**Spectroscopic Measurement of $H(1S)$ and $H2(v'',J'')$
in an H^+ Ion Source Plasma***

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Ph.D. Thesis

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MASTER

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Abstract

Low-pressure H_2 discharges have been used for some time as sources of H^- ions. These discharges contain many different species of particles which interact with each other and with the walls of the discharge chamber. Models exist that predict the populations of the various species for given macroscopic discharge parameters. However, many of the cross sections and wall catalyzation coefficients are unknown or somewhat uncertain. Therefore, it is of interest to measure the populations of as many of these species as possible, in order to determine the validity of the models. These models predict that H^- is created predominantly by the two-step process of vibrational excitation of hydrogen molecules followed by dissociative attachment of slow electrons to these vibrationally-excited hydrogen molecules. Many different collisional processes must be included in the models to explain the dependence of the various populations upon macroscopic parameters.

This work presents results of spectroscopic measurements of the density and translational temperature of hydrogen atoms and of specific rotationally-

and vibrationally-excited states of electronic ground-state H_2 , in a discharge optimized for H^- production, as well as conventional measurements of the various charged species within the plasma. The spectroscopic measurements are performed directly by narrowband, single-photon absorption in the vacuum ultraviolet. The highest vibrational and rotational quantum numbers observed are 8 and 15 respectively. The results for the atomic concentration are in agreement with conventional models. The inferred atom recombination coefficient can vary with wall conditions, but is reproducible and has a value of approximately 0.6 on tungsten-covered copper walls for normal operating conditions. The experimental results on the H_2 vibrational distribution are in good agreement with the results of a model similar to those found in the literature. The vibrational distribution is found to be characterized by a temperature and to be primarily excited by the thermal electrons. The wall relaxation rates of the vibrationally-excited molecules correspond to 10–40 wall collisions. Finally, the H^- density was measured and compared to a model that uses the neutral species measurements as input. The results are consistent, but the role played by the superthermally populated molecules of high rotational excitation is still ambiguous. Suggestions for future research are given.

Dedication

To my parents, Barbara Carson and Leo Stutzin, for bringing me up to be the fabulous human being I am today; to my sister, Candace, for giving me the motivation to leave home, go to college and get a real education; and to Maureen, for pointing out the fact that physicists are not gods, apart from the rest of sweltering humanity.

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Glossary

Symbol	Definition
I_d	discharge current
V_d	discharge voltage (at cathode)
P_d	discharge filling pressure
n_e	electron density
$n_{e,f}$	primary electron density
n^-	H^- density
n^+	total positive ion density
kT_e	electron temperature
$kT_{e,f}$	primary electron temperature
kT_i	ion temperature
n_H	atomic hydrogen density
n_{H_2}	molecular hydrogen density
v''	vibrational quantum number (lower electronic state)
v'	vibrational quantum number (upper electronic state)
J''	rotational quantum number (lower electronic state)
J'	rotational quantum number (upper electronic state)
Δv	$v' - v''$
ΔJ	$J' - J''$
$n(v'')$	density of molecules in given vibrational level
$n(v'', J'')$	density of molecules in given rovibrational level
kT_H	translational temperature of atomic hydrogen
kT_{H_2}	translational temperature of molecular hydrogen
$kT(v'', J'')$	translational temperature of given rovibrational H_2 level

Symbol	Definition
Π	line density (integrated path density)
l	path length
r	radius
R	internuclear separation
$\ln \Lambda$	Coulomb Logarithm
μ	magnetic moment
α	factor that n_{H_2} is reduced by when discharge is on
γ	atom recombination coefficient (per bounce)
γ_{recom}	atom recombination rate
λ	wavelength
λ_0	center wavelength for a given transition
$\Delta\lambda$	generic 1/e half-width in wavelength
λ_{vuv}	center wavelength of VUV probe beam
$\Delta\lambda_{vuv}$	1/e half-width of VUV probe beam, in wavelength
ω_1	angular frequency of (doubled) laser beam from dye laser #1
ω_2	angular frequency of laser beam from dye laser #2
ω_{vuv}	angular frequency of VUV probe beam (at center)
$T(\lambda)$	wavelength-dependent transmission of plasma
$a(\lambda)$	wavelength-dependent absorbance of plasma
A	absorbance of plasma, integrated over wavelength in the neighborhood of a specific transition
$I_{on(off)}$	normalized VUV probe beam signal (discharge is on or off)
f	oscillator strength
r_e	classical electron radius
$\sigma, \sigma(\lambda)$	generic symbol for a given cross section

Symbol	Definition
G	integral of σ over wavelength for a particular photon absorption transition
V_{probe}	voltage of Langmuir probe
I_{probe}	current drawn by Langmuir probe
I_e	electron current to Langmuir probe
$I_{e,\text{sat}}$	saturation electron current to probe (at plasma potential)
V_p	plasma space potential
ϵ	electron kinetic energy
$n_d(\epsilon)$	electron density per unit interval of kinetic energy
S	effective collecting area of Langmuir probe
m	mass of electron
e	unsigned electron charge
M	mass of heavy particle
V_a	DC voltage used in Druyvesteyn method
V_b	AC voltage used in Druyvesteyn method (peak to center)
ω_b	angular frequency of AC voltage used in Druyvesteyn method
$I_{2\omega}$	amplitude (peak to center) of Fourier component at $2\omega_b$ of Langmuir probe electron current
F	photon flux per unit area per pulse
V_{accel}	extraction voltage for positive or negative ions
K_{ions}	total production rate of ions in discharge chamber
Γ_{extract}	extracted H^+ current

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Chapter I

Overview of Physics Relevant for H^+ Ion Sources

A. General Discharge Physics

Partially-ionized plasmas are common in nature and in the laboratory. Planetary and solar upper atmospheres are natural examples of gases that have partial degrees of ionization. On earth, partially-ionized plasmas are found in ion sources, many types of lasers, various forms of lighting, and various laboratory equipment, such as ion gauges and ion pumps. A plasma sustained by man-made external electric fields is usually termed a discharge. The simple fluorescent light is a good example of a weakly-ionized discharge. CW gas discharge lasers, such as the helium-neon laser, have similar discharge characteristics. Partially-ionized gases usually have electromagnetic properties that are primarily influenced by the ionization that exists in the medium, as is well known. They also have kinetic properties that are strongly influenced by the charged particles. There are two main reasons for this effect. First, charged particles are generally more likely than neutral particles to interact with other particles in the discharge, just as free-radical neutrals, such as hydrogen atoms, are more likely to interact with other species than a stable particle, such as a hydrogen molecule. Also, charged particles can receive energy from electric fields that is far in excess of the thermal energy, which cannot be more than 0.3 eV because any solid container would melt. This increased kinetic energy leads to faster reaction rates because a) more reaction channels are open, b) the cross sections for many processes peak far above threshold, and c) the reactants have larger velocities.

A key issue for the understanding of any discharge is the dynamics of energy transfer from the charged species to the neutral species and from the

discharge as a whole to the outside world. In almost all discharges, the power that enters the discharge comes from an electric field that gives energy directly to the electrons and ions that subsequently excite the neutral species by various mechanisms, but mostly via direct collisional excitation. The power that leaves the discharge usually leaves in the form of photons or in the form of kinetic and internal energy of charged particles that collide with a solid surface, thereby transforming the energy into heat. The electrons usually have most of the kinetic energy in the discharge, for several reasons. One reason is that electrons have a very low transfer rate of energy to neutrals by elastic collisions because of the large mass imbalance, something that is not true for ions. Also, in a given electric field, electrons have a higher acceleration and thus regain their energy after a collision more quickly. Finally, in some types of man-made discharges, some of the electrons are born at high potential energy relative to the body of the plasma. Most energy lost by electrons during binary collisions is lost during inelastic collisions:

where X refers to the (undefined) gas atom or molecule and * indicates some type of internal energy, such as rotational, vibrational or electronic excitation, or the energy of ionization or dissociation. The energy transfer per inelastic collision, usually in the range of 5–20 eV, is much larger than the energy loss per elastic collision, which is ~0.01 eV for a 20 eV electron incident on a hydrogen molecule. The cross section for elastic collisions is larger than for inelastic collisions, but only by factors of 10–100, so inelastic collisions still dominate, except at very low energies, ≤ 1 eV or so, where the latter are not allowed on energetic grounds. An electron will have a much higher speed

than an ion of the same energy, so that the rate of collisions is greater for electrons than ions, all else being the same. These properties are typical of most discharges.

The presence of neutral particles almost always has a strong, albeit indirect, influence on discharge characteristics. For example, in the positive-hydrogen-ion sources developed at LBL as part of the fusion-energy neutral-beam program, it was desired to have the fraction of atomic ions as close to unity as possible.¹ The fraction of atomic ions is given by the degree of dissociation of the hydrogen, which is in turn sensitive to many effects: the electron energy distribution function (EEDF), the distribution of the H₂ molecules within the various vibration levels of the ground electronic state, and the rate of surface-catalyzed recombination of atoms to molecules. Only the first item in the list, the EEDF, is a true 'plasma' effect, and even it is affected strongly by the neutral species in the discharge. The overall point is that the various species in a discharge interact with each other in a complicated manner that is often indirect and yet, at the same time, very important.

Static or quasi-static discharges can have several different types of mechanisms for sustaining the density of charged particles. One can divide discharges into two types, those in which there is no outside source of charged particles and those in which there is a mechanism for introducing charged particles into the discharge. In the former case, each electron created by an ionization event creates exactly one new electron on the average, otherwise the plasma would experience either an increase or decrease in density. RF and microwave are examples of this type. In the latter case, there are several different mechanisms for producing charged particles by external means. One technique is photoionization induced by externally-produced radiation. If a photon has enough energy to ionize a molecule or atom, there is almost always

a non-zero chance that it will:

although photoionization cross sections tend to be relatively low, in the range of 10^{-17} cm^2 or less. Also, the ionization energies of hydrogen and the noble gases are greater than 10 eV. There are few DC light sources, coherent or otherwise, that have much power in this spectral range. However, Lyman-beta lamps exist that employ cooled LiF windows.² A moderate plasma would be created by exposing the output of this lamp to a chamber filled with xenon. Mercury lamps emit copious amounts of photons at 2536 Å. Light of this wavelength can ionize cesium, for example.

Another method to sustain the charged particle density is to inject them from outside the discharge, a method employed for the data this thesis concerns. It is not generally practical to inject ions, as they must usually be created by another discharge. Free electrons can be created by thermionic emission by a hot surface, however. In this process, some of the electrons in the high energy tail of the EEDF of the solid material have enough energy to overcome the work function and are emitted into free space. The current density of emitted electrons is extremely small at thermal temperatures, but can become large at high temperatures ($\sim 3000 \text{ }^{\circ}\text{K}$ for tungsten). These electrons must be helped along by an electric field that pulls them away from the solid material if any reasonable current density is to be achieved, thus these electron emitters are always biased negative with respect to their surroundings. In many realistic cases, the current is limited by the space charge rather than by the thermionic emission. A third technique that is related to both of the above methods is the use of the photoelectric effect to free electrons

from solid conductors, and to let them 'fall' into the plasma by appropriate electric fields. This process undoubtedly assists true thermionic emission in most hot-cathode discharges because a typical plasma produces a prodigious amount of radiation in the UV and VUV, where the quantum efficiency of metals is highest. A simple calculation shows that photo-enhanced thermionic emission is a small fraction of the total thermionic emission for this work. In any case, there is no practical difference between the two 'types' of electrons. Photoemission can be important in cold-cathode discharges however. Lastly, secondary electrons generated by ion impact at the cathode will be pulled into the plasma by the cathode sheath. This effect is quite important in cold-cathode discharges, especially those operated on the left-hand side of the Paschen curve.

The general ingredients in a hot-cathode "multicusp" discharge are shown in Fig. 1-1. The metal chamber functions as the anode of the discharge and surrounds the plasma region. Electrons are emitted from the cathode, travel through the chamber in complicated paths, losing energy by inelastic collisions, and eventually will diffuse out of the plasma and impact a metal surface where they are absorbed. Additional electrons and ions are created by ionization events caused by the initial electrons:

Magnets are placed around the discharge container forming a set of magnetic line cusps to assist in preventing the charged particles from reaching the walls where they recombine with almost unit probability. Returning to the plasma formation mechanism, electrons are emitted at thermal energy (~0.3 eV) by the

Hot cathode, ~100 V negative

Permanent Magnets

XBL 908-2592

Fig. 1-1 Conceptual schematic of hot-cathode, multi-cusp discharge

cathode, typically a tungsten wire heated by direct current, and are pulled away from the cathode by the electric field of the cathode sheath. This statement requires explanation. If the anode area exposed to the plasma is much larger than the cathode area, then the space potential of the plasma will 'lock' to anode potential, that is, it will be relatively close to anode potential. Discharges that have a relatively small anode to cathode area ratio can experience mode-flipping, a form of bistability, in which the plasma potential depends on the history of the discharge. This behavior did not occur with the discharge apparatus used for this thesis. The potential drop between the cathode and the plasma space potential takes place in a sheath surrounding the cathode of thickness a few times a Debye length, which is ≤ 0.1 mm for this work. The plasma potential is almost always positive with respect to anode. Even with magnetic shielding, which effectively decreases the anode area, this is still usually true. The reason is that, in steady-state, the total flux of electrons and ions to the wall must be equal (assuming singly-charged ions). This implies that density ratio n_e/n_i must be equal to $(m_e/M_i)^{1/2}$ very near the wall. But then Boltzmann's law implies that the space potential very near the wall (the wall itself is defined as being at zero potential) must be more negative than the plasma space potential V_p by approximately $1/2 \times \ln(M_i/m_e) \times (kT_e/e)$, or approximately a factor of 4 times kT_e for a hydrogen discharge.³ For the data presented in this thesis, the influence of the superthermal electrons and the magnetic shielding of the walls decreases this factor to ~ 2 in the body of the discharge.

Magnetic shielding of the chamber wall generally has the effect of making the plasma more efficient by decreasing the loss rate of charged particles to the walls of the chamber, particularly the energetic ionizing electrons. The magnets are typically arranged in lines of alternating polarity, hence the name

multi-cusp. The magnetic geometry is of the minimum-B type. The electrons are affected more than the ions because they have smaller gyroradii and thus are constrained to the field lines more closely.⁴ Also, higher energy electrons are better confined because the elastic scattering cross section by both neutrals and charged particles decreases with increasing energy, at least past approximately 10 eV.⁵ The magnitude of the magnetic field in the central region of the chamber scales as r^n , where r is radius and n is the number of magnet cusp periods. The angular dependence of the field strength is weak in this region (see Fig. 1-2). Electrons that travel through this central, quasi-field-free region of the discharge do not have a constant magnetic moment μ because adiabaticity will always be broken for weak enough fields. However, μ is conserved for r greater than some r_0 and thus some electrons are turned around by the magnetic mirror effect. In the absence of collisions or collective effects (a gross idealization), charged particles cannot penetrate the cusp regions because the conservation of kinetic energy and canonical momentum together prevents the particles from reaching areas of space where the vector potential has an absolute value greater than some limiting value. Thus, ideally, the charged particles cannot reach the walls by going across the field lines and most particles cannot reach the walls along the field lines because of the magnetic mirror effect. In the real world, collisions invalidate the conservation laws, and flux to the walls is greatly enhanced. However, because the particles 'bounce' at least a few times before they reach the walls, they will be much more isotropic, an important criterion for reliable analysis of probe data. The thermal electrons are estimated to make ~100 bounces on the average for typical discharge parameters in the data used for this study.

The physics of the electrons in the discharge is of prime importance for understanding both electrodynamic effects and reaction dynamics. We now

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Fig. 1-2 Diagram showing magnetic field lines and contours of constant $|B|$. Arrows show magnet orientation. Contour values are 0.01, 0.03, 0.1, 0.3, and 1 kG-cm and kG respectively. Calculation assumes infinite-length magnets. From a program by John Trow.

more carefully discuss what happens to the electrons and why there are effectively two groups of electrons in a thermionic-cathode discharge. As previously discussed, electrons are emitted from the hot tungsten cathodes and are accelerated through the cathode sheath into the body of the plasma. These electrons are called primary electrons. Typical values for the cathode bias, the plasma potential and the sheath thickness are -100 Volts, +4 Volts, and 0.1 mm, respectively. The probability of an electron passing through the cathode sheath ionizing a hydrogen atom or molecule in the sheath is very small for the pressures relevant to this work, 2 to 30 mTorr, because the mean free path for ionization is large compared to the sheath thickness. Initially these electrons have an energy proportional to the cathode bias minus the plasma potential. There is actually a spread of ~5 Volts because of the voltage difference from one end of the tungsten wire to the other. The Spitzer rate constant for Coulomb collisions of electrons with both ions and other electrons,⁶ given by

$$\langle \sigma v \rangle_{e^- \text{ coll.}} = 7 \times 10^{-6} \frac{\ln \Lambda}{(kT_e)^{3/2}} \text{ cm}^3 \text{ s}^{-1} \quad (1.4)$$

where the Coulomb logarithm $\ln \Lambda \approx 12$ and kT_e is electron temperature in eV, is relatively small at these energies and is thought not to be very important until the electrons have lost most of their energy through inelastic collisions.⁷ The conventional picture of what happens to these electrons is then that the primary electrons follow trajectories that are fairly well described by single particle orbit theory for the given electric and magnetic fields of the discharge, except for the discontinuities that occur when a given electron makes an inelastic collision. However, as we will see, there is considerable evidence that

the primary electrons very rapidly exchange energy with each other by an unknown mechanism, which most likely is a collective effect. The primary electrons reflect from the magnetic fields that effectively hide the wall. However, there is always some leakage, and it is very difficult to calculate based on first principles. The practical goal of these discharges is to have the leakage probability small enough so that the average primary electron will lose most of its energy via inelastic collisions before it impacts a metal wall, where it would be absorbed with probability very close to unity. This goal is accomplished by choosing the pressure high enough so that the rate of inelastic collisions dominates the wall loss rate. The pressure is almost always determined empirically and is in the range of 1 – 10 mTorr for many different discharge configurations.^{8,9} Of course, there is also elastic scattering off the heavy neutral particles that will increase the diffusion of primary electrons across the magnetic field lines and therefore the wall loss rate. This suggests that the energy deposition efficiency of the primary electrons saturates at a value below unity, although this possibility is not usually discussed in the literature. The energy deposition efficiency is defined here as the energy lost by the average primary electron via inelastic collisions divided by the kinetic energy of a primary electron as it exits the cathode sheath.

There exists a population of quasi-thermalized electrons, called secondary electrons, with a temperature of ~2 eV in coexistence with the primary electrons. These electrons are either created by ionization events or were primary electrons that have slowed down via collisions to the point where the inelastic collisions become much less probable, ~14 eV.⁵ Secondary electrons created by electron impact ionization of hydrogen molecules and atoms are born with ~7 eV on the average for primary electron energies of less than 100 eV.¹ Below ~14 eV the only important inelastic collisions are vibrational

and rotational excitation of neutral molecules, which involve energy transfers of ≤ 1 eV. The secondary electrons are very isotropic, well thermalized and have a much higher density than the primary electrons, by a factor of ~ 100 , depending on how exactly one defines the two groups. Coulomb collisions are important at these low energies, as well as momentum transfer (elastic) collisions with heavy neutral particles, because they keep the thermal electrons well mixed. The thermal electrons are imperfectly confined by the magnetic fields and in addition experience higher cross field diffusion rates and have a measured loss time of $25 \mu\text{s}$ for this work. This time scale is the same as for the ions because of quasi-neutrality. The loss of ions and electrons in complicated magnetic geometry is a very difficult problem, as discussed in Chen.¹⁰ However, the fact that the plasma potential is positive with respect to anode implies that electrons are still lost more easily, all else being the same.

Fig. 1–3 shows the EEDF for a hydrogen discharge, measured using the Druyvesteyn method.^{11,12} Note that the EEDF ranges over 4 orders of magnitude. The primary electrons and secondary electrons are actually very distinct and the two groups have very different temperatures and densities. The primary electrons have an effective temperature of ~ 30 eV. The secondary electrons have a temperature of ~ 1.8 eV and obviously are much more numerous. The primary electron density is sensitive to how one decides to define them because the differential density is rising sharply in the region one would be likely to call the border. The hydrogen atom production rate happens to be sensitive to the differential density of electrons near this border region because the cross section for the process of triplet excitation and subsequent dissociation

Fig. 1-3 Measurement of the EEDF in the central plasma region for discharge parameters of DC, 25 A, 90 V, 8 mTorr Hydrogen. Note the obviously distinct primary and secondary electron regions.

is largest in the same energy range. Some of the primary electrons appear to have more energy than those born at the cathode. This effect has been observed by others using more sophisticated experimental techniques.⁹ It is not known if these electrons have gained energy through plasma oscillations, through superelastic collisions, or whether the data interpretation is simply in error. This question will be discussed in more detail in chapter III, section C-2.

