^{1/2} \]

Table (2) displays the sources of error associated with the total cross section measurements. It should be noted that the total per cent error for the ratio \( \sigma_s (2)/\sigma_t (2) \) is less than for either \( \sigma_s (2) \) or \( \sigma_t (2) \) independently. This feature arises since several experimentally measured quantities cancel when the ratio is determined. Hence any systematic errors involving these quantities also cancel.

The individual sources of error in Table (2) will be discussed at length in Section B.

(See Conclusion and Table 10 for revision of results.)
(2) Atomic Hydrogen

(a) Total Ionization Cross Sections

Experiments for the determination of the total ionization cross sections \( \sigma_s(l) \) and \( \sigma_t(l) \) for \( \text{He}^+ - \text{H} \) collisions were conducted several times. Table (3) shows the individual results. Again the \( H_2 \) source chamber pressure \( P_{H_2} \) was monitored on all runs. It remained constant to within 2%. The H atom number density \( n_1 \) was measured by means of electron-target beam reactions at the beginning and end of each run. On Runs 2 through 6 less than 5% variation was experienced in the value of \( n_1 \), although on Run 1 an 18% variation occurred. For each run the average value of \( n_1 \) was used in the calculation of \( \sigma_*(l) \).

The column labelled \( T_{\text{exp}} \) contains the temperature at which \( \sigma_*(l) \) was determined. The columns for \( D^{300} \) and \( D^{1375} \) represent the dissociation fraction obtained at \( T_{\text{exp}} \) using "cold" reference temperatures of 300°K and approximately 1375°K, respectively, in equation (24). The two values for \( D \) on each run are essentially in agreement as expected, since by equation (23) the product
$S_{\text{H}_2^+T^+}$ should remain unchanged for any reference temperature at which dissociation does not occur.

The total statistical error for each cross section value is listed in Table (3), while Table (4) contains a summary of the sources of error associated with $\sigma_s(1)$, $\sigma_t(1)$ and the ratio $\sigma_s(1)/\sigma_t(1)$. These sources will be discussed in Section B.

(b) Mass Analysis of Product Ions

Table (5) shows the results of four experimental runs for the measurements of $\sigma_*(\text{HeH}^+)/\sigma_*(1)$ which were obtained by the method described in Chapter II. It is apparent that Penning ionization is by far the most probable ionization process for $\text{He}^*-\text{H}$ collisions, although associative ionization may also occur.

Also shown in this table are the singlet-to-triplet cross section ratios for total ionization, $\sigma_s(1)/\sigma_t(1)$. The average ratio lies within 10% of the value obtained by the TIC method, which is within the uncertainty attributed to the value.

The uncertainties of all the ratios listed in Table (5) are due mainly to poor statistics for the mass spectrometer ion signals.

(See Conclusion and Table 10 for revision of results.)
(B) Sources of Error Common to He⁺-H₂ and He⁺-H Experiments

(1) Path Length

It was shown in Chapter II, equation (9), that the path length \( l \) of metastables through the target beam is related to the geometrical path length \( l_{geo} \) by

\[
l = l_{geo} \left(1 + \frac{\nu_{T}^2}{\nu_{\star}^2} \right)^{\frac{1}{2}}
\]

\( l_{geo} \) may be readily determined from the geometry of the target beam collimating apertures. The average speeds for the metastable beam and target beam, \( \bar{\nu}_\star \) and \( \bar{\nu}_T \), respectively, must now be evaluated.

In general if \( f(v)dv \) represents the speed distribution function for a collection of particles, then the average speed may be written

\[
\bar{\nu} = \frac{\int_0^\infty v f(v) dv}{\int_0^\infty f(v) dv}
\]

The proper distribution function for the target beam, which effuses from an aperture, is the modified Maxwellian function
\[ f_T(v)dv = \text{constant} \cdot v^3 e^{-mv^2/2kT}dv \quad (29) \]

This function differs from the normal Maxwellian by an extra factor of \( v \), which arises from the fact that the probability of a particle emerging from the aperture is proportional to the particle velocity. Integration yields

\[ \bar{v}_T = \frac{3\pi}{8} \left( \frac{8kT_T}{\pi m_T} \right)^{\frac{1}{2}} \quad (30) \]

where \( k \) is the Boltzmann constant, \( m_T \) is the target particle mass and \( T_T \) is the target beam temperature.

The speed distribution function for the metastable beam is not easily determined. The multichannel array that is used to form the ground state helium beam is composed of many closely spaced tubes each with a large length-to-diameter ratio. Recently Angel and Giles (1972) have measured the speed distribution for atoms emerging from a multichannel glass array. They found that the distribution of speeds was somewhat different than a modified Maxwellian distribution but that the average measured speed was about the same as the average speed calculated for a modified Maxwellian distribution.
Therefore, an average speed corresponding to a modified Maxwellian distribution is assumed for the ground state helium atoms formed in the crossed-beam system.

In the excitation region a continuous beam of electrons travels colinearly with the helium atoms and, since slower atoms spend a longer time exposed to the source of excitation, they will have a greater probability of being excited to metastable states. This may be taken into account by dividing the He(1\textsuperscript{S}) speed distribution function by v. The metastable atoms are therefore assumed to possess a Maxwellian distribution of speeds.

\[
f_*(v)dv = \text{constant} \cdot \frac{v^2_\star}{m_\star} e^{-\frac{v^2_\star}{2kT_\star}} dv \tag{31}
\]

which leads to

\[
\bar{v}_\star = \left(\frac{8kT_\star}{\pi m_\star}\right)^{\frac{1}{2}} \tag{32}
\]

(This assumption will be experimentally tested in the near future).

Combining equations (9), (30) and (32) gives the following expression for path length:
\[ \lambda = \lambda_{\text{geo}} \left[ 1 + \left( \frac{3\pi}{8} \right)^2 \frac{T_T}{T_\ast} \frac{m_\ast}{m_T} \right]^\frac{1}{2} \]  

(33)

If the target atoms are in thermal equilibrium with the furnace walls, \( T_T \) corresponds to the optical pyrometer reading. \( T_\ast \) is the only quantity in equation (33) which has not yet been determined.

The metastable beam temperature does not correspond to room temperature since momentum is transferred from electron to atom during the excitation process, thus raising the effective temperature. From conservation of momentum and energy, and assuming that the electrons are forward scattered (McDaniel, 1964), the final momentum of the helium atom \( P^f_{\text{He}} \) after excitation and momentum transfer is

\[
P^f_{\text{He}} = P^i_{\text{He}} + P^i_e \cdot (1 - \sqrt{1 - \Delta E/E_e})
\]  

(34)

In this equation \( E^i_e \) is the incident electron energy (34eV) and \( \Delta E \) is the energy transferred to the atom from the electron, which is 19.82eV for He(\( 2^3S \)) atoms and 20.61eV for He(\( 2^1S \)) atoms. \( P^i_{\text{He}} \) is the momentum of the
excited helium atom which would result if no momentum transfer occurred.

Since \( \bar{P}_{\text{He}} = m_{\text{He}} \bar{V}_{\text{He}} \), equation (34) may be rewritten

\[
\bar{v}^f_{\text{He}} = \bar{v}^i_{\text{He}} + \frac{m_{\text{e}}}{m_{\text{He}}} v^i_{\text{e}} \left(1 - \sqrt{1 - \Delta E/E_{\text{e}}} \right)
\]

or

\[
\bar{v}^f_{\text{He}} = \bar{v}^i_{\text{He}} \left[1 + \frac{m_{\text{e}} v^i_{\text{e}}}{m_{\text{He}}} \left(1 - \sqrt{1 - \Delta E/E_{\text{e}}} \right)^i_{\text{He}} \right]
\]

\[
= \bar{v}^i_{\text{He}} \left[1 + .377 (1 - \sqrt{\Delta E/34}) \right].
\]

\[
\begin{align*}
&= \begin{cases} 
1.140 \bar{v}^i_{\text{He}} & \text{for singlet metastables} \\
1.134 \bar{v}^i_{\text{He}} & \text{for triplet metastables}
\end{cases} \\
\end{align*}
\]

\( \bar{v}^i_{\text{He}} \) is related to temperature \( T_{\text{He}} \) by equation (32), giving

\[
\bar{v}^f_{\text{He}} = \begin{cases} 
1.140 \left( \frac{8kT_{\text{He}}}{m_{\text{He}}} \right)^{\frac{1}{2}} \left( \frac{8kT^f_{\text{He}}}{m_{\text{He}}} \right)^{\frac{1}{2}} & \\
1.134 \left( \frac{\pi m_{\text{He}}}{\pi m_{\text{He}}} \right)^{\frac{1}{2}} &
\end{cases}
\]

where the effective temperature \( T_{\text{He}}^f \) for the metastable helium beam is related to \( T_{\text{He}}^i \) by
\[ T_{\text{He}}^f = \begin{cases} 1.300 \\ 1.285 \end{cases} T_{\text{He}}^i \] (35)

The desired path length expression may then be obtained by combining equation (35) for \( T_{\text{He}}^i = 300^\circ \text{K} \) with equation (33):

\[ \lambda = \lambda_{\text{geo}} (1 + 0.0145 T/m) \lambda_i \] (36)

for both singlet and triplet metastables. Table (6) shows the values of \( \lambda_e/\lambda \) at two temperatures for both \( H_2 \) and \( H \) target particles, assuming \( \lambda_e = \lambda_{\text{geo}} \). Also shown are the values of \( \lambda_e/\lambda \) which would be applicable if a distribution function \( f(v)dv = ve^{-mv^2/2kT}dv \) had been used for the metastable atoms. A comparison of \( \lambda_e/\lambda \) between the two distribution functions shows a 20% variation for \( H \) and 15% variation for \( H_2 \). Consequently these variations were used as the percentage uncertainties in the ratio \( \lambda_e/\lambda \).

(2) Metastable Beam Current

(a) High Rydberg Levels

It is possible for high Rydberg levels of helium, i.e. levels characterized by large principal quantum
number \( n \), to be populated in the excitation region. Atoms with \( n > 200 \) possess sufficiently long lifetimes to enable them to arrive at the interaction region. These atoms may possess large chemiionization cross sections on the order of \( 10^{-14} \text{cm}^2 \) (Hotop and Niehaus, 1968), which would therefore interfere with measurements of \( \text{He}(2^3S, 2^3S) \) cross sections. However it should be noted that helium atoms possessing principal quantum numbers \( n > 200 \) will be ionized in an electrostatic field greater than about 2 volt/cm within a mean time of \( \sim 10 \mu \text{sec} \). The charged particle deflecting plates located on the helium beam axis are operated continuously throughout all chemiionization experiments with fields of 50 volt/cm. Even though atoms with high Rydberg levels may have been produced in the excitation region, they would have been field ionized and therefore lost from the beam prior to entering the collision chamber.

Nonetheless the following experimental check was made in an attempt to establish the presence (or absence) of high Rydberg levels. Hotop and Niehaus (1967) have shown that highly excited helium atoms \( \text{He}^{**} \) will undergo collisional ionization with several gases, one of which is \( \text{SF}_6 \).
They find the cross section for $\text{He}^{**} + \text{SF}_6 \rightarrow \text{He}^+ + \text{SF}_6^-$ to be $(0.76 \pm 0.08) \times 10^{-12} \text{cm}^2$. Therefore the mass spectrometer system was tuned to the $\text{He}^+$ peak and $\text{SF}_6$ was used as the target beam. The helium beam was run in the usual manner. There was no indication of $\text{He}^+$, thereby implying the absence of a sufficient number of highly excited helium atoms to interfere with present experiments.

(b) Photons

The excitation region is a source of photons as well as metastables, since many helium atoms will be excited to levels that can decay to the ground state by electric dipole radiation.

If a substantial number of photons are directed along the helium beam axis, they will interfere with chemionization measurements in two ways: (1) photoionization of the target beam, causing an unwanted contribution to the production signal and (2) ejection of photoelectrons from the metastable atom detector, leading to a false $i_\ast$ reading.

The most abundant photon is likely to be the $^2\text{P}-^1\text{S}$ 584Å photon since the $^2\text{P}$ state has a high probability of being both directly excited by e-$\text{He}(^1\text{S})$ collisions and
populated by cascade from the higher-lying levels. At this wavelength the photoionization cross section for $H_2$ is approximately $7 \times 10^{-18}$ cm$^2$ and for $H$ is believed to be about $2 \times 10^{-18}$ cm$^2$ (Massey and Burhop, 1971). Therefore even if the photon and metastable fluxes were comparable, $S_*(1)$ due to $He^*-H$ collisions would be altered by less than 1%, and $S_*(2)$ due to $He^*-H_2$ collisions would be affected by about 3%.

The photoelectric yields for a 584Å photon may be comparable with secondary electron yields due to metastable impact. For instance, the photoelectric yield for a tungsten surface may be .15 (McDaniel, 1964) and for many other surfaces may be on the order of .1. However, only the measured current for $He(2^3S)$ will be affected by photoelectric ejection. This may be understood as follows.

If $i_p$ is the photon flux in the helium beam then, with the helium discharge lamp on, a current $i'_on = \gamma t' + \gamma p$ = $i'_t + i'_p$ will result, instead of $i'_t$. If the quench lamp is turned off, a current $i'_off = \gamma s i'_s + \gamma t i'_t + \gamma p$ will be measured. Subtracting the two current readings then gives $i'_s$, the correct singlet current.
A beam attenuation experiment, utilizing the gas cell of Figure (4), was therefore performed to determine the photon content of the helium beam. Argon gas was introduced into the gas cell and a plot of the log of back plate current i' as a function of gas cell pressure was made. A significant photon contribution would produce a curve similar to the one in Figure (8), the rapid attenuation of i' at low pressures being due to elastic scattering and chemionization reactions. As the metastables are consumed, the rate of attenuation would fall off until finally no metastable atoms remain. The high pressure region of constant slope, corresponding solely to photoabsorption processes, may then be extrapolated back to zero argon pressure in the gas cell to obtain the contribution to back plate current due to photons.

The actual curve that resulted from a plot of ln i' vs. gas cell pressure gave no evidence of a break in slope anywhere between $1 \times 10^{-7}$ torr and $1 \times 10^{-2}$ torr, which is the expected result in the absence of photons.

To ensure the validity of the beam attenuation vs. gas cell pressure method, the electron beam energy in the excitation region was increased to 150eV and a similar
experiment was conducted. A 20% photon contribution to back plate current was found.

(c) Secondary Electron Ejection Coefficient

The values of $\gamma_s$ and $\gamma_t$ were measured according to the method outlined in Chapter II. This method resulted in a 12% uncertainty in $\gamma_s$ and $\gamma_t$ and a 7% uncertainty in the ratio $\gamma_s/\gamma_t$. Details of the problems associated with $\gamma$ measurements using a gas cell technique have been discussed by Rundel et al. (1972), so that only a qualitative description will be given here.

Measurements of the secondary electron current leaving the back plate of the gas cell and the ion current resulting from Penning reactions with argon are complicated by several factors. Metastable atoms may be elastically scattered in the gas cell and strike the sides of the gas cell instead of the back plate. The back plate current may also be affected by the collection of Penning ions produced from He$^*$-Ar collisions.