The constituents of a weakly-ionized gas are hardly ever in a true Maxwellian equilibrium. There are several ways to see that this is so. The primary reason is that the plasma is strongly interacting with the wall of the discharge chamber, which is very nearly room temperature in most situations and is at most 0.3 eV (white-hot tungsten!). However, the characteristic energy of the charged particles is hardly ever this low, except in afterglows. The reason is that electrons created from electron-impact ionization (a process that generally requires more than 10 eV itself!) have of order 5 eV at birth. The electrons are lost by some process or other, usually wall collisions, long before they have enough time to lose their energy. Thus two very different energy scales, room temperature and ~5 eV are always present in discharges. A local quasi-equilibrium is reached in some discharges, typically those in which the pressure is very high so that the equilibration times are short. For example, a high pressure flame or a high-pressure arc, i.e. a welding arc, can be in local thermodynamic equilibrium (LTE) in some cases. The condition necessary for LTE to be valid is that the equilibration time must be much shorter than the time required for a particle to travel a gradient length. That inequality is grossly violated for the data this thesis concerns, as will be seen. Therefore, the concept of temperature is not really very meaningful here. Sometimes a species can be in an isolated quasi-equilibrium. It is the crux of Langmuir's paradox that electrons often seem to be much better thermalized with each

other than can be explained by rate equations.¹³ The secondary electrons in discharges are often assumed to behave as though they were Maxwellian. Data has shown that this assumption is quite valid, within certain restrictions.¹⁴

B. Hydrogen Discharges

Hydrogen is commonly used in discharges for various reasons. From the theoretical point of view, hydrogen atoms and molecules are the simplest systems that can be used and thus are the most amenable to calculation. This is true not only in discharges but in many other situations. From the practical point of view, hydrogen is used because there exists a wealth of data related to hydrogen that makes interpretation of observed discharge characteristics easier to understand. Hydrogen is employed for nuclear fusion research because of its high energy yield. Deuterium is actually used mostly in that case, but the physics of deuterium and hydrogen are very closely related because the electronic configurations are the same. The only difference comes from the small variation in the reduced electron mass, usually a negligible effect, and from the substantial variation of the reduced nuclear mass in molecular structures. The change in the reduced nuclear mass can be dealt with easily within the Born–Oppenheimer approximation if the relevant potential surfaces and R-dependent matrix elements are known, where R is the internuclear separation. For molecular hydrogen, the actual electron wave functions are amenable to calculation, so this criterion is satisfied.

Many different species of particles can exist even within a simple hydrogen discharge. A partial list is H_2 , H , e^- , H^+ , H_2^+ , H_3^+ , and H^- . Only H^+ and H^- have no excited states and thus they are the only well-defined objects on a quantum level. Hydrogen atoms have various electronic states that are easily excited by photons and electrons. However, because the radiative decay rates

are so much faster than the electron impact pumping rates, it turns out that the populations of the excited states of the hydrogen atom are small enough to be negligible for the purposes of this paper. The charged particles in the discharge mix the metastable $H(2s)$ state with the $H(2p)$ state via the Stark effect, causing the two decay rates to become comparable. The $H(2s)$ population is not important because of this effect. The remaining molecular structures, H_2^+ , H_3^+ , and H_2 , all can have rotational, vibrational and electronic excitation. States that only have rotational and/or vibrational excitation are stable against radiative decay for all practical purposes, because electric dipole transitions are not allowed for homonuclear molecules. Magnetic dipole and electric quadrupole decay rates are orders of magnitude smaller than other rates relevant here and are neglected. Electronic excitation is somewhat more complicated. All states that have electric-dipole-allowed (i.e. fast) decays have very small populations for that reason and are not relevant here. H_2 has one metastable state, the $c^3\Pi_u^-$ state, that has a calculated radiative lifetime of ~ 1 ms in the $v'=0$ vibrational level and ~ 100 μ s in the other vibrational states.¹⁵ This state is readily populated from the ground state by electron impact and has been the subject of some attention.¹⁶⁻¹⁸ The gas quenching rate was recently measured and found to be rather high.¹⁹ The bound electronically-excited states of H_2^+ have very shallow potential wells²⁰ and are believed to be scarcely populated for this reason. H_3^+ does have several metastable electronic states and it is possible that these states are important in these discharges. Unfortunately, there are not enough calculations or data to do justice to an analysis here. The limited data available seem to indicate that metastable H_3^+ reacts similarly to electronic ground state H_3^+ .^{21,22}

The reason that the various excited states of the molecular species must be treated as distinct states is that the cross sections and/or rates for various

processes can have a strong dependence on the degree and type of excitation. For instance, the rate of dissociative attachment of electrons to hydrogen molecules,

in the $v''=9$ state is $\sim 10^5$ times larger than that for molecules in the $v''=0$ state, assuming an electron temperature of 1 eV.²³⁻²⁶ The corresponding factor is $> 10^7$ for deuterium! Another example, that is of astrophysical interest, is the variation of the cross section for dissociative recombination of H_3^{+} ,

with the vibrational quantum number v'' . In that case, different vibrational levels are estimated to have rates that are different by a factor of ~ 100 .²⁷ Thus a small fraction of molecules in an excited state may contribute most of the rate for a given collisional process. If the time scale of reshuffling between sublevels of some state is small compared to the other relevant time scales, then the sublevels may be treated as one unit, using appropriately averaged rates. However, this condition is not met for the different vibrational populations of H_2 in the discharge discussed here.

There is one other collision partner in these discharges: the surface of the chamber wall. The chamber walls are extremely important because they catalyze certain reactions that would proceed many orders of magnitudes slower otherwise. The most important processes are neutralization of charged particles,

recombination of atoms,

and relaxation of internal energy in H_2 ,

These will be discussed in order.

Wall neutralization of ions and electrons is important because, although all three positive hydrogen ions have fast rates for recombination with H^- ,²⁸⁻³¹

and H_2^+ and H_3^+ have fast rates for recombination with electrons,^{32,33}

the rate constant for radiative recombination of H^+ with electrons,

is much smaller.³⁴ The reason is that all energies above threshold are favored when the intermediate complex consists of multiple nuclei because the recombined structure, which is highly unstable, can dissociate to two or more neutrals in a vibration time period, 10^{-14} s. This scenario is not the case for H^+ because an isolated H-atom in a positive energy state can only decay to a bound state by an electromagnetic process, which has a time scale of order 10^{-9} s. Radiative recombination is usually more important in tokamak (high Z) plasmas and in space plasmas, where no surfaces exist.

The catalytic recombination of atoms on surfaces is important for similar reasons. Picture two atoms approaching each other in free space. If they are in a relative electron spin 1 state, then they are in the non-binding $b^3\Sigma_u^+$ state. If they are in a relative spin 0 state, then they are in the vibrational continuum of the $X^1\Sigma_g^+$ state. In either case, the only mechanism for the atoms to bind into a molecule involves a radiative decay that is electric-dipole forbidden:

where it is understood that the initial state is in the vibrational continuum. The latter case is spin disallowed on top of that! Therefore the free space atom-atom recombination rate is extremely small. If there is a third body present, such as a hydrogen molecule, it can take away the energy and still conserve momentum:³⁵

Three-body recombination can be important at high densities, but for the low densities of this work (10^{14} cm^{-3} or less), it is completely negligible. Thus, wall recombination of atoms is the only significant loss mechanism for atoms for most discharges. Note that H^+ ions are converted to H-atoms with almost 100% efficiency when they leave the plasma and impact a surface. The reason is that, even if a proton is reflected, its energy is very likely to be reduced and the proton will not be able to travel back to the plasma because of the plasma potential, and therefore the proton will simply bounce until it becomes an atom.

Internal energy can also be changed by wall collisions. The change is usually a decrease for hydrogen molecules because the wall temperature is small compared to the stored energy of any electronic or vibrational excitation. Rotational transitions can also occur, as can collisions that transform the internal energy from one form to another. If the internal energy is in the form of electronic excitation, the probability is close to unity that the energy will be lost on the first wall bounce. The lost electronic energy sometimes appears in the form of kinetic energy of an ejected free electron, a process that lends itself to detection of metastable Hg atoms for instance.³⁶ In the case of vibrational and rotational excitation of molecules, it is not known what the wall relaxation probability is per bounce in most instances, including the cases relevant to this study. It is not even clear how well characterized the condition of the walls is, in this experiment or others. The probability of a vibrationally-excited hydrogen molecule losing all or part of that vibrational energy during a surface collision

is of some interest. Conflicting data exists within the literature on this subject. This thesis attempts to shed light on this issue.

C. The H^- Question

H^- has been observed many times in low- and medium-power discharges in densities comparable to the electron density, a fact that was not explained for some time. The following paragraph briefly summarizes a much more detailed account given by Hiskes.³⁷ On general grounds, it was surprising because H^- is rather fragile, having an electron affinity on 0.76 eV, and also would be expected to have a large rate for recombination with positive hydrogen ions. Early data also indicated that H^- was more likely to come from a portion of the discharge when the electrons where cool and the power density was low compared to the central portion of the discharge.³⁸ Polar dissociation of H_2 by electron impact,³⁹

was thought to be the source at first but it was determined that the cross section for this process is too small to account for the observed H^- density. It also did not explain the observed spatial variation mentioned above. The cross sections for electron collisions with H_2^+ or H_3^+ yielding H^- (plus anything):

were measured by Peart and Dolder.^{40,41} The energy dependence and magnitude of these cross sections was not enough to explain the measured H^-

densities. Dissociative attachment to H_2 ($v''=0$) has resonances at ~ 3 and 10 eV but the cross section for this process is also extremely small, $\sim 3 \times 10^{-20} \text{ cm}^2$.⁴² It was suggested by Kuchinskii that vibrationally-excited H_2 should have a larger cross section for dissociative attachment than vibrationally-unexcited H_2 , based on the potential curves for H_2 and those of H_2^- .⁴³ This suggestion was correct, but the enhancement was not quantitatively determined until the theoretical work of Wadehra and Bardsley.²⁴⁻²⁶ Allan and Wong subsequently verified the enhancement up to $v''=4$ for H_2 .⁴⁴ Although the theoretical values by several authors are in good agreement for much higher states,^{23,25} the experimental results have not been extended. Indirect evidence exists that the dissociative attachment cross sections for $v''>4$ are at least comparable to those of $v''=4$ and probably larger.⁴⁵ The calculations show that the rate of dissociative attachment of electrons with a temperature of ~ 1 eV increases with v'' up to $v''=9$ where it saturates and then decreases slowly.^{23,25}

It remained to determine what the vibrational distribution of hydrogen molecules is in a discharge. There is ample energy in the secondary electrons to populate high vibrational levels of H_2 in a discharge; the internal energy of $H_2(v''=9)$ is only 3.6 eV. The cross section for (low energy) electron impact excitation of $H_2(v''=0)$ to $H_2(v')$,

was measured by Ehrhardt, et al. for $v'=1-3$, and was extended to $v'=1-6$ by Allan.^{46,47} The cross section was found to decrease almost exponentially with increasing v' . There are a number of processes that can affect the vibrational distribution; unfortunately, the rates for most of these processes are not

known experimentally, primarily because of the difficulty of producing selected rovibrational states of hydrogen (or most other) molecules in the laboratory. The constituents that are believed to be important for determining the H_2 vibrational distribution are e^- , H-atoms, H_2^+ , H_3^+ , and the walls of the discharge chamber, i.e., almost everything except H^- itself. Several authors have generated sophisticated computer models to model the vibrational distribution in a discharge of conditions similar to those employed in this work.⁴⁸⁻⁵⁴ These models generally predict that the populations decrease sharply (factor of 10 roughly) with each additional vibrational quantum up to $v''=5$ and then decrease very mildly (factor of ~ 1.3) with v'' up to $v''=12$. A semi-log graph would then have a plateau feature, as can be seen in the references. The molecules in the vibrational plateau are thought to be formed by electron impact excitation of thermal molecules into the primary singlet states, the B and C states, that subsequently decay radiatively with known branching ratios to the X state, yielding a broad and relatively flat vibrational distribution:

The effective cross sections for $H_2(v''=0) \rightarrow H_2(v'>0)$ were calculated by Hiskes and recently indirectly experimentally verified by Ajello, et al.^{55,56} The hydrogen molecules of vibrational quantum number $v'' \geq 5$ are thought to be destroyed mostly by wall collisions, although the rate of electron-impact induced $\Delta v''=\pm 1$ transitions is thought to be significant. This implies that the high v'' state populations should scale linearly with discharge current, assuming the cold molecule population is not too dissociated. The molecules in the initial 'steep' region ($v''=0-3$) are believed to be quasi-thermalized with

each other in the sense that they are most likely to be created or destroyed by $\Delta v = \pm 1$ electron-impact induced cascade transitions. Some experimental data exists for the vibrational distribution in typical H_2 discharges. Coherent Anti-Stokes Raman Scattering (CARS) was employed to measure the vibrational distribution in a discharge of somewhat higher pressure and less power than that used here. Results up to $v = 3$ were obtained.^{57,58} More recently, Resonance Enhanced Multi-Photon Ionization (REMPI) was employed to measure the vibrational distribution of molecules effusing from a hole in the side of a discharge chamber, up to $v = 5$.^{8,59,60} The second in a series of experiments yielded the first experimental confirmation of the predicted plateau region. The scaling of the $v = 5$ population with discharge current qualitatively agreed with model predictions.

Although the two-step process of H^- production via dissociative attachment to vibrationally-excited H_2 has never been directly proven to be the main channel for H^- formation in discharges, several experiments have shown that the proposed mechanism is clearly consistent with the data. Bacal and coworkers performed the early experiments which indicated a non-linear production mechanism.^{61,62} Leung and Kunkel showed that the H^- production in a low-voltage H_2 -Xe discharge was not affected by the lack of positive hydrogen ions, and that the H^- dependence on discharge voltage agreed with theory.⁶³ Fukumasa, et al. showed that different wall materials produce different H^- densities, even though the electron temperature and density and the positive ion species ratio were unchanged.⁶⁴ Leung also observed similar relative H^- dependence on wall material.⁶⁵ It is difficult to directly show the correlation between vibrationally-excited H_2 and H^- because one cannot independently control the variables. Changing any one of the various macroscopic discharge parameters (current, pressure, voltage, magnetic

geometry, wall material, etc.) changes many of the microscopic variables. A clean *gedanken* experiment would simply be to illuminate the discharge chamber with light at the proper frequency (ν), such as to greatly enhance the production rate of a given $H_2(\nu'', j'')$ state (s) that is believed to be an important intermediate step in the H^- production process.

H^- is easily destroyed by collisions with other particles and the walls of the device. The cross section for electron collisional detachment,

has been measured and yields very high destruction rates for electron temperatures much above 1 eV.^{66,67} This explains why H^- is often observed to have the highest density in the cool plasma edge: H^- is created at high rates everywhere, but is destroyed much more rapidly in the body of the plasma. The reverse reaction of H^- creation, associative detachment,

also has a large cross section at low relative energies (≤ 1 eV), therefore high H-atom density can be detrimental to high H^- density.^{68,69} The process of dissociative attachment contributes only a small fraction of the total H-atom creation rate, therefore high H^- density does not necessarily imply high H-atom density. Mutual neutralization (see Eq. 1.11) with the various positive hydrogen ions also causes a high loss rate for H^- and forms a fundamental obstacle to high H^- densities in some sense, because these plasmas are always quasi-neutral.

It has been proposed that an additional source of H^- could be dissociative

attachment of the metastable $c^3\Pi_u^-$ state of H_2 ,¹⁸

This issue has been investigated experimentally by Bonnie, et al.,^{16,17} and the density of metastable H_2 was found to be rather small, $\sim 3 \times 10^{-9} \text{ cm}^{-3}$. This is small enough so that even if the calculated dissociative attachment cross sections¹⁸ are too small by a factor of 10, this channel would still be a small contribution to the total H^- formation rate.

H^- can also be produced by hydrogen atoms or protons impacting a surface at moderate energy ($\geq 100 \text{ eV}$) and picking up one or two electrons, respectively, as the particle reflects:⁷⁰

This has been demonstrated repeatedly and is, in fact, the basis of H^- ion sources ('surface' sources) under development at LBL and elsewhere.⁷¹

However this process is critically dependent on the surface having a low work function.⁷¹ For this reason, elements such as cesium and barium have been employed as the surface coating. The conversion efficiency for tungsten, which has a work function of 4.5 eV, is very low (of order 10^{-5} H^- created per proton impact), and therefore it is not of consequence here.

D. Scope of This Thesis

This thesis is an experimental examination of most of the constituents of a medium-power hydrogen discharge in a discharge chamber empirically

designed for the maximum extracted H^- ion current density. The emphasis is on direct spectroscopic measurements of the density and temperature of the plasma-produced neutral species, hydrogen atoms and rotationally- and vibrationally-excited hydrogen molecules, for which theory is abundant and data scarce. The electrons in the discharge are measured using both the conventional Langmuir technique and the more powerful Druyvesteyn method. High voltage extraction has been used to measure the species fractions of the positive hydrogen ions and the extracted negative ion current, along with the electrons. The H^- density has also been measured in the region of the plasma that is adjacent to the extractor and that is known to have a high negative ion density. Some effort is made to determine at least approximately the spatial variation of the density and temperature of the electrons and the neutral species. The quantities that are not measured are the rovibrational energy distributions of the molecular hydrogen ions and metastable hydrogen atoms and molecules.

The overall goal of this thesis is to measure as many of the constituents as possible, but particularly the neutral species, in the discharge of interest and to compare the results to that of three staged models. The models presented are similar to those that have been discussed in the literature. This is done for various discharge parameters, for both DC and pulsed operation. By determining the scaling laws and time scales for the different species, correlations may be determined that illustrate how various species influence one another. This thesis does not aim to exactly determine cross sections or rates, but to qualitatively further the understanding of discharges optimized for volume production of H^- , and to determine what the most important unanswered questions are in this regard. In particular, this thesis addresses the predicted mechanism of H^- via the two-step process of vibrational

excitation of hydrogen molecules followed by dissociative attachment of electrons to those molecules yielding H^- .

The first phase of modeling calculates the atom and positive ion density using measured electron data as input, as well as the measured atom and electron temperatures. The atom recombination coefficient employed in the model was measured directly using a discharge perturbation technique. The agreement between the data and the model results is very good. The second phase of modeling predicts the vibrational distribution of the molecules in the discharge, using measured electron and atom data as input. The rate of vibrational relaxation via wall collisions was measured in the afterglow of a pulsed discharge and found to be in the range of 10–40 bounces for $v=1-5$. Employing the measured wall relaxation rates, rather than calculated values, in the model gives much better agreement with the vibrational distribution data. The model indicates that thermal electrons are the primary vibrational excitation agent. Finally, the last stage of modeling predicts the H^- density based on the rovibrationally-excited molecule populations. The measured H^- density is consistent with calculated using mild extrapolations of the measured rovibrational distribution, but the role of very highly rotationally-excited molecules ($J'' \approx 25$) is unclear. The scaling with current for the density of excited molecules and H^- ions indicates that most H^- is produced from molecules of at least moderate ($J'' \geq 7$) rotation.

Chapter II

Discharge Modeling

A. General Considerations for Modeling

Several models of the atomic and molecular physics occurring in the discharge are presented in this thesis. Almost no assumptions are made regarding temperatures, that is, the models are simply based on the relevant kinetic equations. There are three phases of modeling, and each phase is independent of the others. In all three cases, measured values of the electron parameters are used as inputs to the models. The first phase of modeling calculates the balance between molecules, atoms, and positive ions in the discharge. Any internal energy of molecules and ions is ignored in that phase, as is the presence of H^- ions. The second phase calculates the distribution of hydrogen molecules within the various vibrational levels of the ground electronic state. The measured, not calculated, atom density is used as an input for this phase. The last phase of modeling calculates the H^- density in the magnetic filter region using measured values for the atom density and molecular vibrational distribution. In this manner, one can test each phase of the modeling separately and incorrect model predictions do not propagate. The models are essentially zero-dimensional and employ rate constants that are averaged over the volume of the discharge (except for the H^- density modeling, which must necessarily use local values). However, a provision is made to account for the fact that the volume of the plasma is substantially less than the volume of the actual discharge chamber V_{chamber} , 6.5 liters, because of the magnetic shielding. (The reader is referred to Chapter III, section 1 for a more detailed description of the physical chamber and the magnetic geometry). As illustrated by Fig. 5-3, the plasma has a moderately well-defined border.

The electron density and temperature fall together and are roughly proportional to each other in the fall-off region. The volume-averaged rates are the product of the rate constants relevant to the center of the discharge multiplied by an effective volume factor which is generally in the range of 0.2. In essence, the effective volume factors are a crude attempt to account for the fact that the plasma parameters are very inhomogeneous over the chamber volume.