During the measurement of Penning ion current a correction must be made for the elastically scattered metastables which strike the collecting surface and eject
secondary electrons.

In addition, the magnitude of the metastable beam as it enters the gas cell at high pressure is less than the value at zero gas cell pressure since argon gas that streams out of the gas cell will attenuate the metastables by elastic scattering and Penning ionization.

Other factors which must be considered include secondary electron ejection due to Penning ion impact on gas cell electrodes and variations in the value of $\gamma_*$ depending upon the angle of incidence of the metastable atom.

(3) Electron Beam Current

$i_e$ was measured with a cylindrical Faraday cup which was biased to prevent escape of secondary electrons. Successful collection of all electrons was demonstrated by applying a sufficient voltage to saturate the current. All experiments were performed using a voltage bias within the saturated current region.

The same electrometer was used for monitoring both $i_*$ and $i_e$. However, in the event that a different load resistor in the electrometer was used for $i_e$, a small
correction to the current reading was required, since the actual value of the load resistor was slightly different from the value printed on the electrometer dial. This correction was never larger than 4%.

To ensure that the electron beam passed completely within the target beam, the electrons were electro-
statically focused and collimated by an aperture located 4.5 cm from the interaction region. The collimating apertures along the target beam path were correspondingly larger in the vertical dimension to facilitate the passage of the electron beam within the target beam.

(4) TIC Ion Signal

When the product ions formed by He*-hydrogen col-
lisions are being extracted from the interaction region, the electrostatic field must be of sufficient strength to result in saturation of the ion signal. Therefore tests for signal saturation were made. Figure (9) shows the results for He*-H collisions. It is evident that the product ion signal has reached a maximum value by the time a 3 volt/cm extraction field has been applied. The signal produced by He*-H₂ collisions saturated with a
slightly lower extraction field. As a result all ion signal analysis involving He*-hydrogen collisions used extraction fields ≥ 3 volt/cm.

Determination of the hydrogen atom number density involves the measurement of $S_e$, the ion signal resulting from e-H collisions. It was stated in Chapter II that energetic protons, formed from electron collisions with the undissociated molecules of the target beam, will have less than a 1.5% effect on the TIC signal as long as all thermal energy ions are collected. The validity of this statement may be seen from Figure (10), the signal saturation curve for e-H collisions. The TIC ion signal has saturated at an extraction field of about 2-3 volt/cm. Therefore all determinations of $n_1$ utilized extraction fields ≥ 3 volt/cm.

Since ion signal saturation for He*-H$_2$, He*-H and e-H collisions was obtained, the uncertainty in each of these signals was assumed to be solely statistical in nature.

The thermal ion contribution to the signal arising from e-H$_2$ collisions contains an uncertainty due to counting statistics but also a 1-2% error due to the
extrapolation techniques of Figure (5). Both of these
uncertainties have been included under statistical error
in Tables (1) and (2).

The efficiency $\epsilon$ with which the TIC counting system
detects an ion after extraction from the interaction region
is assumed to be independent of how the ion was formed,
because all ions, after extraction, are subjected to the
same accelerating voltages on the TIC electrodes. How-
ever, a variation in $\epsilon$ may occur if the gain of the
Johnston MM-1 particle multiplier is strongly dependent
upon the mass of the incident ion. The gain of the
multiplier in the crossed-beam system was not directly
measured for various ions, but previous experimental
evidence (Aitken et al., 1971; Rundel et al., 1969)
suggests that the MM-1 multiplier detects 5-10KeV ions
with about the same efficiency, regardless of ion mass.
Therefore, since chemiionization cross sections depend
on the ratio $S_*/S_0$, collection efficiency factors cancel
and need not be known.

(5) Ionization Cross Sections for e-Hydrogen Collisions

(a) Molecular Hydrogen
Cross sections for electron impact ionization of \( \text{H}_2 \) and \( \text{H} \) were obtained from a compilation of experimental data by Kieffer and Dunn (1966). This compilation includes data on both total ionization cross sections \( \sigma_{e}^{\text{tot}} \) and cross sections for the production of energetic ions, \( \sigma_{e}^{\text{diss}} \). The value obtained by Rapp and Englander-Golden (1965) was used for \( \sigma_{e}^{\text{tot}} \). The results of two other experiments (Schram et al., 1964; Harrison, 1956) lie within about 15% of this value, the value of Schram et al. lying lower and the value of Harrison higher. As a result, a 15% uncertainty was assigned to \( \sigma_{e}^{\text{tot}} \).

Rapp et al. (1965) also measured the cross section for production of ions having kinetic energies greater than 2.5eV. Referring to Figure (11), it is evident that dissociative ionization occurs almost entirely by transitions from the ground electronic state of \( \text{H}_2 \) to the repulsive \( ^2\Sigma_u^+ \) potential curve which, for Franck-Condon transitions, produces protons having kinetic energies greater than 2.5eV. Very low energy protons might be expected to arise from transitions to the repulsive part of the \( ^2\Sigma_g^+ \) curve for weak violations of the Franck-Condon principle (the dotted line transition of Figure 11), but
such violations never exceed about 1% of the total ionization (Dunn and Kieffer, 1963). Therefore the value of Rapp et al. for energetic proton production from e-H₂ collisions was used as \( \sigma_{e}^{\text{diss}} (2) \).

Since the value of \( \sigma_{e}^{\text{diss}} (2) \) is less than 4% of the value for \( \sigma_{e}^{\text{tot}} (2) \), the uncertainty in \( \sigma_{e}^{\text{tot}} (2) - \sigma_{e}^{\text{diss}} (2) \) was assumed to be equal to the uncertainty in \( \sigma_{e}^{\text{tot}} (2) \) alone.

It should be noted that the apparatus used by Rapp and his co-workers measured total ion current, so that his quoted cross sections actually represent the following sum:

\[
\sigma_{e}^{\text{tot}} = \sigma_{e1} + 2\sigma_{e2} + 3\sigma_{e3} + \cdots
\]

\[
= \sum_{i=1}^{\infty} \sigma_{ei}
\]

where \( i \) refers to the charge on the ion and \( \sigma_{ei} \) is the cross section for producing an ion with multiple charge \( i \). In contrast, the particle multipliers used in the present crossed-beam apparatus provide one count per ion regardless of its charge state, so that the appropriate ionization
cross section would be

\[ \sigma_e = \sum_{i=1}^{\infty} \sigma_{ei} \]

No correction for molecular hydrogen need be made however, since only a repulsive curve exists for \( \text{H}_2^{++} \) which results in rapid dissociation into \( \text{H}^+ + \text{H}^+ \), as shown in Figure (11).

(b) Atomic Hydrogen

Fite and Brackmann (1958) measured the cross section for \( e + \text{H} \rightarrow e + \text{H}^+ + e' \) and found excellent agreement with theoretical calculations using the Born approximation for electron energies \( \geq 300 \text{eV} \). It is therefore expected that their cross section value at \( E_e = 960 \text{eV} \) is accurate to within about 5%.

(C) Sources of Error Unique to He*-H Experiment

(1) Constant Mass Flow and Thermal Equilibrium

In Chapter II it was assumed in the derivation of the expression for \( \sigma_*(1) \) that constant mass flow applied at all furnace temperatures and that the gas inside the furnace had reached thermal equilibrium. For a gas which
does not dissociate in the temperature range of interest, equation (10) holds for e-target gas collisions:

\[ S_e = e \sigma \left( \frac{I_T}{v_T} \right) \frac{r_i}{e} \]

where the number density \( n_T \) has been written as the target beam intensity \( I_T \) divided by the average target atom speed \( v_T \). If thermal equilibrium with the furnace walls exists for the gas, equation (18) may be used to give

\[ S_e T_T^{1/2} = \text{constant} \times I_T \]

where \( T_T \) is the furnace temperature value obtained with the optical pyrometer and, if constant mass flow applies so that \( I_T \) is a constant,

\[ S_e T_T^{1/2} = \text{constant}. \tag{37} \]

It is therefore evident that if \( S_e T_T^{1/2} \) is a constant for all temperatures of interest, then constant mass flow and thermal equilibrium have been established.