One criterion for a zero-dimensional model to be valid is that any mean free path λ_{mfp} should be at least comparable to a chamber diameter, 20 cm presently. As will be shown, this criterion is satisfied for almost all neutral particles and the electrons, but is not satisfied for the ions generally. We first specialize to the case of a fast particle (i.e., electron) moving through a slow target medium. In that case, λ_{mfp} is given by

$$\lambda_{\text{mfp}} = \left(\sum_i \sigma_i n_i \right)^{-1} \quad (2.1)$$

where σ_i refers to some cross section and n_i refers to the corresponding target density. In the present case, the dominant term is given by inelastic collisions with hydrogen molecules or atoms (elastic collisions are ignored at this point). The density n_{H_2} is $\sim 2 \times 10^{14} \text{ cm}^{-3}$ at typical parameters and the total inelastic cross section for electrons in the range of 1 to 100 eV on H_2 is no more than $2 \times 10^{-16} \text{ cm}^2$, yielding λ_{mfp} of 25 cm (neglecting rotational excitations, which involve very small energy transfers, of order 0.05 eV).^{1,5} Actually, the situation is more favorable than this estimate indicates because the stated cross section applies to the primary electrons, and these energetic electrons generally must undergo about 4 inelastic collisions to lose their initial energy,

approximately 100 eV. Also, those fast electrons are confined to a small cylinder of diameter ~ 10 cm and length ~ 15 cm by the magnetic cusp fields. For slow electrons (≤ 10 eV), the total inelastic cross section is no more than $5 \times 10^{-17} \text{ cm}^2$ and thus λ_{mfp} increases to 100 cm.⁵ Thus the gradients in electron density and temperature are not caused by inelastic collisions, but mainly by elastic collisions with H_2 ($\sigma \approx 1.5 \times 10^{-15} \text{ cm}^2$) and the reduced mobility across the magnetic field lines.⁵ An alternative viewpoint that is probably a more realistic and physical picture of thermal electron mobility is that the thermal electrons will go wherever the ions go, because the ambipolar electric fields will dominate other forces. For instance, the plasma density in the discharge chamber under discussion has a much flatter radial profile when the discharge gas is argon, because the ion gyroradius is so large that the magnetic fields barely confine argon ions at all.

In the case of a slow-moving heavy particle, such as an ion or molecule, λ_{mfp} is given by a more complicated expression which includes the effect of a relatively stationary target and a background of much faster particles, namely electrons:

$$\lambda_{\text{mfp}} = v_{\text{th}} * \left\{ v_{\text{th}} \left[\sum_i \sigma_i n_i \right] + n_e \langle \sigma v \rangle_e \right\}^{-1} \quad (2.2)$$

where n_e is electron density, v_{th} is the thermal velocity of the heavy particle in question, and $\langle \sigma v \rangle_e$ is the rate constant for all electron-impact loss processes, appropriately averaged. In practice, the EEDF is assumed to be the sum of two components, corresponding to the thermal and primary electrons. The appropriate symbols for density and temperature are n_e , kT_e , $n_{e,f}$ and $kT_{e,f}$

respectively (note that because $n_{e,f} \lesssim 0.02 n_e$, $n_{e,thermal} = n_e$ to a very good approximation). We first estimate the mean free path for neutral particles, hydrogen atoms and molecules. The first term in the braces of Eq. 2-4 can be ignored because there are no significant neutral-neutral reactions and because the ion density is relatively low. Concentrating on the second term in the braces, one obtains a value of 150 cm for λ_{mfp} , based on typical values for v_{th} , $n_{e,f}$, and $\langle \sigma v \rangle_e$ are 2×10^5 cm/s, 2×10^{10} cm $^{-3}$, and 7×10^{-8} cm 3 /s, respectively.¹ There is one exception to this general trend for neutral particles: molecules in very highly vibrationally-excited states ($v'' = 9$) have such a large rate constant (10^{-8} cm 3 s $^{-1}$) for dissociative attachment:

that λ_{mfp} is reduced to ~ 3 cm in the body of the plasma for a discharge current of 300 A ($n_e \approx 1 \times 10^{13}$ cm $^{-3}$).^{23,25} However, for more typical values of n_e , $\sim 10^{12}$ cm $^{-3}$, this value increases to 20 cm.

Some of the hydrogen ions have mean free paths that are short compared to a chamber length. H_2^+ and H_3^+ have such a fast rate for recombination with thermal electrons

that the corresponding mean free paths (caused by these reactions only) are of order 5 cm at 35 A of discharge current.¹ Also, the mean free path for H_2^+ due to the reaction

is only ~0.5 cm at typical discharge parameters.¹ Therefore, even in the absence of magnetic fields, ions would experience several reactions before impacting the chamber wall. However, the atomic hydrogen ion H^+ has a relatively long mean free path because there are no reactions involving it that have significant cross sections at energies typical of these discharges (a few eV). Hydrogen plasmas tend to become dominated by H^+ when the wall reaction rates are relatively small, that is, for high power and large scale lengths. The mean free path for H^+ , $\lambda_{\text{mfp},\text{H}^+}$, is a sensitive function of position within the discharge chamber. In the central portion of the discharge, this quantity is reduced to ~1 cm because of the large rate constant for collisional detachment:⁶⁷

In the fall-off regions of the plasma, where the electron temperature is ≤ 1 eV, $\lambda_{\text{mfp},\text{H}^+}$ increases significantly, to ~20 cm. However, H^+ ions are somewhat immobile in those regions for several reasons. First, the H^+ ions are prevented from escaping the plasma by the plasma potential. Secondly, the cross field diffusion velocity is not too large. Therefore, the physical scale length for the H^+ density can be very short, of order 1 cm, as can be seen in the data of Leung, et al.⁷²

B. Molecule, Atom, and Positive Ion Balance

Some fraction of the molecules in a hydrogen discharge will be dissociated into atoms. The atoms are created by molecular dissociation at the hot

tungsten filaments, by electron impact dissociation of molecules, and by recombination of ions, either with other charged particles or at the walls of the discharge chamber. Hydrogen atoms are mainly destroyed by wall recombination. Also, some of the molecules will be ionized by primary electrons. H^+ , H_2^+ , and H_3^+ are all stable ions and generally are found in very roughly equal proportions in low-pressure discharges. Any model that predicts the ion or atom density will necessarily have to predict the other, because the two are highly-interdependent in most circumstances. Fig. 2-1 pictorially illustrates the reaction paths under consideration presently.

In the first phase of modeling, we use the measured EEDF as an input to the model and calculate the equilibrium distribution of H_2 , H , H^+ , H_2^+ , and H_3^+ . The model is very similar to that of Chan, et al., except that the electron data is measured rather than calculated.¹ H^- is ignored in this model, as well as rovibrational excitation of H_2 . This neglect is justified because the plasma-averaged H^- density is small enough that the corresponding rates are much smaller than other rates considered here. Treating all of the H_2 molecules as a single unit is justified because the cross sections of interest here do not depend strongly on the degree of internal excitation, in contrast to the cross sections relevant for H^- formation. The general topic of internal energy dependence of the various rates will be discussed further in subsequent paragraphs.

It is assumed that the plasma composition (i.e., density and species ratio of positive hydrogen ions) is homogeneous. The justification for this assumption is that the density of the primary electrons, which are responsible for creating the ions and secondary electrons in the first place, are very well distributed throughout the field free region of the discharge chamber, by arguments discussed in the section 1. Also, the cold gas density is uniform throughout the

Also

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Fig. 2-1 Diagram of reaction paths for processes involving the balance of molecules, atoms, and ions. Dominant pathways are indicated by heavy arrows.

entire chamber. Therefore the plasma creation rate, which is proportional to the product of the two above densities, is uniform in the field-free region of the discharge chamber. There could be a difference however in the freshly-made plasma (i.e., in the central region of the chamber) versus the plasma that is diffusing across the magnetic fields to the wall. In fact, it is almost certain that the fall-off region of the plasma has a higher fraction of H_3^+ than the central region, because of reaction 2.5. Nevertheless, we will assume that the species ratio of positive hydrogen ions is not a function of position.

The mechanics of the model are simple. Because the total number of protons is conserved, the species densities are expressed (in the computer) in proton equivalent densities. We obtain differential equations for the density of each species:

$$\frac{dn_i}{dt} = \left(\sum_{j \neq i} a_{i \leftarrow j} n_j \right) - \left(\sum_{j \neq i} a_{j \leftarrow i} \right) n_i \quad (2.7)$$

where the a 's are constant volume-averaged rates based on the measured EEDF. There is only one non-linear term (see Eq. 2.5), which can be treated in an artificial manner, iteratively (actually only one iteration is needed), and so the final set of rate equations is a set of coupled linear differential equations. Thus the solution is obtained by conventional matrix methods. The steady-state solution we seek is proportional to the eigenvector $\hat{e}_{\text{zero}}$ of the zero eigenvalue, which is a necessary eigenvalue of the matrix because conservation of particles forces the rate matrix to have a zero determinant. The eigenvector is trivial to determine with a computer. The proton-equivalent eigenvector is then converted to conventional densities in an obvious manner and scaled according to the total H^+ density in the

chamber. However, the total H_2 density during discharge operation is not the same as for cold gas at the same flow rate. The primary reason is that the gas is heated significantly by the discharge; dissociation and ionization play a much less important role for the present parameters. The actual density during discharge operation is typically 2/3 of the cold gas filling density. A more quantitative discussion is deferred until chapter IV. The ion densities (which are volume-averaged essentially) are also divided by the effective volume factor, so that they reflect the density relevant to the central region of the discharge (which is the measured quantity). The non-linear term corresponding to Eq. 2.5 uses the H_2 density as a scaling factor for the corresponding rate. The computer model does not have a mechanism to guarantee the physical requirement of quasi-neutrality. Therefore a comparison of the calculated total ion density versus the assumed electron density is a crude test of the self-consistency of the model. One does not expect 5% agreement, but a factor of two would be poor. The reactions considered in the model are listed below:

The cross section data for binary reactions 2.9, 2.11–2.15, and 2.20 are taken directly from Chan, et al.¹ The data for electron-impact-induced H_2 dissociation (reaction 2.10) via the $b^3\Sigma_u^{+}$ state (the dominant triplet channel) and the $B^1\Sigma_u^{+}$ state is taken from references 73 and 74, respectively. The hot filament dissociation rate was measured directly by measuring the atom density under no discharge conditions. The H-atom wall loss rate had been previously measured at identical circumstances, so the rate of H_2 dissociation could be directly calculated. The rate was found to be $\sim 28 \text{ s}^{-1}$ (per molecule) and to vary little over the temperature range that corresponded from 5 A to 100 A of discharge current. This rate implies that $\sim 40\%$ of all molecules that impact the filaments (area of $\sim 10 \text{ cm}^2$) are dissociated. We note here that, for reactions 2.14 and 2.15, the molecule channel is assumed to have twice the rate of the the two atom channel. This assumption is based on several experimental measurements of the H_3^{+} branching ratio for similar reactions.^{22,75} The rates involving surfaces require additional assumptions to be made. The ions are assumed to have probability unity of being neutralized on the first wall bounce. The time scale for ion (or electron) loss was measured

using probe techniques and found to be $\sim 25 \mu\text{s}$ at DC discharge parameters of 25 A, 90 V and 8 mTorr. However, this value must be a weighted average for the different positive ions. For the discharge conditions of that measurement, the measured $\text{H}^+ : \text{H}_2^+ : \text{H}_3^+$ ratio was approximately 30%:5%:65%. For lack of other information, it is assumed that the loss rates for the ions scale as $M^{-1/2}$, which leads to time scales of 20, 28, and $34 \mu\text{s}$ respectively. These values were also assumed to scale as $(kT_e)^{1/2}$. The hydrogen atom wall recombination coefficient γ is defined as the probability that a hydrogen atom impacting the surface will return as half of a molecule. The atom recombination rate γ_{recom} will then be given by

$$\gamma_{\text{recom}} = \frac{\gamma A_{\text{chamber}}}{V_{\text{chamber}}} \sqrt{\frac{kT_{\text{H}}}{2\pi M_{\text{H}}}} \quad (2.21)$$

where the symbols have obvious meanings. Note that kT_{H} is the measured atom temperature, which is assumed to be isotropic. Evidence will be presented in subsequent chapters which indicates the validity of this assumption. Practically speaking, γ is treated as an unknown and is varied to fit the data. However, γ can also be measured directly by operating a DC discharge with a small pulsed perturbation (that has very short rise and fall times) and measuring the characteristic time scale for the atom density to re-equilibrate. This argument assumes that the atom recombination rate dominates the effective molecule to atom rate; that assumption turns out to be true by a factor of ~ 100 . The value of γ derived from this perturbation method does not agree with the value of γ derived from measurements of the decay of the atom population in the plasma afterglow (even after accounting for the different atomic temperatures). A more complete discussion of the value for γ

is deferred to Chapter IV. The rate constant for H_2^+ destruction corresponding to reaction 2.20 is assumed to be $4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, corresponding to an estimated value for the ion temperature of 0.3 eV (see Ref. 1 for a discussion of the uncertainty of this rate). The model results are not sensitive to this value, because this channel of H_2^+ destruction dominates in all cases.

The effective volume factors were determined empirically. The radial profile of the plasma density is shown in Fig. 5-3. It is assumed that the fall off of thermal electron density and temperature at the end of the discharge chamber opposite the filter section has a scale length comparable to the radial scale length, because the field strength is approximately the same. The magnetic fields generated by the filter rods are somewhat weaker on the other hand and the plasma will extend in a little closer to the filter plane. The estimated volume for the thermal plasma component is $\pi \times (5.5 \text{ cm})^2 \times 17 \text{ cm} \approx 0.25 \times V_{\text{chamber}}$. The primary electrons are even more sharply confined, and their estimated volume is $\pi \times (5 \text{ cm})^2 \times 14 \text{ cm} \approx 0.17 \times V_{\text{chamber}}$. There is an additional complication: the effective volume factor for electrons on neutrals is simply 0.25 or 0.17, because the neutral densities are assumed to have no gradients in the chamber, but, the effective volume factor for electrons on ions is much higher, because the ion and electron densities are highly correlated. That factor will also be different for thermal electrons on ions compared to primary electrons on ions. The ratio of the two above factors is $\sim 2/3$. The end result of all this was that the following procedure was used: The primary electron EEDF and the thermal electron EEDF were both measured in the central portion of the discharge. However, the primary electron density was scaled down by the $2/3$ factor mentioned above, so that it corresponded to the average over the region of space corresponding to the thermal plasma. Then the computer calculated volume-average rates for neutral heavy particles by

multiplying the rates for the center of the plasma by 0.25. The volume averaged rates for ions were taken as is (which effectively had a 2/3 factor already). This method at least guarantees that the electrons-on-neutrals rates should be right if the effective volumes from above are correct, and that the electrons-on-ions rates should be fairly accurate.

In actuality, these factors may be regarded as heuristic adjustments to some degree, and the values chosen were influenced somewhat by the agreement of the model with the measured electron and atom densities which, after all, are at least as accurate as these effective volume factors. Also, the effective volume factor corresponding to the thermal plasma depends somewhat on pressure and discharge voltage. In particular, increasing the pressure decreases the cross-field diffusion rate of ions (and therefore thermal electrons) to the walls, as can be seen in the data on the ratio of electron density in the filter region to that in the central region of the discharge chamber. Increasing the discharge voltage increases that same ratio, because the primary electrons can penetrate further into the filter region before being turned around. Ideally, one should measure the EEDF as a function of position throughout the chamber (non-perturbatively, for all the relevant combinations of discharge parameters!) and include transport for the ions in the model, however, that enormous amount of effort was not even performed by Hopkins, who devoted his entire thesis to EEDF measurements.⁹ An approximation that might be fairly good would be to assume that the EEDF is only a function of the vector potential (taking zero at the chamber center), measuring the EEDF carefully along a radial profile, and using a computer to calculate the vector potential throughout the chamber (this can be done if all materials in the vicinity, including the magnets themselves, have a magnetic permeability of unity, as is true for samarium-cobalt magnets). However, even this task would be a

strenuous effort best reserved for an ion source that is of greater practical importance.

The astute reader will note that little mention has been made of diffusion, an effect that would obviously complicate the analysis. The justification for this assumption is discussed. First of all, the VUV absorption measurements of the atom density and temperature show that the atom temperature has a relatively weak dependence on filling pressure from 2 to 20 mTorr (other discharge parameters held fixed). Also, the atom temperature measured in the magnetic filter region agrees very well with the temperature inferred from VUV data in which the beam travels through the center (and presumably the hottest zone) of the discharge. This data is relevant because atoms diffusing through a thick soup of cold molecules (measured kT_{H_2} is ~ 0.06 eV) will be thermalized. Both diffusion and thermal relaxation involve the same basic mechanism, momentum transfer via elastic collisions, therefore evidence against thermal relaxation is also evidence against diffusion being important. The estimated diffusion time scale γ_{diff} for the lowest order mode of this chamber is estimated at $\gamma_{diff} \approx D/l^2$, where D is estimated to be 2×10^6 cm²/s (Ref. 76) and the effective l is ~ 6 cm (this quantity is always about 60% of a chamber radius for a geometry in which the three perpendicular length scales are similar). Thus, $\gamma_{diff} \approx 18$ μ s, which is less than but comparable to the inferred values for the atom loss rate. Actually though, the diffusion equation is not valid at these low densities because the implied diffusion velocity can be larger than the (one-directional flux-averaged) thermal velocity! Strictly speaking, one needs to perform a Monte Carlo calculation, but that was not done for practical reasons.

We add here that the effective volume factors and various electron parameters used in this phase of modeling are retained for the next phase of

modeling without alteration and that this phase of modeling (which is not really new information) serves primarily as a benchmark test of the consistency of the 'easy to get' measurements. As will be seen, the agreement is generally very good for a system as complicated as an electric discharge in a low pressure gas.

Finally, we discuss the issue of the dependence of various rates on the internal energies of the reactants, and why the present model yields rather accurate results despite ignoring any internal energy dependencies. As discussed in chapter I, the hydrogen atoms have such fast radiative decay rates that only a very small fraction ($\ll 1\%$) are not in the $n=1$ state. This is still true even considering the strong trapping of Lyman-alpha photons, which have a mean free path of roughly 1 cm at line center. That leaves the hydrogen molecules and the molecular ions. The fundamental reason that internal energy can be ignored for ionization of the molecules is that the cross sections for ionization have only a weak dependence on the vibrational quantum number⁷⁷ and that most molecules are in the lowest vibrational level, and thus the ionization cross section properly averaged over the vibrational distribution will be scarcely different than that for $v''=0$. The rate for H_2 electron impact dissociation does have a strong dependence on the vibrational level,⁷² however, the proper average is again not significantly different from the $v''=0$ rate because the fraction of molecules in higher vibrational levels is small. That leaves the various rates involving molecular ions, which are known to have considerable internal energy in low-pressure discharges of this type. The vibrational distribution of H_2^+ created by electron impact ionization of room temperature H_2 has been measured and it was found that the average internal energy of the ions was 0.8 eV.⁷⁸ A recent experiment concluded that the H_3^+ ions from an unspecified ion source had an average internal energy of

2.1 eV.²² Generally, one would expect that the rates for reactions 2.13–2.15 would be strongly dependent on the internal energy of the relevant ions. It may be that the rates for transformation of these particles are much higher than those corresponding to internal energy transfer (to H₂ presumably), and thus the ions have the internal energy distribution that they were born with, which should be fairly independent of discharge parameters. If the preceding supposition is true, it would imply that the cross sections for the molecular ions do not depend strongly on the parameters of the ion source from which they originated, and thus, that the literature cross sections are indeed accurate for the present discharge.

C. Vibrational Distribution of Hydrogen Molecules

The second phase of modeling attempts to calculate the distribution of hydrogen molecules within the various vibrational manifolds of the ground electronic state of H₂, the X ¹Σ_g⁺ state. As stated in Chapter I, this model is not intended to have the sophistication of the models found in the literature.^{49,53,54} The division into rotational sublevels is ignored, primarily because data regarding binary reaction rates and wall coefficients is extremely scarce. Most of the basic assumptions are the same as those discussed in the previous two sections. First, the model is essentially a zero-dimensional model that simply uses volume-averaged rate coefficients as in the previous section. The effective volume factors and electron data are exactly the same as used in the previous section. Secondly, the model generates the results by determining the eigenvector corresponding to the zero eigenvalue of a set of coupled linear differential equations that contain the information on the rates for H₂(v'') → H₂(v') for arbitrary v'', v' in the range of 0 ≤ v'', v' ≤ 9. In steady-state, the total number of molecules is conserved. The non-linear

terms corresponding to the molecular relaxation reaction

are very small compared to other relevant rates,⁷⁹ because the pressures of interest presently are relatively low, and therefore these terms are neglected in the model. The process of recombinative desorption of atoms recombining into excited hydrogen molecules at the walls of the discharge chamber is not included because of evidence (presented in subsequent chapters) that this contribution is very small for the discharge parameters used here. The formation of vibrationally-excited H_2 by reactions 2.14 or 2.15 is ignored because there is a complete lack of data on the subject. The formation of vibrationally-excited H_2 by wall neutralization of H_2^+ or H_3^+ ions is also ignored. Thus the processes of ionization and dissociation are treated as conversion to $v''=0$. The reactions included in the model are

The references are, respectively, Ref. 80 for Reaction 2.23, Ref. 49 for 2.24,

Ref.'s 74 and 81 for 2.25, Ref. 82 for 2.26, Ref. 53 for 2.27, Ref. 73 for 2.28, and Ref.'s 23 and 25 for 2.29. The literature data for reactions 2.23 and 2.24 are for several discrete electron and atom temperatures, respectively. The calculations were performed using the temperatures closest to the measured values; the model results are fairly insensitive to the temperatures selected. The wall relaxation coefficients are computed using the measured gas temperature; the branching ratios are from Ref. 82 and the loss-per-bounce coefficients are either from Ref. 82, estimated based on the present data, or simply varied to fit the data. For the electron-impact ionization cross sections, we use the scaling suggested by Hiskes, namely that $\sigma_{v''} = \sigma_{v=0} \times (1 + v''/14)$.⁴⁹ The electron impact dissociation cross section data in Ref. 73 was used to calculate rate constants for $v''=0, 2, 5$, and 8 , for various electron temperatures. The other rate constants for other vibrational levels were estimated by 'eye'. The results are not very sensitive to the exact values chosen because the process of dissociative attachment has the same effect (in the model), but the cross sections are significantly larger. There is an assumption implicit in reaction 2.29, which is that most H^- created in the discharge chamber is destroyed by collisional detachment or by mutual neutralization which will effectively convert the H^- ion into a free atom. Recycling of H^- back into the form of $H_2(v'')$ via associative detachment is neglected because the atom density is so low that the corresponding rate is a small fraction of the other two aforementioned rates, even in the filter region.^{68,69}

Unfortunately, as will be seen in chapter V, this model is not necessarily a very good description of the physical situation because a non-negligible fraction of the population within the various vibrational levels is found in the states of high rotational ($J'' \geq 10$), and molecules with that much rotation cannot be expected to behave the same as molecules that are rotationless,

specifically, one expects them to be significantly more fragile and reactive. For instance, the rate constant for dissociative attachment is very sensitive to the value of the rotational quantum number. For example, the rate constant for $\text{H}_2(2,23)$ is $\sim 10^4$ times larger than that for $\text{H}_2(2,0)$.²⁶ The increase with increasing J'' is not quite so dramatic for higher vibrational levels, but it is still an important effect that is not taken account of properly by the model. Cross section calculations for the various processes, such as electron and atomic collision (de-)excitation, must include the effect of rotation before a truly realistic model can be developed.

D. H^- Density

The last phase of modeling simply predicts the H^- density in the magnetic filter region. The model is very simple in the sense that there is really only one source term, corresponding to dissociative attachment to vibrationally-excited molecules, and two destruction terms, corresponding to ion-ion mutual neutralization and associative detachment of hydrogen atoms to H^- ions. The model must necessarily use local values for the densities and temperatures of the electrons and ions.

Several simplifying assumptions are made that substantially ease the complexity of the model. Transport is neglected, which is equivalent to assuming the time necessary to travel a gradient length is less than or comparable to the relevant scale times for creation and destruction, a criterion which is approximately satisfied at typical parameters. Another very important assumption is that the rate for collisional detachment (see reaction 2.6) is low enough to be neglected compared to other destruction mechanisms, in the filter region. Actually, the cross section is not accurately known in the energy range from threshold (0.75 eV) to about 5 eV (see Ref. 67), but it clear from

many different experiments that it must increase in such a way that the rate constant for collisional detachment is very sharply increasing with electron temperature from 0 to ~5 eV. J. R. Trow calculated the rate constant in his thesis for various electron temperatures using a quasi-linear extrapolation for the cross section, and found that it had the value of 5×10^{-9} , 7×10^{-8} , and $3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 0.5, 2.0, and 5.0 eV, respectively.⁸³ The important point is that, in the body of the plasma, the rate for H^- destruction by this mechanism is very high, $\sim 10^5 \text{ s}^{-1}$, whereas in the magnetically filtered regions of the plasma, the rate drops to a relatively negligible value.

The dissociative attachment rate constant $\langle \sigma v \rangle_{\text{AD}}$ is a weighted average of the rate constants from Ref. 26, which gives values for a wide variety of H_2 rovibrational states. In that work, the assumed electron temperature is 1 eV, which is higher than the actual values in the magnetic filter region of the plasma, typically 0.5 eV. However, as discussed in that work, the dependence of the rate constant on electron temperature is almost flat for kT_e in the range of 0.5 to 2 eV, for the states that have a large rate constant, i.e., the states that contribute the bulk of the averaged rate. In fact, the rate constant for the optimal J'' state of a given vibrational level almost always has the same value, $1-2 \times 10^{-8} \text{ cm}^3/\text{s}$, for a wide range of vibrational levels.

A very useful approximation that is rather accurate was illustrated by Gauyacq.²³ He showed that the peak of the cross section, for the endothermic reactions, can be closely approximated by a single-valued function of the internal scaled energy E_{scaled} , which is defined as

$$E_{\text{scaled}} = E_{\text{true}} - \frac{J(J+1)\hbar^2}{MR_x^2} \quad (2.30)$$

where R_x is the internuclear distance corresponding to the crossing point of the potential curves for H_2 and the $H - H^-$ system, $\sim 2.9 a_0$, J is the rotational quantum number, and M is the mass of the hydrogen atom (see Fig. 6 of Ref. 23). However, the approximation is not completely accurate, especially for large values of J ; also, there is limited data for exothermic reactions. Therefore it was decided to use only Ref. 26, for the sake of consistency. The numerical results of Gauyacq and Wadehra agree well when a straightforward comparison is possible.^{23,26}

The primary H^- destruction mechanism included in the model is the process of ion-ion mutual neutralization. The rate constant for $H^- - H^+$ mutual neutralization has been the subject of considerable controversy,³¹ but it appears that the value is in the range of 0.3 to $1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ for low energies ($\leq 1 \text{ eV}$). The cross section for $H_2^+ - H^-$ neutralization was measured to be $\sim 50\%$ higher than the corresponding H^+ rate, but at somewhat higher energies.²⁹ There is no data that we are aware of regarding $H_3^+ - H^-$ mutual neutralization, however, this cross section is undoubtedly fairly large and increasing rapidly with decreasing energy for small relative energies ($\leq 1 \text{ eV}$). One might also expect that the cross section is somewhat larger than the corresponding H^+ cross section, simply because of the larger size of the ion. It was decided, for lack of better information, that the mutual neutralization rate constant $\langle \sigma v \rangle_{MN}$ for all three positive ions could be assumed to have the value of $1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, independent of energy (the cross section for $H^- - H^+$ recombination scales as $E^{-1/2}$ at low energy, so $\langle \sigma v \rangle$ has no energy dependence). The majority of the ions are dominated by H_3^+ for most discharge conditions of interest presently, so this estimation seems entirely reasonable.

The other destruction mechanism that can be important in some

circumstances is the process of associative detachment of hydrogen atoms to H^- yielding $H_2(v'', J'')$ and an electron.^{68,69} The associative detachment rate constant $\langle \sigma v \rangle_{AD}$ is almost constant over the energy range of interest and has a value of $\sim 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 0.129 eV. Because the atom density is relatively low, this process is not very important compared to ion-ion loss rates, but may become more significant at higher pressures ($> 20 \text{ mTorr}$).

Dissociative attachment to the molecular ions or metastable H_2 is neglected. The dissociative attachment cross sections have been measured for H_2^+ and H_3^+ , and calculated for $H_2 c^3\Pi_u^-$, and the corresponding rates have been calculated by Trow for various electron temperatures.^{18,40,41,84} The rates are smaller than $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in all three cases regardless of electron temperature. Therefore, by very simple arguments, the contribution from the ions alone cannot exceed 0.002 of the total ion density (given the value for ion-ion neutralization assumed presently). Such a small contribution can safely be ignored. The $H_2 c^3\Pi_u^-$ metastable density was measured by Bonnie, et al. in a similar discharge^{16,17} and found to be $\sim 3 \times 10^9 \text{ cm}^{-3}$ (at 30 A of discharge current). That is much less than the ion density and thus the H^- contribution is correspondingly less.

The predicted H^- density is then simple to calculate, once one determines the $H_2(v'', J'')$ distribution and thus the dissociative attachment rate constant $\langle \sigma v \rangle_{DA}$ properly averaged over all $H_2(v'', J'')$ states. One obtains the following formula for the time derivative of the H^- density, which is necessarily zero in steady-state, from which the H^- density n^- can be trivially determined:

$$0 = n_{H_2} n_e \langle \sigma v \rangle_{DA} - n^- \left\{ n^+ \langle \sigma v \rangle_{MN} + n_H \langle \sigma v \rangle_{AD} \right\} \quad (2.31)$$

where n^+ is the total positive ion density, which is approximately equal to n_e if $n^-/n_e \ll 1$, a condition which is usually true. The numerical values turn out such that associative detachment could almost be neglected for the rather low atom densities measured presently. We reiterate that transport is neglected, and that it is possible that this approximation is not a very good one. Obviously, H^- does exit the plasma at the filter, otherwise it could not be extracted! However, due to the strongly inhomogeneous characteristics of the plasma and the magnetic fields in the filter region, it was decided that any model that accurately included transport would require more effort than was justified.

It is useful to make a few quick observations regarding the H^- density. The maximum value of $\langle \sigma v \rangle_{DA}$ for even the most favorable $H_2(v'', J'')$ state is $\sim 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. We can therefore approximate the rate constant as that value multiplied by f_{good} , the fraction of molecules in 'good' (v'', J'') states. Also, loss via associative detachment is usually not important, so we can neglect it. Then n^- is independent of the electron density:

$$n^- = (0.1) f_{\text{good}} n_{H_2} \quad (2.32)$$

If f_{good} is so large that the predicted n^- is comparable to n_e , then the above equations are no longer valid because n_e and n^+ are no longer equal. In that case the scaling is different and n^- can be shown to increase only as the square of f_{good} .

Chapter III

Experimental Procedure

A. H⁻ Ion Source

1. Physical Description

The discharge chamber used for this thesis has been empirically designed for high absolute H⁻ density and is very similar to that used by Kwan, et al.⁸⁵ A conceptual illustration of the chamber is shown in Fig. 3-1 and a much more realistic schematic is shown in Fig. 3-2. The chamber is made out of copper and is cylindrically shaped, with an inside length of 23 cm and an inside diameter of 20 cm. Ten vacuum ports are located on the midplane of the chamber, symmetrically spaced azimuthally, allowing installation of various diagnostics. At two of the ports, located opposite to each other, a semi-circular tungsten filament protrudes ~83 mm into the chamber, mounted on metal chucks that are isolated electrically from the chamber by ceramic feedthroughs. The filament chucks are protected from sputtering erosion by boron nitride cylinders. The chucks are also strongly shielded from charged particles by the magnetic fields. Two other ports have the gas inlet valve and a connection to a high-precision capacitance manometer (MKS Baratron 170M). The calibration of the unit was checked periodically using an U-tube oil manometer and was measured to be accurate to 1% at pressures greater than 50 mTorr, and to be linear to within 2% from 1 to 1000 mTorr. A retractable Langmuir probe and an ion gauge (protected by a 90° bend) are mounted on yet another two ports. In addition, two other ports (again opposite each other) have attached differential pumping apertures and associated plumbing, through which the diagnostic VUV beam travels. Sets of strong samarium-cobalt magnets that have a remnant field of 8200 Gauss are attached to the sidewalls of the chamber,

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Fig. 3-1 Conceptual schematic of volume-produced H^- source.

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Fig. 3-2 Schematic diagram of discharge chamber, viewed from filter flange end. The filter rods are imbedded in the filter flange, except in the 7.5 cm diameter cut-out section at center. Only roughly to scale.

in an alternating polarity, line-cusp configuration. The period of the magnet arrangement is 5. One end of the cylinder has four rows of magnets in a line-cusp array, oriented to make the cusps quasi-continuous at the junction. The other end of the cylinder has four columns of much weaker magnets in rods which pass through the vacuum chamber very near the end wall. This last set of magnets serves to create the so-called magnetic filter region where the reduction in fast electron density (relative to the plasma body) allows H^- to exist in high density. The strength and spacing of the magnets, as well as the distance of the magnet plane from the end wall (~ 1 cm), was determined to be optimal for H^- extraction by previous experimental work on an almost identical chamber.⁸⁶

The magnetic field characteristics are described in more detail because they are important to discharge characteristics. End effects are initially ignored. The field strength scales as approximately as r^n except very close to the chamber wall, where r is radius and n is the magnet period. The center of the discharge chamber is quasi-field-free and the plasma particles are well mixed within this region. The definition of field-free is not immediately clear. The practical definition is the boundary of the region where the primary electrons can travel (based on single particle motion), assuming they were born on axis. The justification for this statement is that the primary electrons create the secondary plasma constituents, so that the spatial profile of the secondary electrons will roughly approximate the region of space where the primaries travel. Actually the secondary electrons have higher cross field diffusivities because of Coulomb collisions and therefore have a broader spatial extent than the primary electrons. The local electron temperature is cooler in the 'spill-over' regions. This effect is important for the magnetic filter region, where it is desired to have a large density of cool (≤ 1 eV) electrons, in order to maintain a

high dissociative attachment rate and a small collisional detachment rate simultaneously. The plasma radial profile was measured on the midplane using a movable Langmuir probe that entered the plasma through a field cusp. The results are shown in Fig. 3-3. The falloff in density begins at a radius of ~ 4.5 cm and is a factor of four smaller at a radius at 6.5 cm. It is interesting that the product of $B r_l$ for a 100 eV electron is 34 G-cm, where B is magnetic field and r_l is gyroradius, because that product is the numerical value of the vector potential at 4.6 cm radius (Lines of force have a constant value of the vector potential in two-dimensional magnetic geometry, also see Fig. 1-2). At the end of the chamber opposite the filter region, the strong line-cusp fields function similarly to the sidewall line cusps, shielding plasma from the end wall while generating a relatively small field in the center of the chamber. The magnetic filter region is of more interest. As previously mentioned, the strength of the magnetic field in the magnetic-filter region and the distance between the filter midplane and the extraction hole have been chosen empirically to maximize the extracted H^- density. Selecting too weak a field allows H^- -destroying fast electrons in, but selecting too strong a field decreases the thermal electron density and therefore the dissociative attachment rate. The optimum field actually depends on the discharge power (or vice versa), as can be seen in the data of Kwan, et al.⁸⁵ The maximum extracted H^- current for the different filter strengths was almost the same in all three cases (at the optimum discharge power in each case) for the different filter strengths.

The overall vacuum system is only a high vacuum (10^{-6} Torr) design, as are all the volume H^- sources the author is aware of. This is important because processes that take place at the wall, such as atom recombination, affect the discharge chemistry strongly. Experiments that involve surface reactions are much more likely to be subject to hysteresis and non-reproducibility than

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Fig. 3-3 Plot of measured electron density and temperature as a function of radius. Note that fall-off is independent of discharge voltage. Other discharge parameters: DC, 20 A and 8 mTorr. Measured along a path through the center of a cusp.

those involving only volume reactions, as is well known. The condition of the discharge chamber walls must be at least reproducible, day after day, for the results of this experiment to mean anything. The condition was satisfied for this data.

2. Operation

The schematic of the electrical connections necessary for running either a DC or pulsed discharge are shown in Fig. 3-4. Separate arc power supplies were used for the two modes of operation. The tungsten filaments were heated in parallel by resistance heating, using a DC power supply that could supply 10 Volts at 400 Amperes, which was more than sufficient to heat the two 1.5 mm diameter filaments. Both outputs of this supply were floating. The discharge arc power supply (DC or pulsed) had its positive terminal connected to the discharge chamber, which functioned as the anode. The chamber was connected to ground via heavy copper braid. It was essential to operate the discharge with an one-point ground, otherwise discharge noise spread throughout the electronics. The negative side of the arc power supply was connected to the the negative side of the filament heating power supply, which was electrically connected to the filament chucks.

The electrical set-up was slightly different for DC and pulsed operation. For DC operation, the discharge voltage was measured directly at the cathode with an ordinary laboratory multimeter. The current was measured using an accurate shunt (< 0.5% error) and another millivolt range multimeter. Several different power supplies were used over the course of the experiment, but they were all similar, supplying 30-50 Amperes at 150 to 300 Volts. All were SCR-fired which means they all had similar electronic noise pollution characteristics, specifically, spikes at 360 Hz. These spikes propagated to the

detector pre-amplifier and did add to the noise of the data, but this was not a significant problem. Broadband RF noise that was clearly originating in the discharge also reached the pre-amplifier, but again this was almost always small. A fan-cooled ballast resistor was inserted between the negative leg of the arc power supply and the filaments during some of the DC operation. The resistor value varied, but was in the range of 1 to 4 Ohms. The resistor provided greater discharge stability as well as some overcurrent protection in case of a short.

The power supply for pulsed operation was designed and assembled by the electronics department of the MFE group at LBL and is shown in a very simplified form in Fig. 3-5. Conceptually, the supply was simply a capacitor bank gated by high-power fast transistors that were gated by an isolated phototransistor. The inherent rise and fall time of the gate was approximately 1 μ s. The actual discharge current did not usually rise this fast for several reasons. First, the inductance of the cables from the supply to the actual discharge chamber slowed the rise time to $\sim 5 \mu$ s at high currents (i.e., 300 Amperes). Also, the conductance of the plasma (due to space charge effects at the filaments) took a finite period of time to rise, especially at high discharge current and low discharge voltage. The time scale of the latter effect was usually the limiting factor. The discharge voltage was measured in the power supply using a 100:1 resistor divider network. The discharge current was measured using a current transformer (Pearson 1114) that had very fast time response (~ 20 ns) and a long droop (~ 50 ms). The current transformer had enough current-time capacity so that saturation was never a problem. When the discharge was operated in the pulsed mode, the usual parameters were 1 ms long pulses every 90-100 ms. These parameters were adjustable and could be changed if necessary. At very high currents (>350 Amperes) it was necessary to

Switch detail

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Fig. 3-5 Schematic of pulsed arc power supply. Only the key components are shown. Switching time is $\sim 1 \mu\text{s}$ into pure resistive load.

reduce the length of the pulse because the charging supply could not supply enough current. The VUV measurements could be taken at any time during or after the pulse, although the electronic noise at the end of a large current discharge pulse (caused by an inductive spike) made measurements difficult in the first 50–100 μ s after turn-off.

In several instances the plasma was operated DC and pulsed simultaneously. In this case the DC arc power supply and the usual SCR filament heating supply were connected to one filament, while the pulsed power supply was connected to the other filament. This type of operation is desirable because one can observe the effect of a small periodic perturbation on the discharge. The pulsed filament was heated with a high-current, step-down transformer. The output of a 110 Volt variac was connected to the input side of the transformer. This arrangement had some pulse to pulse variation because the thermal time constant of the filament was not enormously large compared to the heating cycle time (120 Hz), but the effect was small (<5%).

To run a discharge the gas pressure was first set by adjusting the flow of hydrogen into the chamber with a needle valve. This was always performed with the discharge off. The barocell was zeroed as necessary by comparison with an ion gauge mounted on the discharge chamber. There was a turn-on transient for both DC and pulsed operation which lasted on the order of a minute (for pulsed operation this was averaged over many pulses naturally). During this time, the measured pressure initially decreased very rapidly (faster than response of manometer), then slowly increased until it reached a stable value (time constant was $\sim$ 20 seconds). The temporary drop in pressure is caused by a net loss of gas throughput which is almost certainly due to hydrogen atom coverage of the discharge chamber walls. The opposite effect

occurs when the discharge is terminated. The desorption indicates that there is probably a layer of atoms that is very loosely bound to the surface, besides others that are chemisorbed to the surface. These effects could also be produced simply by heating or cooling the filaments to/from the H_2 dissociation temperature ($\sim 2000\text{ }^\circ\text{K}$), although the magnitude of the pressure changes was somewhat reduced. In any case, no measurements were made during these transient periods. The equilibrium pressure during pulsed discharge operation is the same as the pressure without discharge. For DC discharge operation, the stable pressure is usually higher than the pressure set without the discharge, by approximately 5% at 35 A of discharge current. Unfortunately, we are in the gray area between molecular flow and viscous flow for the pressure and scale lengths used, so exact calculations are difficult. One can definitely say that the gas at the barocell head will have been cooled to room temperature and any atoms will have been recombined (the capacitance manometer is connected to the discharge chamber using $\sim 30\text{ cm}$ of 6 mm inside diameter copper tubing).

3. Condition of Chamber Walls

The monolayer surface coverage time of the discharge chamber walls is only 5 seconds, assuming a base pressure of 10^{-6} Torr, temperature of $300\text{ }^\circ\text{K}$, unity sticking probability, a saturation coverage of 10^{15} cm^{-2} , and a (hydrocarbon?) mass of 100. The base pressure in the discharge chamber is really somewhat worse, $\sim 6 \times 10^{-6}$ Torr. The reason for this poor limit is the small area of the differential pumping holes used to let the laser light through the source. This set-up is believed to be not too different from that used in the work of Eenshuistra, et al. and that of Bacal and coworkers.^{8,61,62,87,88} The larger sources used by Kwan, et al., Hanada, et al. and McAdams, et al. presumably have much higher effective pumping speeds because the extraction

apertures have much more total area.^{85,89,90}

Reproducible data was obtained despite the above mentioned difficulties, and it is believed that this data is relevant to other experiments because of the rather simple conditions necessary to produce it. The chamber and accompanying vacuum system were leak checked with a commercial leak checker that had a detection sensitivity of $\sim 2 \times 10^{-9}$ sccm of He. After the chamber was brought up to air (actually dry argon), it was rough pumped quickly and pumped by a turbo pump (via some plumbing shown in Fig. 3-8). The base pressure in the chamber was measured by a mTorr ion gauge (Varian) attached to the side of the source with a 90° bend (so the gauge would not be covered with evaporated tungsten coming from the filaments). The emission of the ion gauge was calibrated for H₂ against the capacitance manometer, so true base pressure was corrected by a factor of 2.4, the sensitivity ratio for hydrogen and water (very likely the chief constituent of the background). After a day of pumping (or less in most cases), the base pressure had almost reached its terminal value, $\sim 6 \times 10^{-6}$ Torr. A electric discharge was then operated until the measured absorption peaks reached their equilibrium values. The time necessary to reach these values was generally 3 hours or less. After this had been done once, it was not necessary to repeat it each day. The absorption measurements were very close to their base values after a few minutes of discharge operation. The source was generally given a half-hour warm-up period, to be safe.