The validity of equation (37) was established for \( H_2 \)
up to the temperature at which dissociation started, as discussed in Section A of this chapter. For higher temperatures there is indirect evidence which suggests that mass flow remains constant and thermal equilibrium exists. This evidence was obtained by replacing $H_2$ with He and recording $S_e T^{1/2}$ for various temperatures from 300°K to 2600°K. The signal $S_e$ was measured by both the TIC system and the mass spectrometer system. $S_e T^{1/2}$ was found to remain constant. Since the gas flow conditions for He and $H_2$ were similar, it is a good assumption that constant mass flow and thermal equilibrium existed for the target gas mixture of $H_2$ and H used in the chemiionization experiments.

(2) Furnace Ions and Electrons

The installation of a new tungsten tube for use as the hydrogen atom furnace created an undesirable effect at high operating temperatures: production of ions and electrons from impurities in the tungsten tube, some of which were directed toward the interaction region.

Appropriately directed furnace ions interfered with the TIC signal in the following manner. These ions,
modulated at the chopper wheel frequency, were able to enter the interaction region and subsequently be extracted into the particle multiplier as a spurious contribution to the signal arising from neutral beam interactions. This problem was eliminated by biasing the interaction region and surrounding electrodes slightly positive (+10 volts), so that the low energy furnace ions were not able to overcome the potential barrier.

Furnace electrons interfered with the mass spectrometer system. For this system the interaction region was maintained at +960 volts. Electrons which left the furnace travelling toward the interaction region were accelerated to an energy of 960eV, thereby attaining velocities greatly in excess of the target beam velocities. Ionization of the target beam particles by electron impact then occurred, and if the mass spectrometer was tuned to the H\(^+\) or H\(_2\) peak an anomalous signal was observed. However, the magnitude of this effect could be easily determined by shutting off the projectile beam. The remaining signal was then attributed to ions formed by collisions between furnace electrons and target atoms (and molecules).

After several hours of furnace operation at high
temperatures, these effects could no longer be observed.

(3) Modulation of Background $\text{H}_2$ Gas

In order to achieve the desired target beam intensity the target beam source chamber was ordinarily operated at about $1 \times 10^{-4}$ torr. As a result there was a net effusive flow of background gas toward the collision chamber, some of which coincided spatially with the target beam and therefore was modulated by the chopper wheel. The only effect on a molecular hydrogen target beam was to increase the apparent density of $\text{H}_2$. The determination of $\sigma_*(2)$ was not affected.

Much more serious effects arose when the furnace produced a partially dissociated beam, since the background species was no longer identical with the target beam species. The dissociation fraction measurement and the TIC ion signals $S_e$ and $S_*^*$ were each affected differently. Therefore use was made of a moveable shutter, which was mounted so that it could be rotated in front of the aperture and prevent the effusing beam from reaching the interaction region while at the same time permit the background gas to flow unimpeded. The desired signal $S$ was therefore
determined by subtracting the signal obtained with no shutter (designated by \( S' \)) from the signal obtained with shutter (designated by \( B \)).

The corrected expression for dissociation fraction then becomes

\[
D = 1 - \frac{(S'_H - B'_H)_{TH}}{(S'_H - B'_H)_{TC}}
\]

\[
= 1 - \frac{(S'_H \frac{1}{h})_{TH} \left(1 - \frac{B'_H}{S'_H} \frac{1}{h}\right)}{(S'_H \frac{1}{c})_{TC} \left(1 - \frac{B'_H}{S'_H} \frac{1}{c}\right)}
\]

The values of \( \frac{B'_H}{S'_H} \) for \( T = 300^\circ K, 1385^\circ K, \) and \( 2585^\circ K \) have been measured and lead to

\[
1 - \frac{B'_H}{S'_H} = \begin{cases} 
.99 \pm .5\% & \text{at } T = 300^\circ K \\
.97 \pm .5\% & \text{at } T = 1385^\circ K \\
.92 \pm 1.2\% & \text{at } T = 2585^\circ K
\end{cases}
\]

The values of \( D \) listed in Table (3) are the corrected values, using the results above. The percent error accompanying \( D \) in Table (4) includes the statistical error
quoted above and a 2% error associated with reading the furnace temperature with the optical pyrometer.

The TIC ion signal \( S_e \) may be written in terms of \( S'_e \), the signal with no shutter, and \( B_e \), the background signal, as

\[
S_e = S'_e - B_e = S'_e (1 - B_e/S'_e)
\]  

For a furnace temperature of 2585\textdegree K, \( B_e/S'_e \) was measured to be .073 \pm 20\%.

An expression similar to equation (40) holds for \( S'_e \), but the value of \( B_e/S'_e \) at \( T = 2585 \textdegree K \) was measured to be less than .01. This result was expected because (1) the chemiionization cross section for He\(^*\)-H\(_2\) collisions is much smaller than for He\(^*\)-H collisions and (2) the number density of H is significantly larger than the modulated background H\(_2\) density.

(4) HeH\(^{+}\) Production From He\(^*\)-H\(_2\) Collisions

The cross section ratios presented in Table (5), obtained in the manner described at the end of Chapter II,
are representative of He*–H collisions only if negligible HeH\(^+\) and H\(^+\) signal contributions arise from chemionization of the undissociated molecules in the target beam. Therefore preliminary investigations were made concerning the nature and abundance of ion products formed from He*–H\(_2\) reactions.

Table (7) shows the results obtained with the present apparatus as well as those reported by Hotop and Niehaus (1968) and Penton and Muschlitz (1968). Individual singlet and triplet contributions are reported only for the present results. Upper limits only could be placed upon HeH\(^+\) and H\(^+\) production cross sections due to the corresponding extremely low ion signals.

It is instructive to calculate the ratio \( S_\ast(\text{HeH}^+)/[S_\ast(\text{HeH}^+) + S_\ast(\text{H}^+)] \) which would result if the HeH\(^+\) signal was formed entirely by He*–H\(_2\) collisions, assuming \( D = 0.75 \) and equal collection efficiencies for HeH\(^+\) and H\(^+\):

\[
\frac{S_\ast(\text{HeH}^+)}{S_\ast(\text{HeH}^+) + S_\ast(\text{H}^+)} \approx \frac{0.1\sigma_\ast(2)n_2\lambda_2}{0.1\sigma_\ast(2)n_2\lambda_2 + \sigma_\ast(1)n_1\lambda_1} = \frac{1}{1 + \frac{\sigma_\ast(1)n_1\lambda_1}{0.1\sigma_\ast(2)n_2\lambda_2}}
\]

(41)
Using \( D = 0.75 \), equation (19) gives \( n_1/n_2 = 4.23 \). Table (6) gives \( l_1/l_2 = 1.4 \), and Tables (1) and (3) give \( \sigma_s(1)/\sigma_s(2) = 10 \) and \( \sigma_t(1)/\sigma_t(2) \approx 5.9 \). Therefore the final expression in equation (41) has a value \( \leq 0.003 \) for both He\((2^1S)\) and He\((2^3S)\). Comparison of this value with the experimentally determined value for \( \sigma_*(\text{HeH}^+)/[\sigma_*(\text{HeH}^+)+\sigma_*(\text{H}^+)] \) listed in Table (5) shows that He*-\(H_2\) collisions contribute less than 3% to the HeH\(^+\) signal. The total percent error listed in Table (5) includes this uncertainty.