The possibility of mercury contamination of the source chamber altering the discharge chemistry was investigated and the conclusion was that there is no evidence of this process occurring. In order to reach the discharge chamber, the mercury would have to migrate from the mercury oven through effectively four stages of differential pumping to the discharge chamber. The details of the

investigation are reserved for Appendix 1, but the results are quickly summarized here. First, a careful examination of the visible emission spectrum of the discharge yielded no evidence of mercury atom emission. A quantitative upper limit on the mercury density is no more than 10^{10} cm^{-3} , and is probably at least a factor of 10 less (the excitation cross section data is of dubious quality). Also, H^- measurements using the photodetachment method were performed when the discharge chamber was on the VUV absorption test stand (and therefore presumably contaminated if any contamination ever took place). However, these results agreed well with data taken almost a year earlier on a different test stand, before the source had had the chance to become contaminated). Finally, no day to day or hour to hour variation of the neutral species data was observed.

Despite the fact that we could generate reproducible data, it was also found that the characteristics of the walls of the chamber could be changed by operating the discharge in a high-power (pulsed) mode (i.e., 300 A discharge current as opposed to 25 A usually) in which the tungsten filaments were much hotter than usual and therefore had a much higher evaporation rate. That the walls in fact did change after running in what will henceforth be called 'high-power' mode as opposed to 'low-power' mode was ascertained by measuring four different quantities: the thermal electron parameters, the atom density, the $\text{H}_2(v'',J'')$ density (for certain (v'',J'') combinations), and the H^- density (by the photodetachment technique). These quantities were measured in the low-power DC mode at discharge parameters of 35 A, 90 V, and 8 mTorr. In one case the history of operation was all low-power (but the terminal values had long been reached); in the other case, the discharge was run at high-power parameters (1 ms pulses @ 10 Hz) for twenty minutes or more immediately previously. It was observed that the atom density, the $\text{H}_2(1,1)$, $(1,5)$, $(1,9)$, $(2,1)$,

(3,1), (4,1) and (5,1) populations, and the H^- density all decreased by a factor of ~ 2 , and that the electron temperature and the plasma potential had decreased by small but measurable amounts. All of these data indicate that the walls somehow became better at 1) recombining atoms into molecules, and 2) more effective at relaxing vibrationally-excited molecules (which in turn relax the thermal electrons that excite those molecules). It also indicates that the hydrogen atoms are not the primary relaxation agents for $H_2(v'',J'')$. It is very interesting that the H^- density correlates with the $H_2(v'')$ density, but what was cause and what was effect is not unambiguous. The wall-catalyzed atom recombination rate and $H_2(v'')$ relaxation rate were measured directly when the walls were in the 'high-power' state and found to be significantly decreased. The observed recovery time (under vacuum) from 'high-power' walls to 'low-power' walls varied, but always was on the time scales of hours, and the effect sometimes lasted overnight partially. The source could also be recovered quickly by bringing the chamber up to air or argon (the argon line undoubtedly had some impurities in it.) The tungsten deposited during high-power operation is exposed to a very large H-atom flux during the discharge and is assured of being instantly H-atom passivated. Also, we see no evidence of wall pumping during the low-power mode after the high-power mode, other than the initial turn-on transient which lasts approximately one minute and is present even in the case of no high-power history. Therefore the discrepancy is not simply a loss of particles. The base pressure in the source decreases somewhat after high-power operation, and recovers on the same long-term time scale as the measured discharge constituents, an interesting clue.

Several statements can be made regarding this hysteresis effect, but none definitely explain the behavior. If the recovery time is attributable to

re-coverage by impurities, then the partial pressure of the impurities which are important must be a very small fraction of the measured base pressure. This is certainly possible, as it is expected that the main constituent of the base pressure is water. A residual-gas-analyzer (RGA) is not available, unfortunately. It is possible that the nature of the change of the surface is chemical, and that the low-power data applies to walls that are actually tungsten covered with some impurity, and that the high-power case applies to pure(r) tungsten surfaces (that are H-atom passivated). The background oxygen density and the presence of small DC electric fields (2 V/cm!) are known to affect the formation of steps on tungsten surfaces.⁹¹ Another possible explanation could be grossly increased surface roughness caused by very rapid tungsten deposition. A very rough surface would clearly be more effective at catalyzing certain reactions simply because one macroscopic surface collision could involve several microscopic surface collisions. Indeed, in the limit of the surface as a black body, all hydrogen flux would return to the volume as molecules at 300 K, regardless of the incoming form: H^0 , $\text{H}_2(\text{v}^{\text{v}}, \text{J}^{\text{v}})$, H^+ , etc. It is not clear what would cause the surface to lose the roughness. The wall is well-cooled at all times, and the energy of bombarding ions or neutrals is only 5 eV. Another possible effect is related to the fact that commercially available tungsten often has considerable carbon contamination.⁹² Perhaps operating the filaments at very high temperature causes some amount of carbon to contaminate the walls of the device. The carbon will be removed from the walls at some unknown rate by the process of methane formation. Practically speaking, it is not possible to further investigate this issue with the equipment available to the MFE group presently.

The key question with regards to the observed wall hysteresis effect is, how does this data relate to that of other experiments? We believe that we can

separate most existing experiments into either the low-power or high-power category with a fair degree of confidence. Generally speaking, the low-power category is characterized by low discharge power (low evaporation rate of tungsten), poor pumping, and poor base pressures in the discharge chamber. 'High-power' is characterized by high discharge power (lots of fresh tungsten), good pumping, and low base pressures. It is believed that the work of Bacal, et al., Bonnie, et al. and Eenshuistra, et al., as well as the low-power data here are at the low-power side of the scale.^{8,61,93} The large-scale experiments of Kwan, et al., Hanada, et al. and McAdams, et al., which all had very large discharge currents (500–1000 A) and relatively good pumping geometry should fall on the high-power side of the scale.^{85,89,90} The increased relaxation of vibrationally-excited molecules observed at high-power may explain why H^- current measured in various experiments does not seem to scale well with discharge power. However this is only speculation at this point. It would be of interest to measure the dynamics of this low-power, high-power effect as a function of the pumping on the source. In particular, it would be of interest to determine whether there is a difference in the base low-power values of the atom density and $H_2(v'',j'')$ densities between those measured in a typical 'dirty' system and those measured in all-metal, bakable, UHV system. The author was not able to perform these experiments for practical reasons.

B. VUV Absorption System

The technique employed to measure the density and temperature of the neutral particles is single-photon absorption, in the vacuum ultraviolet (VUV). Measurement of absolute photon flux is not required, and the oscillator strengths of the transitions involved are known,^{94,95} which allows determination of absolute concentrations of hydrogen atoms and molecules in

specific quantum states. Laser-induced-fluorescence allows spatial concentration profiles to be determined, but absorption, while useful only for measuring line densities, can be made much less susceptible to background signal (from plasma-produced photons collected at the detectors). This is important because the background photon flux is very large. Absorption also requires less extensive optical access to the plasma, as there is no need for large-solid-angle collection optics. Measuring the population of ground-state hydrogen atoms or electronic ground state hydrogen molecules directly requires VUV radiation, from ~94 to ~125 nm for the present data (see Fig. 3-6). Narrow-band tunable VUV is generally available only through non-linear processes in gases, such as four-wave mixing.

Resonant four-wave sum-frequency mixing (FWSM) is a method of VUV production which has been reported for generation of a broad range of frequencies including the Lyman series in atomic hydrogen.⁹⁶ It allows production of large VUV fluxes without phase-matching, and it produces VUV over a wide continuous range of frequencies by changing the frequency of only one of the lasers. A review of the principles and applications of FWSM has been recently published.⁹⁷ Briefly, FWSM is a coherent process in which a non-linear medium, mercury vapor in this application, is exposed to intense electric fields of (angular) frequencies ω_1 and ω_2 , and converts some of the energy from those fields into radiation at $\omega_{\text{VUV}} = 2\omega_1 + \omega_2$. By choosing $2\omega_1$ to correspond to the energy difference of the ground-state and an excited-state of the medium of the same parity, this process is made resonant. The intense electric fields needed generally require high-power pulsed lasers. Fig. 3-7 schematically illustrates the process of FWSM, specific to the present application.

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Fig. 3-6 Energy level diagram of the hydrogen atom and molecule, showing most relevant states. Rotational levels are too dense to show here.

Fig. 3-7 Energy level diagram for mercury, showing the states relevant to the two-photon-resonant four-wave mixing scheme used here. All three of the excited states shown have been used as the resonant state. This specific illustration applies to L- γ generation. VUV loss in the cell by mercury absorption is insignificant.

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1. Experimental Arrangement

A schematic of the experimental apparatus is shown in Fig. 3–8. An excimer laser pumps two dye lasers, which generate the ω_1 and ω_2 beams. These beams are merged in a prism, and are focussed by an achromatic lens into a mercury vapor cell, where the VUV is generated coincident with the original beams. Two stages of differential pumping immediately follow. All three beams are then incident upon a grating which disperses them. The first order VUV beam, the probe beam, is directed towards the plasma of interest, while the second order VUV beam, the normalization beam, is directed onto a detector. Light of all other wavelengths is discarded at this point. After passing through the plasma chamber, which is differentially pumped, the probe beam enters a monochromator which is tuned to allow full transmission of the beam, while rejecting most of the background photon flux from the plasma. Another detector is mounted on the output side of the monochromator. The purpose of the normalization detector is to reduce the statistical noise of the baseline. The statistical noise of the ratio of the signals from the two detectors (at fixed conditions) is much smaller than the pulse to pulse variation of the VUV intensity.

The pump laser is a XeCl excimer laser (Lambda Physik EMG201E) pulsed at ~ 10 Hz. Each pulse provides approximately 450 mJ at 308 nm in 20 ns. The pump beam is directed into two dye lasers (Lambda Physik FL2002E) using a 50–50 beam splitter. The ω_1 dye laser is operated at one of three wavelengths, depending on which mercury–atom excited state is used as the intermediate resonance state. The three states employed are the $(6sns) \ ^1S_0$, where $n=7, 8$, or 9. The corresponding wavelengths are 625, 537 and 510 nm, respectively. The ground mercury state is $(6s^2) \ ^1S_0$. The fundamental beam has ~ 20 mJ of energy in all three cases. An intracavity etalon reduces the linewidth to $\sim 0.05 \text{ cm}^{-1}$,

Fig. 3-8 Schematic of VUV absorption system. Electronics are shown separately.

and a KDP or BBO crystal is used to double the frequency of the emitted light, yielding ~ 3 mJ of frequency-doubled light. Frequency calibration is performed by observing fluorescence of I_2 vapor produced by the fundamental beam in a glass cell.⁹⁸ The accuracy of the calibration is estimated to be $\pm 0.02 \text{ cm}^{-1}$ for the frequency-doubled light. The ω_2 dye laser generates ~ 15 mJ of light, at various wavelengths ranging from 350 to 730 nm, depending upon what final VUV wavelength is desired as well as the intermediate resonance state in use at the time. This laser is operated without an intracavity etalon and the bandwidth is nominally 0.20 cm^{-1} . The frequency calibration of this laser is performed indirectly by observing absorption of generated VUV in krypton, xenon, or H_2 at known frequencies. Both dye lasers were found to have extremely good wavelength agreement with the nominal value. The frequency-doubled beam from the ω_1 laser and the fundamental beam from the ω_2 laser are directed to a calcite Glan-Taylor prism which merges the two beams. The beam paths have been chosen so that the beams are coincident in time, and the various prisms are adjusted to make the two beams spatially coincident. The final alignment is done by optimizing the VUV output.

The two dye laser beams are focussed by a 25-cm focal length quartz achromatic lens into the mercury-vapor cell in which the VUV is generated colinearly with the original laser beams. The design of the cell is loosely based on heat pipe technology.⁹⁹ Two different cells were used over the course of the experiment; the latter version is shown in Fig. 3-9. The cell is constructed out of stainless steel to avoid chemical reactions. The input window is a piece of Suprasil quartz plate. A 0.012-mm thick stainless steel foil is mounted on the exit arm, through which the lasers burn a hole in a few minutes, forming a tight differential pumping constriction ($\sim 0.20 \text{ mm}^2$) that is automatically aligned with the beams. The central region of the cell is heated to $\sim 160^\circ \text{C}$,

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Fig. 3-9 Detail of mercury vapor oven. Definitely not to scale.

yielding a mercury vapor pressure of a few Torr. Helium, typically at a pressure of 30 Torr, is used as a buffer gas to help confine the mercury vapor.

Absorption of the VUV by the mercury itself is possible, but the cross section for this process is small enough so as not to be a problem, except in a few small spectral regions.¹⁰⁰ The helium inlet location and the restrictor discs are chosen so as to minimize flow and turbulence in the central region of the cell. A capacitance manometer is connected to the top arm of the cell to measure the pressure. Water cooling lines are wrapped around the upper and side arms adjacent to the intersection region in order to condense mercury before it travels an appreciable distance. Liquid nitrogen cooling lines on the input arm serve to condense any remaining mercury vapor before it reaches the input window. Two stages of differential pumping immediately follow the cell. The first stage is evacuated by a mechanical pump with an effective pumping speed of a few l/s, and has a pressure of ~1 Torr. The second stage is pumped by a turbo-pump with a pumping speed of approximately 100 l/s. The pressure in the second stage is not measured but is believed to be ~1 mTorr.

The beam passes through another differential pumping aperture into a 35-cm diameter chamber (the 'grating chamber') which contains a blazed grating (Milton Roy, 2400 grooves/mm, blaze angle 5.5° , radius of curvature 100 cm), a two-stage chevron microchannel plate (MCP) detector (Varian 8946ES plates), and a photodiode sensitive to the visible and near UV. The chamber is pumped by a liquid nitrogen trapped diffusion pump, with an effective pumping speed of 600 l/s. The photodiode is used to check system alignment under vacuum by collecting stray light from the grating. The grating is mounted in a homemade two-axis tilter which is controlled by two externally-mounted micrometers. The probe beam is refocused by the grating (actually the focussing is astigmatic) and is directed 45° from the incident beam

through the plasma chamber. The normalization beam detector, shown in Fig. 3-10, is positioned to completely intercept the normalization beam from the grating. A series of biased shields prevents signals caused by charged particles impinging upon the detector. Background signal from this detector, caused by stray light of other wavelengths, is negligible ($< 0.1\%$) compared to the primary signal.

The probe beam passes through the plasma into the vacuum monochromator (Acton VM502, 0.2m), which has its entrance slits at the horizontal focal point of the probe beam. Two collimating discs slightly larger than the beam size are placed on each side of the plasma chamber in order to reduce background photon flux and to allow differential pumping of the plasma source. The monochromator slits are adjusted so that the full beam passes through without attenuation. The probe beam detector, which is similar in construction to the normalization beam detector, is attached to the output side of the monochromator. The frequency resolution of the system is controlled entirely by the narrow VUV bandwidth, not by the monochromator, which acts simply as a tunable narrow-band filter to increase the signal-to-noise ratio at the probe beam detector.

The signal from each MCP detector is sent to a charge-sensitive pre-amplifier (one is Ortec 113, the other is home-made) that has a $50\ \mu\text{s}$ decay time, and is sampled with a gated integrator (Stanford Research Systems SR250) using a $3\ \mu\text{s}$ window and a $1\ \mu\text{s}$ delay. These values were chosen empirically so as to minimize background signal caused by the unavoidable electronic noise generated by the firing of the excimer laser. The linearity of both detectors was verified using screens of known transmission, and the proportionality of the two signals was verified. The integrator output signals are fed into a multiplexer (HP 3495A), whose output is measured by a digital voltmeter

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Fig. 3-10 Generic schematic of microchannel plate detector assembly. Sometimes only one plate is used. Ion shield is necessary only on normalization detector.

(HP 3437A), and collected by a computer (HP 9920) while scanning the frequency of the ω_2 laser(which scans ω_{VUV} also). A complete schematic of the electronics used is shown in Fig. 3-11. Typically data from 100 laser pulses are recorded for each of ~ 50 scan points, although these values were adjusted as necessary, depending on how relevant statistically error was for a given measurement. The spacing of scan points is usually $\sim 0.3 \text{ cm}^{-1}$, approximately the same as the VUV bandwidth. Data recorded between laser pulses is used to remove baseline drift of the boxcar integrators.

Only one spectral absorption line was scanned at a time during actual operation because most of the spectrum is empty space for our (sub-Doppler) resolution. Also, if ω_{VUV} changes too much (of order 200 cm^{-1} or more), the geometrical factor associated with the aiming of the probe beam from the first grating to the monochromator input slit will change (the beam will start to be apertured), yielding a changing baseline.

The estimated VUV flux is about 10^9 photons/pulse, although this quantity depends on the value of ω_{VUV} , particularly when ω_{VUV} is below the ionization threshold of mercury. The estimate was made by comparing the average single photon signal with the full pulse and scaling by the estimated efficiencies of the gratings and detectors. The actual photon yield was unimportant, as long as it was enough to yield a good signal-to-noise ratio. The VUV photon flux was far below saturation intensity in all cases.

To determine the VUV bandwidth, an absorption profile of Kr was measured. The absorption profile of the krypton line at 103.0023 nm has an observed width (FWHM) of 0.30 cm^{-1} . Krypton has a Doppler width of 0.13 cm^{-1} at room temperature. Assuming the linewidth and the laser bandwidth add in quadrature, we obtain 0.27 cm^{-1} (FWHM) for the VUV bandwidth. The VUV bandwidth will actually vary a little with the

Fig. 3-11 Diagram of electronic arrangement used to collect VUV absorption data. The computer controls only the multiplexer and the voltmeter, and is really only a passive component.

wavelength and the oscillator grating order of the ω_2 laser, so the above value is given here merely as a typical bandwidth.

It should be mentioned that the lasers are not completely spectrally pure, which causes the VUV to be spectrally impure also. The fraction of impurity radiation which reaches the primary detector, designated the leakage fraction, is important since this fraction will determine the maximum true attenuation that can be measured. This fraction was reduced, as described in section 3, to $\leq 0.5\%$.

2. Data analysis

The transmission $T(\lambda)$ of the plasma for the VUV probe beam is measured as a function of wavelength in the neighborhood of an appropriate transition by measuring the (normalized) signal from the primary detector with and without discharge in the narrow spectral region surrounding the transition Doppler width, from which the absorbance $a(\lambda)$ and the integrated absorbance A can be calculated:

$$A = \int a(\lambda) d\lambda = \int -\ln [T(\lambda)] d\lambda = \int -\ln [I_{\text{on}}(\lambda)/I_{\text{off}}(\lambda)] d\lambda \quad (3.1)$$

where $I(\lambda)$ is the probe beam signal divided by the normalization beam signal and the subscript refers to the discharge status. The center wavelengths for the atomic and molecular lines are found in references 95 and 101, respectively.

Actually, for most of the data presented, the normalized absorbance was only measured with the discharge on and the baseline was determined by performing a linear fit to the flat line segments on both sides of the absorption structure. The portions of the spectrum that were used for the fit were

determined by the operator for each measurement. It was verified experimentally many times that this procedure produced results indistinguishable from the on/off method. In the case of a close co-incidence, the width of the spectrum measured was expanded if necessary so that 'empty space' was on both sides of any structure observed. The method was also verified by performing measurements with the discharge, filaments, and gas off. During these tests the baseline was fit to the sides of the measurement and thus any peak observed would have to be a systematic error. No peaks were observed within the statistical errors. The advantage of operating the system in this manner, other than the time savings (which was substantial), was that the discharge did not have to be constantly turned on and off for each run, which makes for more consistent data.

The data interpretation is straightforward. We first obtain formulas for the line density Π ($= n l$, where n is average density over path length and l is path) and the translational temperature on the assumption that the VUV probe beam is perfectly monochromatic. Small corrections necessary will be discussed in the subsequent section. The integrated absorbance is proportional to the line density, regardless of the shape of the transition lineshape. The proportionality factor G is the integral of the cross section over wavelength in the region of the resonance, which can be written in terms of the oscillator strength:

$$G = \int \sigma(\lambda) d\lambda = \pi f r_e \lambda_0^2 \quad (3.2)$$

where f is the transition oscillator strength, r_e is the classical electron radius, and λ_0 is the center wavelength of the transition. The line density Π is given by

$$G = \int \sigma(\lambda) d\lambda = \pi f r_e \lambda_0^2 \quad (3.3)$$

The width of the absorption peak is assumed to be determined entirely by Doppler broadening. Fine structure (for the atomic lines), Stark broadening, Zeeman effects, etc. are all very small for the transitions and plasma parameters used presently (although fine structure is not negligible for Lyman- α near room temperature). The operational procedure for determining the translational temperature consisted of performing a least-squares fit of a Gaussian to the observed absorbance profile and then deriving the temperature in the obvious way from the fit. All three variables, center location λ_0 , peak height A_m , and (1/e half-)width $\Delta\lambda$ were allowed to vary during the fit. The initial estimates could be input by hand to the computer but were usually selected by the computer in a trivial manner. These estimates were nonetheless very close to the final result for most of the data. The derived temperature $kT_{H(H_2)}$ is simply given by

$$kT_{H(H_2)} = \left[\frac{\Delta\lambda}{\lambda_0} \right]^2 \frac{Mc^2}{2} \quad (3.4)$$

where Mc^2 is the mass of the hydrogen atom or molecule (in eV).

A plot of absorbance vs wave number is shown in Fig. 3-12 for the H-atom transition $1S \rightarrow 4P$ (Lyman- γ) for typical discharge parameters. In this instance the measured H-atom line density is $2.55 \times 10^{14} \text{ cm}^{-2}$, with an error of ~3%, as discussed in section 3. The path length in the source is 22.4 cm, leading to an average number density of $1.14 \times 10^{13} \text{ cm}^{-3}$. The atom temperature (2/3 of average kinetic energy, assuming isotropy), as determined

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Fig. 3-12 Hydrogen atom absorption measurement using the Lyman-gamma transition. Discharge conditions are DC, 25 A, 145 V, and 15 mTorr. The inferred line density and temperature are $2.55 \times 10^{14} \text{ cm}^{-2}$ and 0.132 eV, respectively.

is measured to be 0.132 eV, and is estimated to be accurate to within 10%.

The oscillator strengths for the H-atom Lyman series transitions are well known and are certainly more accurate than any other quantity in this experiment.⁹⁵ The oscillator strengths for the molecular absorption lines are assumed to be the product of an electronic-vibrational factor, given by Allison and Dalgarno and stated to be accurate to 6%, and the usual Hönl-London factors.^{94,102} Some discussion is warranted on the accuracy of this assumption. Several factors may alter the above simple view and both are discussed by Abgrall, et al. in a paper that combines theory and experiment.¹⁰³ First of all, centrifugal distortion of the potential curves, present for v'' or $v' > 0$, will alter the vibrational wave functions, which means that the overlap integrals used to calculate the oscillator strengths will change. This is true even for $\Delta J=0$ transitions. These corrections could have been calculated in a (rapidly converging) iterative manner by Allison and Dalgarno, but would have required orders of magnitude more computer time because every transition will have its own unique factor. However, as discussed in Ref. 103, these corrections are small for low J values and good original overlap. The second problem relates to the fact that coupling between adjacent high-lying electronic states will have the net effect that the observed individual (v, J) states near close coincidences are really admixtures of the two original states. For example, it is seen in Fig. 6 of the work of Dabrowski that the states ($B^1\Sigma_u^+, v''=12, J''=4$) and ($C^1\Pi_u^+, v''=2, J''=4$) are very close.¹⁰¹ Calculations and experiment in Ref. 103 showed that these states were strongly perturbed. In the present study it was also observed that the oscillator strength of the $C \leftarrow X\ 2 \leftarrow 5\ R(3)$ transition was perturbed. This conclusion was based on measurements of the $C \leftarrow X\ 2 \leftarrow 5\ R(1)$, $C \leftarrow X\ 2 \leftarrow 5\ Q(1)$ and $C \leftarrow X\ 2 \leftarrow 5\ Q(3)$ transitions at fixed discharge conditions. Therefore, no data was taken from transitions that were suspect, as determined

by a figure similar to that of Fig. 6 in Ref. 101 but extended to a wider range of energies.

It is believed that the data presented is not significantly affected by either type of perturbation. This conclusion is based on the results of various measurements. First of all, several different v'_s were usually used for measuring the rotational distribution of a given v'' , because that avoided the necessity of changing dye circulators and realigning the lasers through the vacuum system. The measured distributions (after dividing by the J' -dependent degeneracy values) were very smooth curves. Second, $C \leftarrow X$ Q transitions (which necessarily terminate on the $C^1\Pi_u$ state) are not subject to the admixing problem because the '-' branch of the C state does not couple to the B state. Also, the population of a given (X, v'', J'') state was sometimes measured using different final upper states, and these measurements almost always agreed. For instance, the density of the $C(4,1)$ state was measured using the $C \leftarrow X$ $1 \leftarrow 4$ Q(1) and $B \leftarrow X$ $9 \leftarrow 4$ R(1) transitions and found to agree to within ~10% (this is comparable to the statistical error). Similar comparisons were performed on several rotational levels of the $v''=0$, $v''=1$, and $v''=3$ vibrational manifolds. This inspires confidence in the results of Allison and Dalgarno. Of course, it should be noted that the band strength factors of Ref. 94 are more likely to have problems when both v'' and v' are large, because the overlap integrals of the vibrational wave functions have more cancellation generally. In the few cases where distinctly different values were inferred from measurements using different final states, it was often determined that the cause was a coincidence with an undocumented (by Dabrowski) line, based on measurements of the same initial state, but using a different rotational branch, or based on measurements of the other rotational states within the same vibrational manifold. In some of the cases, the problem

was caused by the admixing effect before the author completely understood it, however, none of this data is presented here.

3. Corrections and Uncertainties

The systematic and statistical errors inherent in this system are discussed. In the first phase of data reduction, the measured absorbance profile must be corrected for the finite VUV bandwidth. This aspect does not depend on the oscillator strength (directly), but only the measured absorption profile and the measured VUV bandwidth $\Delta\lambda_{\text{VUV}}$ (this quantity is a 1/e half-width). Roughly speaking, the reason this correction is necessary is that the average of the logs is not, in general, the log of the averages. More specifically, the measured transmission T at a given will be a convolution of the VUV beam spectral profile with the frequency-dependent exponential absorption:

$$T = \int f_{\lambda_{\text{VUV}}}(\lambda) e^{-\Pi\sigma(\lambda)} d\lambda \quad (3.5)$$

where $f_{\lambda_{\text{VUV}}}$ is the spectral power distribution of the VUV probe beam whose center wavelength is λ_{VUV} , normalized to unity in λ space, and $\sigma(\lambda)$ is the absorption cross section for the transition of interest. We assume the absorption feature is isolated, so that the integral covers only the immediate neighborhood of this particular absorption line. Only in the limit that $\Delta\lambda_{\text{VUV}}/\Delta\lambda_{\text{actual}} \rightarrow 0$ will the transmission be given by the simple expression which we initially assumed is applicable in order to derive Eq. 3.1:

$$T = e^{-\Pi\sigma(\lambda_{\text{VUV}})} \quad (3.6)$$

where $\Delta\lambda_{\text{actual}}$ is the true (1/e half-) width of the absorption feature. It is not possible to determine an analytic correction for general A_m , and $\Delta\lambda_{\text{vuv}}/\Delta\lambda_{\text{actual}}$, where A_m is the maximum true absorbance. However, approximate corrections to the measured line density and temperature can be determined in the limit of finite A_m and small $\Delta\lambda_{\text{vuv}}/\Delta\lambda_{\text{actual}}$ (see Appendix 2). Life is simpler in the limit of small $A_m \ll 1$, which is relevant for most of the $\text{H}_2(\nu, J'')$ data for $\nu \geq 2$, because in that case it is sufficient to expand the exponential in Eq. 3.5 to first order only. The rest of the present paragraph is specific to that case. The measured line density Π will be correct regardless of $\Delta\lambda_{\text{vuv}}/\Delta\lambda_{\text{actual}}$. The correction to the Doppler temperature depends on what shape one assumes for the VUV spectral profile and the transition spectral profile. We assume that both are Gaussian. This is supported by the fact that the measured absorbance profiles are almost always well fit by a single Gaussian function. Also, the uncorrected Doppler temperature measured (at low absorbance) for room temperature H_2 (292° K) is only about 330° K, indicating that $\Delta\lambda_{\text{vuv}}$ and $\Delta\lambda_{\text{actual}}$ must add in quadrature or close to it, which implies that the correction to the measured temperature is simply additive. The correction scales as $M\lambda_0^2$, where M is the mass of the absorbing species and λ_0 is the center wavelength of the transition. M is either 1 or 2 proton masses. The correction numerically is then 40° K for H_2 at 111 nm and 17° K for H at L- γ . The correction is ignored for the hydrogen atom data because it is much smaller than the statistical variation in the measured temperature at fixed discharge conditions. The correction is applied to the hydrogen molecule absorption data.

The statistical error is generally less than 5% for the line density measurement as long as the peak absorbance A_m is larger than 0.2 or so. When A_m decreases beyond this limit, statistical errors become the dominant source

of uncertainty. The line density Π is observed to be less sensitive than the temperature to the statistical noise. This property was verified by numerical computer simulations of noise on a perfect Gaussian. When A_m was very small ($\leq 5\%$), the measured temperature could vary by as much as a factor of two (if the alignment of the VUV system was poor) while the measured line density varied by much smaller factors. Therefore, every effort was made to obtain the best alignment possible when measuring low absorption transitions.

When the peak absorbance A_m is large (≥ 4), the statistical error was small and other systematic errors became important. The systematic error of a line density measurement depends on three factors: the ratio of the transition linewidth to the probe bandwidth, the maximum true absorbance, and the anomalous VUV leakage fraction discussed previously. The latter factor is the one most difficult to estimate accurately. This undesired radiation will not be absorbed by the hydrogen atoms or molecules to the same extent as radiation within the central line, which causes a large error in the attenuation measurement when the attenuation is large. The error introduced determines the maximum true attenuation that can be measured accurately. To reduce the spectral impurities, a VUV absorption spectrum is measured for a transition which should be optically opaque at line center ($I_{\text{transmitt}}/I_{\text{incident}} < 10^{-4}$). With this attenuation, any residual transmission at line center is due to spectral impurities. The alignment of the laser optics is then adjusted to minimize this transmission. A D_2 line was selected [$B \leftarrow X \ 7 \leftarrow 0 \ P(2)$, at $96,686.95 \text{ cm}^{-1}$],¹⁰⁴ as its linewidth (0.62 cm^{-1} FWHM) is wide enough to completely absorb the desired VUV line but narrow enough to give high sensitivity to spectral impurities. At optimum alignment, the fraction transmitted is $\sim 0.3\%$. Practically speaking, this error can be made relatively unimportant simply by using a weak enough transition for a given initial state.

Neglecting the leakage fraction, the fractional error in the measured absorbance caused by the finite bandwidth of the probe beam can be shown to be proportional to the product of the oscillator strength and the square of the VUV bandwidth (see Appendix 2 for details) for a VUV line shape that is Gaussian, and a bandwidth that is small compared to the transition linewidth. This implies that to minimize this error, the VUV bandwidth should be small, and the absorbance should be small.

Numerical analyses were performed to determine the error in the measured line density as a function of the bandwidth ratio, the leakage fraction, and the maximum absorbance. The transition lineshape was assumed to be Gaussian. The probe beam spectral profile was also assumed to be Gaussian, except for the leakage factor, given as a parameter, which was assumed to be so far off center as to be unattenuated. The error is always such as to underestimate the true line density. For the measurement of section 2, where the bandwidth ratio was ~ 11 , the maximum absorbance was 2.2, and the leakage factor was measured to be $\sim 0.5\%$, the line density error was 3%, and was mostly due to the leakage factor, not the bandwidth ratio, which would have given an error of $\sim 0.3\%$ by itself. A study of the error produced by different parameters indicated that the primary source of error in this parameter regime is the fact that the leakage factor is not small compared to the maximum true attenuation.

Steering of the beam by a non-uniform plasma could cause an error in the measurement. A simple calculation was performed to determine the maximum deflection of the beam at the monochromator input slits that could be expected due to a transverse gradient in the atom density (and therefore index of refraction), and it was found that the deflection is very small compared to the slit size. This is to be expected, since the real part of the dielectric function

has a maximum amplitude of the order of the wavelength (~ 100 nm) divided by the $1/e$ length (~ 10 cm), or 10^{-6} . It is noted here also that no off-resonance continuum absorption is observed with the discharge on.

The measurable line density range of the system depends on the temperature of the absorber and the oscillator strength of the transition. Generally, the atomic absorption lines have relatively strong oscillator strengths, while the molecular absorption lines are weaker because the total transition strength is spread among more discrete transitions. Temperatures observed were in the range of room temperature to 0.4 eV, with 0.1 eV being typical for the atoms. The bandwidth of the generated VUV corresponds to a H-atom temperature of $\sim 17^\circ$ K, so any temperature that can be reasonably expected in a plasma can be measured (although at high absorbance and low temperature the error in the measurement becomes larger).

C. Electron Measurements

1. Conventional Probe Analysis

An ordinary Langmuir probe, shown in Fig. 3-13, was used to measure the thermal electron density and temperature, both in the body of the plasma and in the magnetic filter region. The probe is much larger than a Debye length at all times, so that sheath effects are negligible. We therefore use simple probe theory, discussed in Schott, for example.¹⁰⁵ In the plasma body, the effective probe area is simply treated as the total exposed area of the cylindrical probe tip, which is 3.2 mm long and 1.0 mm across, without regard to shape, because the sheath thickness is always very small compared to the tip size for the present study.

The only real question about the probe measurements is that which applies to all probe data: does the probe significantly perturb the plasma? The

Shield (Molybdenum, water-cooled, electrically floating)

Probe tip is molybdenum, has 1.0 mm diameter, extends 3.2 mm past shield. Insulator (alumina) not shown.

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Fig. 3-13 Schematic diagram of Langmuir probe, showing basic probe geometry. This probe was used for ordinary probe data and Druyvesteyn data, but not H^- photodetachment data.

answer is definitely no in the body of the plasma, based on the measured perturbation on the probe induced by the introduction of a second probe. This is not surprising for several reasons. First, the primary electron density is highest in the plasma body, yielding energetic production of new plasma. Also, the diffusion coefficients are largest in this region where the magnetic fields are very weak, so that the density decrease of plasma body caused by the (plasma-destroying) metal probe is spread throughout the central region. The decrease in plasma density observed when a second probe was temporarily installed was found to be mainly caused by the increased loss of primary electrons, not by the loss of thermal plasma constituents. This is known because when the second probe was biased more negative than cathode voltage (which would eliminate all electron current, but increase the ion current to it) the plasma density increased compared to the case where the second probe was at floating potential. The floating potential of the probe is more negative than one might expect, typically -7 Volts, because the primary electron flux is large. Thus the thermal electron current to the probe is actually very small.

Returning to the perturbation problem, the question is more important at the magnetic filter region, because here the effective volume being sampled is smaller. Additionally, thermal plasma constituents are not created here, but must diffuse across the filter field, thus, any additional sink terms are more important. If the dominant loss of plasma is along the field lines (to the filter rods), then the probe is surely a significant perturbation, because the path length between metal surfaces is halved. On the other hand, if the cross-field diffusivities are large enough, then the probe will be less of a perturbation. The situation is really more complicated than this still, because generally speaking, the ion and electron flux is not locally ambipolar in this type of geometry.¹⁰⁶ Initially, a large thin disc (4 mm diameter) was used as the probe tip in the filter

region, oriented normal to the local field lines. However, it became clear that the results were in error because the probe was significantly perturbing the plasma near the knee of the probe characteristic. It was decided to use the ordinary probe tip described earlier, except that the effective area was estimated at 8 mm^2 , because of magnetic field effects. The orientation was such that the tip was pointed towards the center of the discharge chamber. This arrangement results in the least perturbation of the plasma. Even these results showed some evidence of decreased plasma density when the probe was positively biased, but the induced errors appear to be small.

The electronic set-up used to take probe data is shown in Fig. 3-14. A timing box generated pulses at $\sim 3 \text{ Hz}$, which triggered a function generator (Wavetek 148) and a digital voltmeter (HP 3437A). The output of the function generator was amplified with a programmable power supply (Kepco BP100-2M) and sent to the probe through a resistor. The voltage was measured directly at the probe. The current was measured by a high-speed differential amplifier (Tektronix AM 502) that measured the voltage difference across the resistor. The voltage and current signals V_{probe} and I_{probe} went to a multiplexer (HP 3495A) and read by the digital voltmeter. The data was collected and analyzed by a HP 9920 series computer. A typical raw data scan is shown in Fig. 3-15. The data analysis was simple and interactive with the operator. First, the linear portion of the ion saturation regime was selected, along with the floating potential and an estimate of the plasma potential (which was usually very close to the final value determined). The computer subtracted the ion current from the data, leaving the electron current I_e only. The computer then took the natural log of the data and fit the results to two straight lines. One line was based on the data only to the negative side of the plasma potential estimate, and the other was based on that to the right. The

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Fig. 3-14 Langmuir probe trace data collection system. Ramp generator outputs 100 ms ramp at ~3 Hz. Voltmeter collects data in slew mode (~5 kHz).

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Fig. 3-15 Measured Langmuir probe I-V curve for discharge parameters of DC, 25 A, 120 V, 8 mTorr. Measured in the plasma body. Inferred electron density and temperature are 1.79 eV and $1.37 \times 10^{12} \text{ cm}^{-3}$.

x-value of the intersection was taken as the true plasma potential and the y-value as the log of the saturation electron current $I_{e,sat}$. The key assumptions were that

$$\frac{d \ln(I_e)}{d V_{probe}} = \frac{e}{kT_e} \quad (3.7)$$

and that

$$n_e = \frac{I_{e,sat}}{eS} \left(\frac{kT_e}{2\pi m} \right)^{-1/2} \quad (3.8)$$

where e is the unsigned electron charge, m is the electron mass, S is the effective probe collection area, and kT_e is the electron temperature. It was found that iteration did not improve the derived values as long as the initial estimate of the plasma potential was reasonable. The saturation ion current was ignored because the primary electrons distort the ion saturation portion of the probe characteristic. This method of data interpretation is simple and direct, but is subject to some uncertainty, because, in the portion of the probe trace near the 'knee', the assumptions made in the interpretation are no longer true. This whole issue is discussed in numerous sources,^{9,14,107} but there is no good solution as yet, so we will accept this data as is. It is important that the probe be momentarily cleaned by high electron saturation current before any data is taken, so that the surface of the probe is the same material as the body of the probe. If a layer of oxide or something similar exists on the probe surface, the voltage at the surface, which the plasma 'sees', will not be the same as that

measured by the electronics. This problem is most sensitive near the 'knee', where the perturbation would be largest proportionally.

2. Druyvesteyn Method

The Druyvesteyn method is a technique to derive the EEDF directly from the a Langmuir probe trace.^{12,59} This technique is particularly useful for measuring the EEDF at high energies, that is, where the primary electrons dominate and ordinary probe methods fail. Druyvesteyn showed that the second derivative of the electron current $I_e(V_{\text{probe}})$ determines the EEDF. Specifically,

$$n_d(\epsilon) = \frac{\partial n_e}{\partial \epsilon} = \frac{2I_e''}{e^3 S} (2m\epsilon)^{1/2} \quad (3.9)$$

where n_e is the total electron density, $n_d(\epsilon)$ is the electron density per (kinetic) energy interval, V_{probe} is the probe voltage, V_p is the plasma potential, ϵ is the kinetic energy of the electrons, given by $e(V_p - V_{\text{probe}})$, S is the total area of the probe exposed to the plasma, and m and e refer to the mass and (unsigned) charge of the electron respectively. The primes mean differentiation with respect to V_{probe} . Others subsequently derived the same result with less specific specifications on probe shape, the key point being that the probe must be convex and the plasma must be isotropic and reasonably homogeneous, a condition that is certainly true in the plasma body.¹² The data presented in this thesis was measured in the body of the plasma only, using the simple cylindrical tip described in section 1. In general the data from this method is most reliable when the probe bias is more negative than the plasma potential minus a few times the thermal electron temperature (in appropriate units).

The data is more suspect near the 'knee' because the assumptions made in the derivation of Eq. 3.9 start to break down. But in this region an ordinary Langmuir probe trace works just as well. The Druyvesteyn method is particularly useful for measuring the primary electrons, because these are not well measured by ordinary probe trace techniques. There is one complication for the method, and that is that one must subtract the ion current from the total current to the probe. It is assumed for the present data that the second derivative of the total current to the probe (with respect to voltage) is dominated by the second derivative of the electron current, and therefore no correction is made to the raw data. This approximation should be a good one, as discussed by Hopkins, et al., who performed a more sophisticated version of the Druyvesteyn technique on a similar discharge.⁹ The results obtained here were very similar to those obtained by Hopkins, et al., leading the author to have greater faith in the results.

The basic idea behind the experimental arrangement is not new and has been previously employed.¹⁰⁸ The voltage to the probe is sinusoidal with a DC offset:

$$V_{\text{probe}} = V_a + V_b \sin(\omega_b t) \quad (3.10)$$

We can write I_{probe} as a function of V_{probe} , and perform a Taylor expansion around V_a , and assume that it is a good approximation to carry terms only to second order in V_b . The expression for the probe current I_{probe} will be given by (ignoring phase):

$$I_{\text{probe}} = \frac{V_b^2}{4} I'' \cos(2\omega_b t) + (\text{other terms at DC and } \omega_b) \quad (3.11)$$

where I' is understood to be evaluated at V_a . Thus one can measure the second derivative of the probe current by measuring the amplitude of the $2\omega_b$ term. The EEDF is then given by

$$n_d(\epsilon) = \frac{8I_{2\omega}}{e^3 S V_b^2} (2m\epsilon)^{1/2} \quad (3.12)$$

where $I_{2\omega}$ is the amplitude of the 2ω component of the probe current.