(5) Mass Spectrometer Collection Efficiency

An experimental error would arise in the cross section ratios obtained with the mass spectrometer if ions of different masses were collected with different efficiencies. Individual collection efficiencies were not quantitatively measured, but indirect evidence supports the assumption that all ions were collected with approximately the same efficiency. Most ions are produced from He*-\(H\) collisions and are therefore expected to possess only thermal energies (Hotop et al., 1971). The 20 volt/cm electrostatic field applied across the interaction region will therefore extract all ions before they are able to travel any significant
distance from the desired extraction direction. As an added check, the magnitude of the extraction field was varied up to 50 volts/cm, but the cross section ratios remained unchanged.

The Johnston MM-1 particle multiplier, which served as the detector for the mass selected ions, is assumed to have a detection efficiency that is not dependent on incident ion mass (See pp.44 for a more complete discussion).

D. Comparison of Results With Theory and Other Experiments

(1) He*-H Collisions

(a) Theoretical Descriptions

Several calculations of cross sections for chemiionization from He*-H collisions have recently been reported (Fujii et al., 1970; Bell, 1970; Miller et al., 1972; Cohen and Lane, 1971; Cohen, 1972) and the results are summarized in Figure (12).

The calculations were based upon the concept of autoionization, which may be understood with the aid of Figure (13a). The electronic states corresponding to the A*-B system and the A-B*-e⁻ system may be represented by
potential curves $V_1$ and $V_2$, respectively. $V_1$ ($\infty$) represents the excitation energy of $A^*$ while $V_2$ ($\infty$) represents the ionization potential of $B$. Thus the initial electronic state of the $A^*-B$ system lies in a continuum of states belonging to the $A-B^+-e^-$ system. A finite probability then exists for the decay of the initial electronic state into a continuum electronic state degenerate with it, resulting in chemiionization.

The distinction between Penning and associative ionization is illustrated in Figure (13a). $A^*$ and $B$ approach each other from infinity with relative energy $E_K$. If there is a transition to the continuum at an internuclear separation $R_1$, a vertical transition to $V_2$ occurs. (The Franck-Condon principle is assumed to be valid. See, for example, Schmeltekopf et al., 1967.) The ejected electron carries off an energy $E_{el}^1$ so that the $A-B^+$ complex dissociates into $A + B^+$. However, if decay into the continuum occurs at $R_2$, the ejected electron carries off energy $E_{el}^2$, leaving the $A-B^+$ complex in a bound state. Therefore, when the $A-B^+$ complex is formed within the shaded portion of Figure (13), i.e. below the dissociation limit, associative ionization occurs. Otherwise, Penning
ionization results.

A theoretical calculation of chemiionization cross sections requires knowledge of the potential curves $V_1(R)$ and $V_2(R)$ and $\Gamma(R)$, the probability for decay from the initial discrete electronic state to the final continuum state.

Bell (1970) used an impact parameter formalism to find the ionization cross section for $\text{He}(2^3S)$-$\text{H}$ collisions. Fujii et al. (1970) used the method of Fano (1961), involving a complex adiabatic potential $W(R) = V(R) - i\Gamma(R)/2$ to obtain this cross section. Both Bell and Fujii et al. used single-configuration wavefunctions composed of product wavefunctions for the two isolated atoms. It is presently believed that the potential curves obtained using these simple wavefunctions are incorrect and that as a result the calculated cross sections of Bell and Fujii et al. may be incorrect. (Cohen, 1972).

Two recent large-scale configuration interaction (CI) calculations have been reported concerning chemiionization of $\text{H}$ by $\text{He}(2^3S)$. Miller and Schaefer (1970) used sophisticated wavefunctions to derive potential energy curves for $\text{He}^*\text{H}$ (321 configurations) and $\text{HeH}^+$ (51 configurations)
which are very different from the ones belonging to Fujii et al. Miller et al. (1972) then calculated the auto-
ionization probability and the cross sections for chemiioni-
zation of H by He(2\textsuperscript{3}S).

The second large-term CI calculation was performed by Cohen (1972) in an attempt to substantiate the results of Miller and his co-workers. Cohen constructed the He\textsuperscript{*}H potential curve using a stabilization method, whereby the number of configurations used for the wavefunctions was gradually increased until the potential curve ceased to change significantly. He found that stabilization occurred only after at least 14 (appropriately chosen) configurations were used, thus demonstrating that the potential curves of Bell and Fujii et al. were not stabilized but that the curves of Miller had achieved stabilization.

Cohen subsequently calculated the total ionization cross section for He(2\textsuperscript{3}S)-H using the curves and auto-
ionization probability of Miller et al. He then argued that the autoionization probability involving He(2\textsuperscript{1}S) collisions should be approximately the same as for He(2\textsuperscript{3}S) and, with the proper He(2\textsuperscript{1}S)-H potential curve, calculated $\sigma_{s}(l)$. 
It is evident from Figure (12) that the present experimental results concerning He*-H collisions are in very good agreement with the CI calculations of Miller et al. and Cohen. The agreement for $\sigma_s (l)$ is somewhat worse than for $\sigma_t (l)$ but this may be due to the assumption of equal autoionization probabilities for the He($2^1S$)-H and He($2^3S$)-H systems. The measured cross section ratio $\sigma_s (l)/\sigma_t (l)$ is in excellent agreement with the calculated value of Cohen. The calculated ratio of associative ionization to total ionization is somewhat smaller than the measured value but is still in good qualitative agreement.

(b) Other Experimental Results

The cross section for ionization of H by He($2^3S$) was measured in a flowing afterglow system by Shaw et al. (1971). The flowing afterglow apparatus is shown in Figure (14). High purity helium was flowed down the Pyrex tube at a bulk velocity of about $10^4$ cm/sec. Some of the helium was excited to the $2^3S$ and $2^1S$ states, but He($2^1S$) was rapidly converted to He($2^3S$) by reactions of the type $e + He(2^1S) \rightarrow e + He(2^3S) + .79$eV. The mean metastable density across the tube at a given distance down the
afterglow was measured by optical absorption of the 3889Å \((2^3S-3^3P)\) line produced in source \(S\).

The hydrogen atoms were produced by dissociation of \(H_2\) with a microwave discharge located in a side tube. These atoms were injected along the flow tube axis.

The loss rate of \(\text{He}(2^3S)\) due to reactions with the injected gas was then determined after taking into account the loss rates due to \(\text{He}(2^3S)-H_2\) reactions and diffusion to the tube walls. Since this loss rate was related to the rate constant \(k_l\) for \(\text{He}^*-H\) reactions, the chemiionization cross section was therefore obtained as \(\sigma_t(1)=k_l/\bar{V}_r\) where \(\bar{V}_r\) was the average relative velocity between metastable helium atoms and hydrogen.

Figure (12a) shows the value for \(\sigma_t(1)\) obtained by Shaw et al. (1971). Since the average relative velocity in the flowing afterglow system corresponded to 300°K gas temperatures, close agreement with the present value obtained at a much higher average relative velocity is not expected. However, the theoretical predictions for \(\sigma_t(1)\) at 300°K are substantially higher than the flowing afterglow result, which may indicate a possible error in the work of Shaw et al.
The only other experiment involving chemiionization of H by He* that has been reported is the work of Hotop et al. (1971). In this experiment a beam of helium metastables, formed in a helium discharge, was crossed by a beam of H₂ which was partially dissociated using an rf discharge. Product electrons resulting from He*-H collisions were analyzed by a retarding potential electron spectrometer.

An estimate for the cross section ratio \( \frac{\sigma_e^{'(i)}}{\sigma_t^{'(i)}} \) was then obtained from the integral electron stopping curves corresponding to He(2¹S)-H and He(2³S)-H reactions:

\[
\frac{\sigma_s(1)}{\sigma_t(1)} = \frac{S_s(1)}{S_t(1)} \frac{i_t}{i_s}
\]

(42)

where \( S_x(1) \) represents the height of the integral stopping curve. Hotop et al. did not possess direct information concerning the value of \( \frac{i_t}{i_s} \), so they performed an auxiliary experiment involving He*-Ar reactions and assumed that the ratio \( \frac{\sigma_s(Ar)}{\sigma_t(Ar)} \) was known from previous work (Hotop et al., 1969). They therefore obtained

\[
\frac{i_t}{i_s} = \frac{\sigma_s(Ar)}{\sigma_t(Ar)} \frac{S_s(Ar)}{S_t(Ar)} = 1.15 \frac{S_t(Ar)}{S_s(Ar)}
\]

(43)
Substituting equation (43) into (42) gave the desired value: \( \sigma_s(1)/\sigma_t(1) = 1.5 \pm 50\% \). This value is significantly smaller than the theoretical calculation of Cohen (1972). Better agreement would result, however, if the value of \( \sigma_s(\text{Ar})/\sigma_t(\text{Ar}) = 1.34 \), obtained by the present crossed-beam apparatus, had been used (Howard et al., 1972), which would yield \( \sigma_s(1)/\sigma_t(1) = 1.8 \).

(2) He*-H\(_2\) Collisions

(a) Theoretical Description

The total chemiionization cross section for He\( (2^3\text{S})-\text{H}_2 \) collisions has recently been calculated by Cohen (1972) using a CI calculation similar to the one used for He\( (2^3\text{S})-\text{H} \) analysis. Table (8) and Figure (15) show a comparison between the measured and calculated values of \( \sigma_*(2) \). The calculated value is an order of magnitude smaller than the experimentally determined values. At present the theoretical calculations are being reanalyzed, since it is possible that the autoionization probability should be larger at large separations between He* and H\(_2\) (Cohen, private communication).
(b) Other Experimental Results

Several values for $\sigma_*(2)$ have been previously reported, and these values are listed in Table (8). The value of $\sigma_s(2)$ obtained with the present apparatus is in good agreement with the flowing afterglow experiment of Schmeltekopf and Fehsenfeld (1970), but the beam-gas cell experiment of Sholette and Muschlitz (1962) is significantly lower. However, Sholette and Muschlitz calibrated their metastable beam intensity by assuming that the secondary electron ejection coefficients $\gamma_s$ and $\gamma_t$ were both equal to .29, the value obtained for $\gamma_t$ by Stebbings (1957) for a contaminated gold surface. Since the value of $\gamma_*$ is believed to be dependent on the nature of the detecting surface (Rundel and Stebbings, 1972), the cross section values of Sholette and Muschlitz are suspect.

Agreement for the value of $\sigma_t(2)$ among the several experiments is poor. In addition to the aforementioned questionable assumptions made by Sholette and Muschlitz, the stationary afterglow results of Benton et al. (1962) were obtained without proper consideration of He$(2^1S)$-to-He$(2^3S)$ conversion by collisions with slow electrons. In addition, since the $H_2$ was exposed to the discharge,
a fraction of it may have been dissociated, excited or ionized, which would have interfered with the determination of $\sigma_*(2)$. As yet there is no obvious reason for the discrepancy between the flowing afterglow results and the present results.
CONCLUSION

Chemionization cross sections were obtained for He\(^{2\text{S}}\text{S,2}\text{S}\)-H\(_2\) and He\(^{2\text{S}}\text{S,2}\text{S}\)-H collisions. Total ionization cross sections were determined for both types of collisions utilizing the TIC (Total Ion Collector) system shown in Figure (2a). The mass spectrometer system of Figure (2b) was then used in the determination of the cross section for HeH\(^+\) production relative to total ion production for He*-H\(_2\) and He*-H collisions. A summary of experimental results is presented in Table (9).

There is good agreement between the present value of \(\sigma_\text{s}(2)\) and the best previously determined (flowing afterglow) value. However a discrepancy exists concerning the value of \(\sigma_\text{t}(2)\). Since great care was taken in obtaining the present value, it is believed that a systematic error may have been made during the flowing afterglow experiment.

The cross section values \(\sigma_\text{s}(1)\) and \(\sigma_\text{t}(1)\), appropriate to He\(^{2\text{S}}\text{S,2}\text{S}\)-H collisions, are in excellent agreement with the most recent theoretical calculations.

Cross sections for HeH\(^+\) production in He*-H\(_2\) and He*-H
collisions are several times smaller than the cross sections for penning ion production in these collisions, in good qualitative agreement with previous experiments and recent theoretical calculations.

The speed distribution for the beam of metastable helium atoms was recently measured using a time-of-flight technique. The electron beam, which normally travels collinearly with the helium beam in the excitation region in a continuous fashion, was pulsed at a frequency of 100 Hz with a pulse duration of 40 μsec. A Johnston Labs. MM-1 particle multiplier, positioned about three meters downstream from the excitation region, monitored the metastable flux as a function of arrival time after the end of each pulse. A plot of multiplier signal versus arrival time yielded the speed distribution of the metastable beam.

The resulting average speed for the metastable atoms was found to be \(1.866 \times 10^5\) cm/sec. This value leads to the following path length ratios:

\[
\frac{\lambda_e}{\lambda_H} = 0.224 \quad \text{at} \quad T = 2585 \, ^\circ\text{K}
\]

\[
\frac{\lambda_e}{\lambda_{H_2}} = 0.707 \quad \text{at} \quad T = 300 \, ^\circ\text{K}
\]
If these ratios are used in equations ( ) and ( ), revised cross section values are obtained, which are shown in Table 10. These revised values are 38.3% higher for He*–H collisions and 25.4% higher for He*–H₂ collisions. All cross section ratios remain unchanged.

Full details concerning the measurement of the metastable atom speed distribution will shortly be published.
REFERENCES


Figure 2a: Total Ion Collector (TIC) System
Figure 3: Hydrogen Furnace
Typical Ion Collection Curve For e-H\textsubscript{2} Collisions

Figure 5
Figure 6
Sweep Rate of Ions Across Mass Spectrometer Exit Plane

\[ y^2 + (\Delta r)^2 - 2y\Delta r \cdot \cos \alpha - r_2^2 = 0 \]

\[ y = \Delta r \cdot \cos \alpha + r_2 \ \text{(neglecting terms of } \Theta (\Delta r^2) \text{)} \]

\[ \Delta y = r_1 - y = r_2 + \Delta r - y \]

\[ = \Delta r (1 - \cos \alpha) \]

\[ \frac{\Delta y}{\Delta r} = 1 - \cos \alpha = \frac{\Delta y}{\Delta B} \cdot \frac{\Delta B}{\Delta r} \]

or \[ \frac{\Delta y}{\Delta B} = (1 - \cos \alpha) \frac{\Delta r}{\Delta B} \]

But \( r = \text{constant} / B \) and \( \frac{\Delta r}{\Delta B} = - r / B \)

Therefore

\[ \frac{\Delta y}{\Delta B} = -r (1 - \cos \alpha) / B = \text{constant} / B \]
Actual TIC Collection Curve For e-H₂ Collisions

Figure 7
Photon Attenuation Curve

Figure 8
Signal Saturation Curve For He\(^*\) - H Collisions

Figure 9
Signal Saturation Curve For e-H Collisions

Figure 10
Fig. 13.2. Potential energy curves for higher energy states of \( \text{H}_2^+ \).