Fig. 3-16 illustrates the experimental apparatus. A function generator (Wavetek 148) generates a sine wave signal of angular frequency ω_b , which was ~ 100 kHz. The $50\ \Omega$ output of the function generator was coupled to the input of a Kepco BP100-2M programmable power supply through a capacitor which decoupled any DC offset coming from the Wavetek. The output of the Kepco power supply was described by Eq. 3.10, where V_a was measured with a laboratory multimeter and was adjusted manually for each data point. Unfortunately, V_a was limited to ~ 100 V by the power supply available. V_b was measured by displaying the AC-coupled output of the Kepco on a well-calibrated oscilloscope. The uncertainty in measuring V_b in this manner is estimated to be $<3\%$ when care is used. The output of the Kepco went directly to the probe via shielded cable. A current transformer (Pearson 4100) measured the center wire current at the probe. The voltage drop along the cable was measured and found to be negligible. The signal from the current transformer went to the signal input of a phase-lock amplifier (Princeton Applied Research HR-8) that used the $2\omega_b$ component of a TTL signal from the function generator as its reference. The phase control on the lock-in amplifier

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Fig. 3-16 Diagram of electronic configuration used for measuring EEDF's by the Druyvesteyn method. Data collection was essentially by hand. All possible sources of false second harmonic signal were checked and found to be negligible (see text).

was empirically set at each data point to maximize the detected $2\omega_b$ signal. The phase did sometimes vary with V_a and other parameters. The lock-in amplifier also had a built-in calibrator signal that was used to check the detection sensitivity of the amplifier.

The operational procedure consisted of first turning on the discharge to the desired parameters and then systematically measuring the $2\omega_b$ amplitude for enough different V_a 's to produce a smooth curve (see Fig. 3-17 for a typical result). V_a ranged from -100 Volts (the limit of the power supply) to the plasma potential, typically + 3.5 Volts. V_b was selected at each V_a using the criteria described previously. When V_a was negative enough to be in the 'primary electron zone,' typically less than -20 Volts, the $2\omega_b$ amplitude was relatively small and therefore V_b had to be made large, 3 - 6 Volts, so that the false second harmonic signal from power supply non-linearities were relatively small. It was fortunate that there was no fine structure in this parameter range, because it would have been smeared out somewhat. The primary to secondary transition usually occurred at $V_a \approx -15$ Volts, and was evidenced by a sharp increase in the slope. The $2\omega_b$ signal was much larger in this range and therefore the minimum V_b could be decreased. This was fortunate because there was structure on a finer scale here and one does not want to smear it out. The plasma potential V_p was measured by determining the inflection point. Although this may be somewhat crude, the resulting error in the calculated EEDF is small (< 5%) except at very small ϵ , where the entire method is more suspect anyway. It is noted that the EEDF derived from this data yields a total n_e that is 80-90% of that derived from the ordinary Langmuir probe technique, and this minor disagreement is believed to arise entirely from the small ϵ portion of the data.

This method can yield extraneous results if care is not taken during the

experiments. First, the assumption is made that the current to the probe is a function of the *instantaneous* probe voltage. This assumption will be true provided that the ion transit time across the probe sheath is small compared to ω_b^{-1} . This criterion is satisfied by several orders of magnitude for the present data. Another possible error is the false introduction of a second harmonic signal in the probe current, which can happen by several different mechanisms. One is the presence of second harmonic content in the voltage waveform; another is non-linear response of the current sensing device, in this case a current transformer. The ratio of the $2\omega_b$ amplitude to the ω_b amplitude was measured for both the voltage and the current at typical parameters, and it was found that the ratio was usually a few percent for the current, but less than 10^{-3} for the voltage. This rules out the first possibility. Also, the second harmonic content was measured when the probe was connected to the plasma by an ordinary resistor instead of the plasma. The resistor value was such that the DC current at V_a was the same as when the plasma was running. It was found that the current transformer signal had an immeasurably low second harmonic content. We therefore conclude that the second harmonic signal coming from the current transformer is actually caused by the non-linear plasma conductivity. However, another assumption was made that must be examined. It was initially assumed that it is valid to use only the lowest order term which had a $2\omega_b$ term in it. Obviously, as V_b increases, this will cease to be valid. Practically speaking, one must choose V_b large enough so that the 'true' $2\omega_b$ term dominates the small false $2\omega_b$ terms arising from experimental imperfections (which scale linearly with V_b usually), and yet small enough so that higher order terms do not contribute. Fortunately, this is easy to do. After the exhaustive tests were made at several different combinations of V_a and V_b , each data point was checked by halving V_b momentarily and observing

whether or not the amplitude of the $2\omega_p$ term decreased by four. However, it became clear that the data for low ϵ was more susceptible to systematic errors, because the Kepco power supply started having significant non-linearities in the output voltage waveform when the plasma impedance was low enough (i.e., as V_{probe} approached V_p). The problem is one of the reasons the numerical analysis of the DC probe characteristic used by Hopkins, et al. is probably superior to the present method, for data regarding thermal electrons.⁹ For this reason, it was decided that only the Druyvesteyn method data regarding the primary electrons ($V_{\text{probe}} \leq -20$ V) would be used in modeling, and that ordinary probe methods were probably better for the thermal electron data.

The measured EEDF for plasma parameters of 25 Amperes, 90 Volts, 8 mTorr filling pressure, and DC discharge is shown in Fig. 3-17. The ordinate covers 4 orders of magnitude. The primary and secondary electron populations are clearly distinct. The primary electron EEDF appears to be described by a negative exponential function with a $1/e$ folding scale of ~ 30 V. This is very similar to the results found by Eenshuistra, et al. and Hopkins, et al.^{9,87} Both of those experiments and the present experiment find a very smooth primary EEDF that is well-described by a 'temperature,' and that the temperature is close to one third of the birth energy of the primary electrons. We note here that a true Maxwellian distribution is not an exponential with this normalization, but rather an exponential function multiplied by $\epsilon^{0.5}$ and other constants. Thus the word was misused in a sense previously. This behavior does not agree very well with modeling calculations regarding primary EEDFs.⁷ The measured EEDFs seem to indicate that the primary electrons somehow thermalize with each other. This is particularly indicated by the fact that there is a measurable electror. energy density at energies greater than the

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Fig. 3-17 Measurement of the EEDF in the central plasma region for discharge parameters of DC, 25 A, 90 V, 8 mTorr Hydrogen. Note the obviously distinct primary and secondary electron regions and the presence of electrons above cathode birth energy.

cathode birth energy. This behavior was also observed by Hopkins, et al.⁹

Several possible explanations for this phenomenon were examined and excluded. First, the cathode voltage has negligible high frequency noise that could smear out the cathode birth energy. Secondly, the rate of superelastic scattering by metastable electronically-excited $c^3\Pi_u^-$ H_2 must very small if the densities measured by Bonnie, et al. are relevant to the present work, which is believed to be the case.^{16,17} Even if one assumes an unrealistically large cross section for superelastic scattering, the rate is so small that $< 0.1\%$ of primary electrons would have a superelastic collision before they lost their energy from other inelastic collisions. It is clear that a rate this small cannot explain the measured high-energy tail of the EEDF. The same is true for superelastic scattering from rovibrationally-excited H_2 , because even though the target densities are higher, the energy gain is so small that an unrealistic number of collisions (i.e., >20) would be needed to explain the anomalous tail. Another possibility is experimental error. There is of course the finite resolution introduced by the non-zero V_b , but the tail extends far beyond $V_p + V_b$, so this cannot entirely explain the data. There exist several remaining possibilities: first, the basic assumptions in the Druyvesteyn method are possibly not valid for this experiment; second, the ion current contribution to the second derivative signal may not be negligible; third, the data may be correct and unexplained thermalization of the primaries may be taking place. We examine these possibilities in order. The assumptions made in the data interpretation are explained in detail in Schott,¹² and it appears that they are all satisfied presently, in particular, it is definitely true that the sheath is thin compared to the probe scale length and that elastic scattering from neutrals is negligible in the sheath. There are several reasons why it is believed that ion current is not a factor. First of all, the measured primary electron density scales as $I_d^{1.02}$,

while the ion current to the probe should scale as $n_e(kT_e)^{0.5}$, which is empirically found to scale as $I_d^{0.80}$, over a range of 10 in I_d . The exponent is approximate, as the determining fit is not perfect, but it is clearly less than unity. Also, as previously stated, Hopkins, et al. found the ion current to be negligible in their more sophisticated analysis. We therefore conclude that the anomalous tail of the measured EEDF's are real, although we cannot explain them. We speculate that some sort of beam-plasma instability may be the cause of this behavior, but the subject will not be investigated further.¹⁰⁹

D. H⁻ Measurement by Probe-Photodetachment Method

The density of H⁻ ions in a hydrogen plasma can be measured by the probe-photodetachment technique first used by Bacal, et al.^{62,110} The idea is straightforward. One first measures the electron density with a probe by standard techniques. Then the increase in electron saturation current is measured immediately after an intense, short pulse of light photodetaches the outer electron from all of the H⁻ ions in the region of the probe. The H⁻ density n^- is then simply given by

$$n^- = n_e \frac{\Delta I_{e,sat}}{I_{e,sat}} \quad (3.13)$$

Several conditions must be satisfied for this method to work. First, n^- should be relatively small compared to n_e , so that the electron parameters in the region of the probe immediately after the light pulse are not significantly different from those before the pulse. This condition is always satisfied for the data presented here. Secondly, the total volume of plasma 'seen' by the probe must be illuminated by the light pulse. This can easily be accomplished by

using a laser beam radius that is much larger than a Debye length. Thirdly, the photodetachment process must saturate, that is $\sigma_{\text{detach}}F$ must be $\gg 1$, where F is the photon flux per unit area per pulse. Fourth, one must be careful not to create additional electrons by any other photon-related process. This is simple in practice because H^- has a large photodetachment cross section at low photon energies.¹¹¹ Lastly, the volume illuminated must be large enough and the time response of the probe current measuring system must be fast enough so that the perturbation of the probe current can be accurately measured. The duration of the 'flat top' is less than 1 μs , because other H^- ions will drift into the photodetached region with the H^- thermal velocity and displace the (very mobile) newly-liberated electrons. Typical H^- thermal energies are a few tenths of an eV.^{25,26} The time scale for generation of fresh H^- in the same volume is much longer, of order 100 μs . Stern, et al. recently published a paper combining experiment and theory that explained how electric fields in the photodetached region arise that are essentially caused by the resulting density gradient of H^- and electrons.¹¹² This effect is very closely related to ambipolar diffusion and sheath formation.¹¹³

A schematic of the electrical circuit used for the photodetachment measurements is shown in Fig. 3-18. The arrangement is very similar to that used by Eenshuistra.¹¹⁴ The normal electron density has already been measured, as described in section C-1, so here we only measure the ratio of H^- to electron density. The probe consists of a very thin wire (0.050 mm diameter) that extends from an alumina insulator ~ 3 mm. A function generator (Wavetek 148) and a programmable power supply (Kepco BP100-2M) were employed to pulse a positive bias to the probe, from -1 V to $+35$ V for a few ms at ~ 3 Hz, in order to avoid heating the probe wire. That voltage was chosen because the measured H^-/e^- ratio increases mildly with V_{probe} up to ~ 30 V.

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Fig. 3-18 Schematic diagram of system used to measure the ratio of H^- density to electron density. Measurements were made in the magnetic filter region. Laser system is not shown.

This behavior was also seen and discussed by Eenshuistra.¹¹⁴ The voltage across the 100 Ω resistor is measured with a differential amplifier (Tektronix AM 502) and determines the relative DC electron density. The excimer/dye laser system is fired near the end of flat top portion of the waveform. The laser pulse has a duration of ~ 20 ns and is effectively a delta function in time. The fast current waveform across the 100 Ω resistor is measured using a fast oscilloscope and a high-pass filter of time constant 10 μ s that effectively filters out the 36 V quasi-DC pulse to the probe. An oscilloscope photograph of the fast peak is shown in Fig. 3-19. The 0.22 μ F capacitor at the output of the Kepco power supply was necessary to insure that the voltage there was constant during the fast pulse. Stray cable capacitance limited the rise time of the electronics to 100 ns. Data collection and reduction is performed manually. The H^+ /electron ratio is simply the ratio of the peak voltage (fast pulse) to that of the voltage from the differential amplifier.

Several issues relating to validity of the data remain to be discussed. First, it was experimentally verified that the signal was saturated as a function of laser intensity by using screens to reduce the dye laser output. The laser was operated at 625 nm. Eenshuistra showed that there is not structure of the photodetachment signal in this wavelength range.¹¹⁴ The signal also had a clear saturation regime with respect to optical alignment of the laser beam. Additionally, tests in argon (which has no known negative ion) yielded a null result. The only possible problem is the finite rise time of the circuit. However, it is clear from looking at the oscilloscope photograph that any necessary correction is small, and thus will be neglected for our purposes. This error will only produce a factor that is the same for all data, thus relative comparisons are still valid exactly.

Fig. 3-19 Oscilloscope photograph showing response of thin wire probe to laser-induced photodetachment of H^- in neighborhood (5 mm) of probe. Finite rise time is caused by stray cable capacitance, but peak magnitude is believed to fairly accurate.

E. Extraction of Hydrogen Ions

1. H⁻ and electrons

H⁻ ions and electrons were extracted from a hole in the discharge chamber wall located in the center of the magnetic filter region, and measured using Faraday cups. The entire apparatus has been described previously by Leung, et al.¹¹⁵ A schematic of the extraction apparatus is shown in Fig. 3-20. The collection apparatus was at or near ground while the discharge chamber and associated power supplies were connected to the negative side of a 15 kV power supply. The accelerator geometry was a simple two-hole system. The first hole was that in the discharge chamber wall and was 2 mm diameter. The second hole had a diameter of 3 mm and was in a thin, flat piece of copper mounted 2 mm away from the discharge chamber hole. Only negatively charged particles can exit the plasma through this hole, so only electrons and H⁻ ions can be in the extracted beam. Weak magnets that separate the electrons from the H⁻ ions are located above and below the beam as it exits the accelerator gap. The accelerator was tested with an argon discharge, as argon has no known negative ions, and found to have no false ion signal caused by electrons reaching the ion cup.¹¹⁵ The H⁻ beam is not optimized for perveance, and probably has very poor beam characteristics, however, the H⁻ Faraday cup covers a large solid angle and should collect all of the beam. The currents are measured by measuring the voltage across a suitably chosen resistor. The actual data is recorded by photographing oscilloscope displays, so the accuracy is ~5%.

The extracted ion and electron current is shown as a function of extraction voltage for three different discharge parameters in Fig. 3-21. In particular, the electron and ion currents are proportional to each other and have the same relative slope. This indicates that the extracted current is a good relative

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Fig. 3-20 Diagram of H^- measuring system. The accelerator is a simple two-electrode design. Either the discharge or the extraction voltage was pulsed, in order to reduce the over loading of the Faraday cups.

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Fig. 3-21 Extracted H⁻ or electron current, as a function of acceleration voltage. Note that the normalized current is independent of discharge parameters and species being extracted.

measure of the actual density inside the discharge chamber, and that the extracted currents are not sensitive to beam focussing effects. However, it also points out the fact that it is not obvious how the extracted current relates to the actual density in the discharge chamber. The simplest assumption would be that the current is the density times electronic charge times the ion sound speed, but that does not explain the variation with extraction voltage. More realistically, the extracting electric field extends into the plasma for some distance and a 'funneling' effect is occurring. This effect could be avoided large area extraction, but this was not possible with the equipment available due to power supply limitations. It was decided to operate always with the same extraction voltage, 15 kV, and to use this data as a relative measure only of H^- only. It is clear that is definitely a good measure of the H^- to electron ratio.

The H^- extraction data was performed on a completely separate test stand from where the VUV and electron probe data was measured, several months earlier. Thus, the question arises: is this data relevant to the other data, or in other words, if we could have measured the extracted H^- simultaneously with the VUV measurements, would we have gotten the same results? There are several reasons to believe the answer is yes. First of all, the vacuum system and in particular the discharge chamber was carefully leak-checked before operation. After an up-to-argon filament change, the filaments were gently heated for several hours after a moderate vacuum (1×10^{-5} Torr) had been established. A RGA was mounted on the downstream chamber from the source and the water peak was observed as a check of the vacuum status. While this peak never entirely disappeared, its size had a small terminal value. The source was discharge cleaned for several hours before any data was recorded. Secondly, tests were performed on the H^- extraction data to determine whether the data was repeatable from day to day and to determine

whether opening the chamber to replace the filaments would necessitate a long waiting period for good data. It was found that the H^- data was very reproducible and that surprisingly little effort was necessary to obtain reproducible data, in fact, this data was probably more reproducible than the VUV data. When this data was taken, the author was unaware of the hysteresis effect discussed in section A-3. The log books were reexamined at a later time, and it became clear why the extraction data was valid. For both the low-power DC and high-power pulsed data, the "break in" routine was the same. After an up to air event (to replace filaments), the discharge chamber was pumped on until the base pressure (measured downstream of the chamber) had reached a fair value (mid 10^{-6} Torr range), then hydrogen was flowed through the source while the filaments were mildly heated (monolayer evaporation time equal hours) for some time. Then the discharge was operated in the same manner as the subsequent data, for at least one hour. A small set of data was taken for low-power, pulsed discharges (<40 A) when the chamber walls were clearly in the high-power state. The H^- currents measured under these conditions was significantly less than those measured the DC data operated at the same discharge condition. Unfortunately, it is not clear if one can compare the two data sets directly because two different parameters have changed: DC vs. pulsed and the wall condition.

2. Positive Hydrogen Ions

The fraction of H^+ , H_2^+ , and H_3^+ in the discharge was determined by measuring the extracted positive ion currents with a mass spectrometer. The density ratio was assumed to be that of the currents corrected for the different masses. This apparatus is not shown, but is described in Leung, et al.⁸⁶ The accelerator geometry was the same as in section 1, but the Faraday

cup apparatus was replaced with a 180° mass spectrometer. The spectrometer was at ground while the discharge chamber was at ~ 3.5 kV negative. It was verified that the ratio of the three peak heights was almost independent of extraction voltage, indicating that the results measured are not significantly influenced by focussing effects. The operational procedure was simple. The discharge was initiated and then the extraction voltage was turned on. The current for the electromagnetic analyzer was swept with a ramp (10 seconds total), and the collector signal was measured as a function of the current. Three distinct peaks were clearly visible at fields that agree with the nominal identification of H^+ , H_2^+ , and H_3^+ . Much smaller peaks were detectable corresponding to water and associated ions. The data was recorded on an X-Y recorder and reduced at a later time (see Fig. 3-22 for sample data). The qualitative trends were exactly what is expected for this type of discharge: H_2^+ is very small except at very low pressures, and increasing power favors H^+ over H_3^+ . Generally though, H_3^+ was always found to be the dominant ion for DC operation (< 40 A).

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Fig. 3-22 Output signal from magnetic mass spectrometer. The three peaks are H^+ , H_2^+ , and H_3^+ . Discharge parameters are pulsed, 100 A, 100 V, 7 mTorr. Extraction voltage is 3.7 kV.

Chapter IV

Experimental Results – I

A. Electrons and Positive Ions

The results of the measurements on the charged particles in the discharge are presented in this section. The results are in good agreement with the modeling results in most cases. The parameters of the thermal electrons and the primary electrons have been measured in the center of the discharge in all cases, as discussed in chapter II, sections 1 and 2. The thermal electron parameters were determined using conventional Langmuir probe analysis,¹⁰⁵ while the primary electron characteristics were measured using the AC modulation version of the Druyvesteyn method.^{11,12} The choice of the effective volume parameters, used for the modeling calculations, is discussed at length in chapter II, section 1. The data on the positive ion species ratios was obtained by extracting from the magnetic filter region of the plasma. As will be discussed further, that data may be somewhat different from the true volume-averaged species ratios, and the differences are easily understood qualitatively.

Most of the data obtained applied to DC discharges of modest power. The charged particle data was measured for various values of the three discharge parameters that one can easily adjust: filling pressure P_d , discharge current I_d , and discharge voltage V_d . Because one cannot cover all parameter space for practical reasons, it was decided to take three 'slices' of data; that is, for one parameter scan, the pressure (measured with the discharge off) was varied while the discharge current and voltage were held fixed; for another scan, the current was varied and the other parameters were held fixed, and for the last scan, the voltage was varied while the pressure and current were held fixed. It

was necessary to adjust the filament heater current to achieve independent control of all three parameters. To some degree of approximation and over some finite range, one can assume that the three aforementioned parameters have independent, multiplicative effects on the plasma. The range of pressures, currents, and voltages measured was 2 to 20 mTorr, 5 to 35 A, and 70 to 150 V, respectively. The parameter set of 8 mTorr, 25 A, and 90 V was taken as the center point in parameter space because these parameters are close to optimal for H^- production within the range studied. Generally, increasing the discharge current will always increase the H^- density, and the upper limit of discharge current, 35 A, was chosen simply because that was the limit of the DC power supply available. The range of discharge voltages selected has other criteria. Below 70 V, it is quite difficult to 'pull' much discharge current from the filaments unless the filaments are run significantly hotter than would ordinarily be necessary, because the emission is very strongly space-charge limited, and that higher temperature leads to very rapid filament evaporation, which is undesirable. One can operate at discharge voltages above 150 V without much difficulty, however, this regime is not very interesting for H^- ion sources because the extracted electron current is increasing rapidly with voltage (at least for the particular ion source under study), and that effect is detrimental to extraction of high current ion beams because of related space-charge problems. Also, the primary electrons are not confined as well at higher energies and thus the energy transfer efficiency (from the arc power supply to the plasma) decreases. The range of pressures is also related to practical problems of high-current beam extraction. As subsequent data will illustrate, increasing the pressure generally decreases the electron density (in the filter region). Typically, the H^- density increases with pressure at low pressures, saturates at 10–20 mTorr, and then slowly decreases with increasing

pressure. However, in a real ion source, it is desired to maintain a low operating pressure because the very large cross section for stripping of fast H^- on H_2 ($\sim 10^{-15} \text{ cm}^2$ from 0.1 to 10 keV)¹¹⁶ will cause the extracted H^- beam to be attenuated before it has reached full acceleration energy:

Therefore one chooses an operating pressure based on the balance between the various competing effects, and the chosen pressure must necessarily be lower for ion sources with relatively large extraction areas ($\geq 1 \text{ cm}^2$). Also, increased pressure leads to increased non-uniformity of the discharge, complicating the data analysis.