(from Massey, 1969)

Figure 11
Circles: Fujii et al., 1970

Dashed Line: Cohen and Lane, 1970

Solid Line: Miller et al., 1972
Cohen, 1972

Cross: Bell, 1970

Total Ionization Cross Section Data For
He(2^3S)-H Collisions
Figure 12b

Circles: Fujii et al., 1970

Dashed Line: Cohen and Lane, 1970

Solid Line: Cohen, 1972. $\Gamma_s(R) = \Gamma_t(R)$ was assumed.

Total Ionization Cross Section Data For He(2\textsuperscript{1}S)-H Collisions
Upper Curve: Cohen, 1972 $\Gamma_s(R) = \Gamma_t(R)$ was assumed.

Lower Curve: Cohen, 1972 $\Gamma_s(R)$ was assumed to be equal to the singlet value obtained by Fujii et al., 1970.

Singlet-to-Triplet Total Ionization Cross Section Ratio
Figure 12d

Ratio of Associative to Total Ionization Cross Sections For $\text{He}(2^3S)$–H Collisions

Theory: Miller et al., 1972

Present Work
Figure 13.

Schematic of Potential Curves for A*-B and A-B-e Systems
Figure 14

Flowing Afterglow Apparatus of Shaw et al., 1970.
Upper Curve: Cohen, 1972. Direction of $\hat{V}_* \text{ is perpendicular to a straight line joining centers of the hydrogen nuclei.}$

Lower Curve: Cohen, 1972. Direction of $\hat{V}_* \text{ is parallel to a line joining centers of the hydrogen nuclei.}$

Total Ionization Cross Section Data For He($^3S$)-H$_2$ Collisions.
Table 1

Total Ionization Cross Section Results For He* -H₂ Collisions

<table>
<thead>
<tr>
<th>Run</th>
<th>P_H₂ (torr)</th>
<th>( \sigma_s (\AA^2) \pm \Delta_s )</th>
<th>( \sigma_t (\AA^2) \pm \Delta_t )</th>
<th>( \vec{\sigma}_s / \vec{\sigma}_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.02x10^-4</td>
<td>2.97±.34</td>
<td>3.38±.23</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.02x10^-4</td>
<td>2.09±.41</td>
<td>2.93±.22</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.11x10^-4</td>
<td>2.71±.14</td>
<td>3.01±.09</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.11x10^-4</td>
<td>2.54±.12</td>
<td>2.98±.07</td>
<td></td>
</tr>
<tr>
<td>AVG</td>
<td>1.11x10^-4</td>
<td>2.62±.09 (±3.25%)</td>
<td>3.02±.05 (±1.75%)</td>
<td>0.87</td>
</tr>
</tbody>
</table>

NOTE: The following values were used in determining \( \sigma_s \) and \( \sigma_t \):

\( \gamma_s = 0.49 \)

\( \gamma_t = 0.74 \)

\( \lambda_e / \lambda_{H_2} = 0.565 \)

\( \sigma_e^{\text{tot}} (2) = 0.248 \times 10^{-16} \text{ cm}^2 \)

\( \sigma_e^{\text{diss}} (2) = 0.065 \times 10^{-16} \text{ cm}^2 \)

\( E_{el n} = 960 \text{ ev} \)
Table 2

<table>
<thead>
<tr>
<th>Source of error</th>
<th>Percent error</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{\psi}_s(2)$</td>
<td>$\bar{\psi}_t(2)$</td>
<td>$\bar{\psi}_s/\bar{\psi}_t$</td>
<td></td>
</tr>
<tr>
<td>Statistical</td>
<td>3.25</td>
<td>1.75</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>$\nabla_v^{tot}(2) - \nabla_v^{diss}(2)$</td>
<td>15</td>
<td>15</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$i_e$</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$i_*$</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$\lambda_e/\lambda_{H_2}$</td>
<td>15</td>
<td>15</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\gamma_*$</td>
<td>12</td>
<td>12</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>$\approx 25$</td>
<td>$\approx 25$</td>
<td>$\approx 10$</td>
<td></td>
</tr>
</tbody>
</table>

NOTE: Total % = $\left[ \sum_{i} (\%)^2 \right]^{1/2}$
Table 3

Total Ionization Cross Section Results For He* - H Collisions

<table>
<thead>
<tr>
<th>Run</th>
<th>$\frac{P_H}{T_{exp}}(R)$</th>
<th>$D^{300}$</th>
<th>$D^{\neq 1375}$</th>
<th>$D^{AVG}$</th>
<th>$\sigma_s(\text{Å}^2)_{\text{stat}}$</th>
<th>$\sigma_t(\text{Å}^2)_{\text{stat}}$</th>
<th>$\sigma_s/\sigma_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0/2590</td>
<td>.82</td>
<td>.82</td>
<td>.82</td>
<td>27.77±1.62</td>
<td>17.66±.66</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>≥2.0/2610</td>
<td>.54</td>
<td>.58</td>
<td>.56</td>
<td>27.07±1.73</td>
<td>18.23±1.09</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.0/2630</td>
<td>.83</td>
<td>.81</td>
<td>.82</td>
<td>25.45±1.90</td>
<td>16.50±.83</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.0/2600</td>
<td>.82</td>
<td>.81</td>
<td>.815</td>
<td>23.97±1.92</td>
<td>18.49±1.24</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.0/2535</td>
<td>.77</td>
<td>.75</td>
<td>.76</td>
<td>24.51±1.52</td>
<td>17.23±.83</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.0/2515</td>
<td>.70</td>
<td>.69</td>
<td>.695</td>
<td>27.16±1.36</td>
<td>17.77±.66</td>
<td></td>
</tr>
<tr>
<td>AVG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.14±.67 (±2.56%)</td>
<td>17.64±.33 (±1.87%)</td>
<td>1.48</td>
</tr>
</tbody>
</table>

NOTE: The following values were used in determining $\sigma_s$ and $\sigma_t$:

- $\gamma_s = 0.49$  
- $\ell_e/\ell_H = 0.162$  
- $\gamma_t = 0.74$  
- $\ell_{H_2}/\ell_H = 0.715$  
- $\sigma_{tot} = 0.248 \times 10^{-16} \text{cm}^2$  
- $\sigma_e(2) = 0.112 \times 10^{-16} \text{cm}^2$  
- $E_{eln} = 960 \text{ ev}$
Table 4

<table>
<thead>
<tr>
<th>Source of Error</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \sigma_s(1) )</td>
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<tr>
<td>Statistical</td>
<td>2.6</td>
</tr>
<tr>
<td>( \sigma_e^{\text{tot}} )</td>
<td>15</td>
</tr>
<tr>
<td>( \sigma_e(1) )</td>
<td>5</td>
</tr>
<tr>
<td>( i_e )</td>
<td>2</td>
</tr>
<tr>
<td>( i_e^* )</td>
<td>1</td>
</tr>
<tr>
<td>( \lambda_e/\lambda_H )</td>
<td>20</td>
</tr>
<tr>
<td>( \lambda_H^2/\lambda_H )</td>
<td>-</td>
</tr>
<tr>
<td>( \gamma_* )</td>
<td>12</td>
</tr>
<tr>
<td>D</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>( \sim 25 )</td>
</tr>
</tbody>
</table>

**NOTE:**

\[
\text{Total } \% = \left[ \sum \left( \%_i \right)^2 \right]^{1/2}
\]
Table 5

Cross Section Ratios Obtained With Mass Spectrometer System

<table>
<thead>
<tr>
<th>Run</th>
<th>$\sigma_{<em>}(\text{HeH}^+)/\sigma_{</em>}(1)$</th>
<th>$\sigma_s(1)/\sigma_t(1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Singlet</td>
<td>Triplet</td>
</tr>
<tr>
<td>1</td>
<td>0.085</td>
<td>0.140</td>
</tr>
<tr>
<td>2</td>
<td>0.105</td>
<td>0.125</td>
</tr>
<tr>
<td>3</td>
<td>0.105</td>
<td>0.145</td>
</tr>
<tr>
<td>4</td>
<td>0.100</td>
<td>0.140</td>
</tr>
<tr>
<td>AVG</td>
<td>$0.10 \pm (20%)$</td>
<td>$0.14 \pm (15%)$</td>
</tr>
</tbody>
</table>

NOTE: Percent uncertainties are listed in parentheses.
Table 6

Path Length Ratios

<table>
<thead>
<tr>
<th>Metastable Distribution Function</th>
<th>Target</th>
<th>$T (^{0}K)$</th>
<th>$\ell_e/\ell$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f^*_v dv = v^2 e^{-mv^2/2kT} dv$</td>
<td>$H_2$</td>
<td>300</td>
<td>.564</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2585</td>
<td>.227</td>
</tr>
<tr>
<td>$f^*_v dv = v e^{-mv^2/2kT} dv$</td>
<td>$H$</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2585</td>
<td>.162</td>
</tr>
<tr>
<td></td>
<td>$H_2$</td>
<td>300</td>
<td>.465</td>
</tr>
<tr>
<td></td>
<td>2585</td>
<td>.179</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H$</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2585</td>
<td>.127</td>
<td></td>
</tr>
</tbody>
</table>
Table 7

<table>
<thead>
<tr>
<th>Reference</th>
<th>( \sigma_<em>(\text{HeH}^+)/[\sigma_</em>(\text{HeH}^+) + \sigma_*(\text{H}_2^+)] )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Singlet</td>
</tr>
</tbody>
</table>
| Present Results†                                | .11\(^{\pm}20\)%  
| Hotop and Niehaus (1968)                        | .10\(^{\pm}15\)%                                                                |
| Penton and Muschlitz (1968)                     | .10 \(\{\text{Mixed Beam}\} \)                                                |
|                                                 | Triplet                                                                  |

† Neglects a \( \leq 1\% \) contribution from \( \text{H}^+ \) and \( \leq 5\% \) from \( \text{HeH}_2^+ \).

† Includes a 2\% contribution from \( \text{HeH}_2^+ \).
Table 8

Comparison of Total Ionization Cross Section Values
For He$^+$-H$_2$ Collisions

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\sigma_s(2)$</th>
<th>$\sigma_t(2)$</th>
<th>$\sigma_s(2)/\sigma_t(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Results</td>
<td>2.6$^{\pm}$25%</td>
<td>3.0$^{\pm}$25%</td>
<td>.87$^{\pm}$10%</td>
</tr>
<tr>
<td>Sholette and Muschitz (1962)</td>
<td>.94$^{\pm}$10-25%</td>
<td>1.4$^{\pm}$10-25%</td>
<td>.67</td>
</tr>
<tr>
<td>Benton et al. (1962)</td>
<td>-</td>
<td>6.0$^{\pm}$20-50%</td>
<td>-</td>
</tr>
<tr>
<td>Bolden et al. (1970)</td>
<td>-</td>
<td>1.5$^{\pm}$20%</td>
<td>-</td>
</tr>
<tr>
<td>Schmeltekopf and Feisenfeld (1970)</td>
<td>2.3$^{\pm}$30%</td>
<td>1.5$^{\pm}$30%</td>
<td>1.5$^{\pm}$10%</td>
</tr>
<tr>
<td>Dunning and Smith (1970)</td>
<td>-</td>
<td>-</td>
<td>.67$^{\pm}$25%</td>
</tr>
<tr>
<td>Hotop et al. (1969)</td>
<td>-</td>
<td>-</td>
<td>.57</td>
</tr>
<tr>
<td>Cohen (1972)</td>
<td>-</td>
<td>.05-.10</td>
<td>-</td>
</tr>
</tbody>
</table>

All cross sections are in units of Å$^2$. 
### Table 9

**Summary of Results**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\sigma_*(2)$</th>
<th>$\sigma_*(H_2^+)$</th>
<th>$\sigma_*(HeH^+)$</th>
<th>$\sigma_<em>(HeH^+)/\sigma_</em>(2)$</th>
<th>$\sigma_s(2)/\sigma_s(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He($^1S$)$-H_2$</td>
<td>2.6 (75%)</td>
<td>2.31 (30%)</td>
<td>0.29 (30%)</td>
<td>0.11 (20%)</td>
<td>TIC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mass Spec</td>
</tr>
<tr>
<td>He($^3S$)$-H_2$</td>
<td>3.0 (25%)</td>
<td>2.76 (30%)</td>
<td>0.24 (30%)</td>
<td>0.08 (15%)</td>
<td>0.87 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.83 (20%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\sigma_*(1)$</th>
<th>$\sigma_*(H^+)$</th>
<th>$\sigma_*(HeH^+)$</th>
<th>$\sigma_<em>(HeH^+)/\sigma_</em>(1)$</th>
<th>$\sigma_s(1)/\sigma_s(1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He($^1S$)$-H$</td>
<td>26.14 (25%)</td>
<td>23.53 (30%)</td>
<td>2.61 (30%)</td>
<td>0.10 (20%)</td>
<td>TIC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mass Spec</td>
</tr>
<tr>
<td>He($^3S$)$-H$</td>
<td>17.64 (25%)</td>
<td>15.17 (30%)</td>
<td>2.47 (30%)</td>
<td>0.14 (15%)</td>
<td>1.48 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.63 (20%)</td>
</tr>
</tbody>
</table>

**Note:** All cross section values are in units of $\AA^2$.

Percent error is given in parentheses next to each value.
Table 10
Revised Summary of Results

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\sigma_*(2)$</th>
<th>$\sigma_*(H_2^+)$</th>
<th>$\sigma_*(HeH^+)$</th>
<th>$\sigma_<em>(HeH^+)/\sigma_</em>(2)$</th>
<th>$\sigma_s(2)/\sigma_t(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He($^1S$)-H$_2$</td>
<td>3.26 (25%)</td>
<td>2.90 (30%)</td>
<td>0.36 (30%)</td>
<td>0.14 (20%)</td>
<td>TIC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mass Spec</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.87 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.88 (20%)</td>
</tr>
<tr>
<td>He($^3S$)-H$_2$</td>
<td>3.76 (25%)</td>
<td>3.46 (30%)</td>
<td>0.30 (30%)</td>
<td>0.10 (15%)</td>
<td>TIC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mass Spec</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.48 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.63 (20%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\sigma_*(1)$</th>
<th>$\sigma_*(H^+)$</th>
<th>$\sigma_*(HeH^+)$</th>
<th>$\sigma_<em>(HeH^+)/\sigma_</em>(1)$</th>
<th>$\sigma_s(1)/\sigma_t(1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He($^1S$)-H</td>
<td>36.15 (25%)</td>
<td>32.54 (30%)</td>
<td>3.61 (30%)</td>
<td>0.14 (20%)</td>
<td>TIC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>Mass Spec</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.48 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.63 (20%)</td>
</tr>
<tr>
<td>He($^3S$)-H</td>
<td>24.40 (25%)</td>
<td>20.98 (30%)</td>
<td>3.42 (30%)</td>
<td>0.19 (15%)</td>
<td>TIC</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
<td>Mass Spec</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>1.48 (10%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.63 (20%)</td>
</tr>
</tbody>
</table>

NOTE: All cross section values are in units of Å$^2$.

percent error is given in parentheses next to each value.
ACKNOWLEDGEMENTS

I wish to thank my thesis advisor, Ronald Stebbings, for all the help he has given me throughout this project. I also wish to thank Bob Rundel for his help during the project and for the sincere interest that he has shown in my education. I would also like to thank John Riola, not only for his help on "our" project, but also for his friendship.

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