The experimental results for the plasma density in the center of the discharge and the corresponding model predictions are shown in Fig. 4-1, as a function of discharge current, pressure, and voltage, for low-power, DC operation. Clearly, the agreement is quite good, although there is some disagreement for the dependence on discharge voltage. The model results depend, of course, on the assumed molecule density n_{H_2} . The density is reduced from the cold-gas filling value by a factor α which is assumed to depend on the current and voltage only. The values assumed for the current variation data are given by $\alpha = (1 - I_d/100 \text{ A})$ and the values assumed for the voltage variation data are $\alpha = 0.8, 0.75, 0.7$, and 0.65 for 70, 90, 120, and 150 V, respectively. The value of α for 25 A and 90 V, the discharge parameters used during the pressure scan, is 0.75. These factors are based on extrapolations of the VUV absorption data for $v''=0$ (see Chapter V, section A).

The tendencies exhibited in the thermal electron data are as one might expect, namely, that increased power (in the form of current or voltage) leads to

Fig. 4-1 Comparison of the calculated total ion density vs. measured thermal electron density in the central region of the discharge, as a function of discharge current (a), pressure (b), and voltage (c). The default discharge parameters are 25 A, 90 V, and 8 mTorr.

increased plasma density, and that the plasma density saturates at a fairly low pressure (~5 mTorr), indicating good confinement of the primary electrons. The qualitative disagreement between the model and the measured data for the discharge voltage scan may be related to the fact that more Gauss-cm are required to turn around an electron of higher energy and therefore the effective volume ratio for the primary electrons (not the thermal electrons) increases enough with voltage to account for the discrepancy. However, the thermal plasma density has a radial profile which depends only very weakly on discharge voltage, as can be seen in Fig. 3-3, indicating that the primary electron radial density profile is not significantly different for the voltages under consideration here. Another possible explanation is related to the fact that data on the primary electrons could only be obtained up to 100 V (negative), and that possibly the high-energy tail of the EEDF does not follow the exponential behavior measured up to 100 V. However, neither Hopkins, et al. or Eenshuistra mentioned any such effect in their works.^{9,117} Further discussion relating to this discrepancy is relegated to section D.

The measured results for the electron temperature are shown in Fig. 4-2. These data were used only as inputs to the model and were not predicted by it. Again, the trends are as one would naively expect: the electron temperature increases as the discharge power increases (although current is more effective than voltage apparently) and decreases as the pressure increases. The electrons are cooled by inelastic collisions with the hydrogen molecules, in particular, $v''=0 \rightarrow v''=1$ or 2 excitations, and presumably thermalize with each other so quickly that the electron sea can be considered to lose energy as a whole. The electrons are born with ~7 eV (Ref. 1) and are also probably heated by some type of plasma interaction between the primary electrons and the thermal electrons, although we are not aware of any reference that has carefully examined the

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Fig. 4-2 Measured thermal electron temperature in the central region of the discharge, as a function of discharge current (a), pressure (b), and voltage (c). The default discharge parameters are 25 A, 90 V, and 8 mTorr.

issue under parameters of interest presently.

The measured thermal electron density and temperature in the magnetic filter region are shown in Figs. 4-3 and 4-4, as a function of current, pressure, and voltage. The qualitative trends are all the same as those found in the center of the plasma. The more interesting question is, how does the ratio of the electron density in the filter to the electron density in the center of the discharge vary with the discharge parameters? That data is shown in Fig. 4-5. Clearly, discharge current is not a strong effect. There is a positive correlation to discharge voltage and a fairly strong negative correlation to discharge pressure. The voltage effect is very likely caused by primary electrons penetrating closer to the filter and thus thermal plasma constituents have less magnetic field to diffuse through in order to reach the filter. The pressure dependence is suggestive of a $1/x$ dependence (but is clearly weaker). In any case, the density is a monotonically decreasing function of pressure, which would be expected if diffusion against gas molecules is the primary obstacle to free transport. As discussed in chapter II, section 1, the most realistic physical picture is, as far as cross field diffusion is concerned, that the ions have higher diffusivities than the electrons because they have much larger gyroradii, and the electrons are dragged along by the ambipolar electric fields. It is almost certainly true that the momentum transfer cross section for the various hydrogen ions on H_2 is large (probably greater than 10^{-15} cm^2), and therefore the explanation for the decrease in the density ratio, as a function of pressure, is that the ions (and consequently the thermal electrons) have a harder time reaching the filter because ion-molecule collisions are the chief impediment to cross-field transport.

The behavior of the primary electrons in the center of the discharge was also measured. As Hopkins, et al. initially showed, and as can be seen in

(a)

(b)

(c)

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Fig. 4-3 Measured thermal electron density in the magnetic filter region of the discharge chamber, as a function of discharge current (a), pressure (b), and voltage (c). The default discharge parameters are 25 A, 90 V, and 8 mTorr.

Fig. 4-4 Measured thermal electron temperature in the magnetic filter region of the discharge chamber, as a function of discharge current (a), pressure (b), and voltage (c). The default discharge parameters are 25 A, 90 V, and 8 mTorr.

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Fig. 4-5 Measured ratio of thermal electron density in the magnetic filter region to that in the center of the discharge, as a function of discharge current (a), pressure (b), and voltage (c). The default discharge parameters are 25 A, 90 V, and 8 mTorr.

Fig. 3-17 for instance, the differential electron density $n_d(\epsilon)$ in the 'primary electron region' of the EEDF is described very well by a decreasing exponential function.⁹ Therefore the primary electron data for energies above 20 eV was fit to a function characterized by two quantities, $n_{e,f}$ and $kT_{e,f}$:

$$n_d(\epsilon) = \frac{n_{e,f}}{kT_{e,f}} \exp\left(-\frac{(\epsilon - 20 \text{ eV})}{kT_{e,f}}\right) \quad (4.2)$$

The density integrated over energy is $n_{e,f}$ only if the lower limit of the integral is 20 eV, an assumption that is used presently. However, the various rate constants calculated using this parametrization are not sensitive to the lower limit chosen in the corresponding integral because the cross sections of interest decrease very rapidly below ~20 eV. Thus, one must be somewhat careful when defining how to count the primary electrons.

The results of the primary electron measurements are shown in Figs. 4-6 and 4-7, as a function of varying the discharge current, pressure, and voltage. Typical values of $n_{e,f}$ and $kT_{e,f}$ are 2% of the thermal density and one third of the discharge voltage (times electronic charge), respectively. The fast electron temperature $kT_{e,f}$ is almost invariant with current and pressure, a somewhat surprising result, but one observed by Eenshuistra also.¹¹⁷ Only varying the discharge voltage causes $kT_{e,f}$ to significantly change, at least over the range of parameters measured presently. The primary electron density scales close to linearly with discharge current, in fact, any deviation from linearity is smaller than the uncertainty (estimated at $\leq 5\%$). The linear scaling observed is stronger than the scaling with discharge voltage. The variation with pressure is weaker than the P_d^{-1} dependence that would be expected from simply modeling (and the assumption that wall loss of primary electrons

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Fig. 4-6 Measured density of primary electrons in the center of the discharge, as a function of discharge current (a), pressure (b), and voltage (c). See text for definition of primary electrons. The default discharge parameters are 25 A, 90 V, and 8 mTorr.

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Fig. 4-7 Measured temperature of primary electrons in the center of the discharge, as a function of discharge current (a), pressure (b), and voltage (c). The default discharge parameters are 25 A, 90 V, and 8 mTorr.

is negligible). Therefore the creation rate of ions does not completely saturate with increasing pressure, because that rate is proportional to $(n_{H_2})(n_{e,f})$. It would appear that the measured dependence of $n_{e,f}$ and/or $kT_{e,f}$ on voltage must be incorrect, based on the discrepancy between the model and the data on the thermal electron density as a function of voltage (see Fig. 4-1, also 4-17). Qualitatively, the measured primary electron data indicates that increasing the discharge voltage does not increase the power entering the plasma, but the data on the resultant products of the primary electrons, such as thermal plasma and H-atoms, indicates that increasing the discharge voltage does increase the power entering the plasma. However, the fractional increase is still weaker than that for current in general generally. Eenshuistra also observed a substantial decrease of the directly measured $n_{e,f}$ with increasing discharge voltage, despite an increase in the densities of the resultants.¹¹⁷ The behavior of $kT_{e,f}$ can probably be explained in a very qualitative way by the simple assumption that the primary electrons somehow exchange energy with the thermal electrons, and that this process is more efficient when the energy (i.e., voltage) of the primaries is lower. In particular, moderate energy primary electrons (i.e. 50 V) are probably more likely to transfer some of their energy to the thermal plasma than higher energy primaries (i.e. 150 V). Obviously, the specifics must depend on the magnetic geometry of a given chamber and other parameters. The data does indicate that the neutral pressure and thermal plasma density have surprising weak effects on the fast electron temperature.

The energy deposition efficiency of the primary electrons can be calculated from the measured density and temperature of the primary electrons. The potential production rate is proportional to the discharge current. The energy lost by a primary electron during an ionization event, E_i , is about 20 eV and the 'turn on' energy of the ionization cross section is about 20 eV, so a first

estimate is ~4 ions/primary electron. Actually, there is a branching ratio factor because the primary electrons also cause electronic excitations in the H₂. The true production rate K_{ions} is given by

$$K_{\text{ions}} = \frac{\tau_i E_i}{\sigma_i E_i + \sigma_{\text{exc}} E_{\text{exc}}} \frac{I_d (V_d - 20 \text{ V})}{E_i} \quad (4.3)$$

where E is the energy lost by the primary electron in an inelastic collision and the subscripts refer to ionization and excitation. The first factor is the fraction of energy expended in the form of ionization, and is approximately 2/3, depending on the exact values assumed for the ionization and excitation cross sections.^{1,55} The actual value of the rate for discharge parameters of 25 A, 90 V is then ~4 × 10²⁰ s⁻¹. The measured production rate of ions created by the primary electrons is given by n_{H₂} n_{e, f} <σv>_{ionize} V, where V is the volume of the space filled by primary electrons, previously estimated at 1.1 l, and the rate constant has a value of ~3 × 10⁻⁸ cm³/s. The values for the densities refer to the 8 mTorr data and the actual ion production rate is about 1.4 × 10²⁰ s⁻¹, yielding an efficiency of only 35%. It is not clear what happens to the other energy, but much of it is lost as fast primary electrons travel along the magnetic field lines and collide with the chamber wall at high energy. It is well known that the wall of a discharge chamber will have the highest heat load where the magnetic cusps cross the surface of the chamber. During preliminary experiments using a poorly cooled chamber, the wall was observed to glow with a moderate yellow color at some of the cusp-wall intersections! Also, one can clearly see the fast electrons trapped along the field lines simply by observing the visible emission visually. The emission volumes are continuous and not significantly weaker near the wall, thus the magnetic

mirror effect is clearly not very effective in confining the primaries. There is also undoubtedly some transfer of energy from the primary electrons to the thermal electrons, but the associated transfer rate is not known.

The ratio of the densities of three positive hydrogen ions has been measured by extraction from the filter region of the discharge chamber and has also been calculated for the same variation of discharge parameters as in the previous section. A comparison of the data and the model results is shown in Fig.'s 4-8, 4-9, and 4-10. Clearly, the agreement is rather good, both in qualitative trends and in terms of the absolute fractions. The trends can be rather neatly summarized: increasing the gas pressure converts H_2^+ to H_3^+ by the reaction

and increased power generally converts H_3^+ to H^+ . These behaviors are well known and have been observed before.¹

The discrepancies between the data and the model can be primarily attributed to the fact that, as discussed in chapter II, section 1, the ion species is not uniform throughout the discharge chamber because the mean free paths are not necessarily short compared to a chamber length, in fact, they are almost always shorter. One consequence of that fact is that H_2^+ will be greatly attenuated by reaction 4.1 before it reaches a chamber wall, thus one expects that the data will definitely have a lower H_2^+ fraction and possibly a higher H_3^+ fraction than the model. Also, H_2^+ and H_3^+ have a significant chance of recombining with an electron before they reach the wall, but H^+ has a negligible probability of doing that, therefore one might expect that H^+ is

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Fig. 4-8 Measured (a) and calculated (b) species ratios of the positive hydrogen ions, as a function of discharge current. Data is based on ions extracted from filter region, with a correction for the different masses. Other discharge parameters are 90 V and 8 mTorr.

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Fig. 4-9 Measured (a) and calculated (b) species ratios of the positive hydrogen ions, as a function of pressure. Data is based on ions extracted from filter region, with a correction for the different masses. Other discharge parameters are 25 A and 90 V.

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Fig. 4-10 Measured (a) and calculated (b) species ratios of the positive hydrogen ions, as a function of discharge voltage. Data is based on ions extracted from filter region, with a correction for the different masses. Other discharge parameters are 25 A and 8 mTorr.

enhanced in the data relative to the model. When the above qualifications are taken into account, which tend to increase the measured H^+ fraction and decrease the H_3^+ fraction compared to the model results, the agreement between the data and the model is excellent.

Some data was also obtained at very high discharge currents (up to 300 A). The discharge had to be operated in a low duty-cycle (~ 0.01), pulsed mode (~ 1 ms pulses) because of power supply considerations, not to mention the problem of cooling the actual chamber. Operating in this 'high-power' mode caused the characteristics of the discharge chamber walls to change (transition time ≈ 20 minutes), as discussed in chapter III, section A-3. While the change in the wall condition caused only minor variations in the plasma parameters, the induced changes of the atom density and vibrationally-excited H_2 density were significant (factor of two decrease). The operating voltages were necessarily somewhat higher (120 V was more typical) for that data because otherwise space charge rather than filament temperature limited the achievable discharge current. Modeling was performed for only one set of high-power parameters (250 A, 120 V, 8 mTorr). There are several reasons for this. First, the agreement between the model and the data is much worse than for the low-power discharge conditions, for reasons that are not clear. Secondly, the data obtained for high-power operation is generally of poorer quality than the DC data, both for the probe measurements and the VUV data, because various background noise sources were greatly increased. Finally, it turns out that the VUV data on the vibrationally-excited molecules is much more incomplete because the molecules are extremely hot rotationally. No data could be obtained on the primary electrons because the method used presently is not applicable for short discharge pulses. The measurement technique for the thermal electron data was significantly cruder than for the DC

data (see next paragraph). The method used to obtain the species fraction data is easily amenable to pulsed operation and therefore that data for pulsed operation is the same quality as for DC operation.

The Langmuir probe data analysis was simpler for the pulsed mode of discharge operation. The thermal electron data was measured using straightforward probe techniques as usual; however, a computer analysis was not possible because of the limited data rate possible with the equipment available (each discharge pulse lasted only 1 ms or less, and the maximum data transfer rate was only ~ 2 kHz). Also, electronic noise caused by inductive effects could not be prevented from reaching the Langmuir probe electronics, slightly altering the measured I-V characteristic (but only on the 'ion' side). Therefore the data collection method consisted of simply photographing simultaneous oscilloscope displays of the probe current and voltage, and estimating the electron temperature as the plasma potential (times electronic charge) divided by two, the same ratio that was observed for the DC data (for which better measurements were possible). The plasma density was estimated based on the electron saturation current and the estimated electron temperature using the usual formula (see Eq. 3.8). To check this method, one curve was analyzed manually (the electronic distortion mentioned above could be subtracted out), and the results of the two methods agreed quite well (15%). The additional uncertainty of the electron density and temperature is easily comparable to the uncertainty inherent with any probe technique.

The data for the thermal electron characteristics during high-power pulsed operation over a range of discharge parameters is not presented, as most of the results will not be of interest presently. The measured electron density and temperature in the center of the discharge are $\sim 7.5 \times 10^{12} \text{ cm}^{-3}$ and $\sim 3.3 \text{ eV}$, respectively, at discharge parameters of 250 A, 120 V, and 8 mTorr.

The discharge pulses lasted 600 μs and had a 10.5 Hz repetition rate. The measurements were performed near the end of the pulse. Other measurements of the time dependence of the ion and electron saturation currents showed that the plasma reached equilibrium in $\sim 200 \mu\text{s}$. The primary electron density and temperature were estimated as $2 \times 10^{11} \text{ cm}^{-3}$ and 40 eV for modeling purposes. The model results for the above parameters yielded a total ion density of $1.4 \times 10^{13} \text{ cm}^{-3}$, which disagrees with the measured electron density by almost a factor of two. The disagreement is difficult to understand. The only variable parameter is the true H_2 density during the pulse which is unknown. Simple flux conservation arguments cannot determine n_{H_2} because the chamber pump-out time ($\sim 0.5 \text{ s}$) is much longer than the discharge pulse. VUV measurements cannot determine n_{H_2} either, because of the problems of the very hot rotational distributions (even for $v''=0$ at these currents) and the cold gas outside the discharge chamber (due to imperfect differential pumping). Therefore, n_{H_2} was estimated to be $\sim 1.2 \times 10^{14} \text{ cm}^{-3}$ ($\sim 45\%$ of the cold gas filling pressure), because this molecule density yielded good agreement for the measured atom density. The atom temperature and the wall recombination coefficient γ were accurately known for these parameters (0.35 eV and very close to 1, respectively). However, the positive ion species data is also in poor agreement with the model. Performing modeling calculations for other assumed primary electron and molecule densities yielded the result that no matter how these parameters varied (within reason), the agreement was always poor, for at least one of the three modeling results: the plasma density, the positive ion species ratio and the hydrogen atom density.

The failure of the model for this supposedly well-understood collection of processes suggests that the two subsequent phases of modeling cannot be taken

seriously either, for high-power operation. However, it is clear from a variety of indicators that the primary electron density must be much higher than during DC operation. The thermal electron density has increased by a factor of six compared to the 25 A, 90 V DC data. The atom density has also increased by about a factor of 3, despite a wall loss rate that has increased by almost 3 (see next section). The electron and atom temperatures are also both significantly higher, despite their rather weak scaling with power.

The calculated ion species ratio did not agree well with the measured ion species ratio, and the qualitative corrections discussed in reference to the DC data do not improve the agreement. The measured species ratio of $H^+ : H_2^+ : H_3^+$ is 74%:7%:19%, while the corresponding calculated quantity is 91.5%:4.3%:4.2%. The measured H_2^+ fraction is higher rather than lower than the calculated quantity. That indicates that either: the H_2 density during the pulse is greatly decreased compared to the cold gas value, or that possibly the internal energy distribution of the H_2 (and consequently H_2^+) is so different during the high-power operation that the reaction 4.1 has a significantly different rate constant, in particular, that it is lower. There is some evidence to support this proposition. As discussed in Chan, et al., two different groups found different values for the rate constant of reaction 4.1.⁷ The group that found the smaller value used a merging beam apparatus in which the H_2 studied was produced by neutralization of fast H_2^+ in a gas cell. H_2 formed in such a manner is very likely to have a different internal energy distribution (in particular, more internal energy) than room temperature H_2 , which was used in the other experiment which found a value a factor of 2 higher. The H_2^+ is believed to have had similar distributions in both experiments, and to be similar to that measured by Busch and Dunn,⁷⁸ who measured the vibrational distribution of H_2^+ produced by electron impact ionization (near 100 eV) of room temperature

H₂. That data, together with the present data, suggests that the increased internal excitation of H₂, and possibly H₂⁺, in a high-power discharge effectively decrease the rate constant for reaction 4.4.

The measured H₃⁺ fraction that is more than a factor of 4 larger than the model calculations. This discrepancy is more difficult to explain. We suggest several possibilities, all of which are speculative in nature. First, it may be that the H₃⁺ internal energy distribution appropriate to a high-power discharge is different from that in low-power discharge and that, correspondingly, the dominant product of fast-electron impact on H₃⁺ is H₂⁺ + H rather than H⁺ + (neutrals). Another possibility is that the rate for recombination of H₃⁺ with electrons yielding neutrals is decreased by altered internal energy distributions. The latter suggestion is indicated by the model results, which predict that the main loss of H₃⁺ is by free-space binary recombination.

B. Atomic Hydrogen – Density and Temperature

The results of the VUV absorption measurements on atomic hydrogen are presented in this section. The measured density is compared with the modeled density, and the agreement is generally quite good. The only atom loss mechanism, wall-catalyzed recombination, is parametrized by γ , the probability of an atom impacting the surface returning as half of a molecule. This quantity can be determined both by varying it so as to fit the model results to the data, or by the more direct technique of measuring the time scale for the atom density to change when the discharge conditions are slightly perturbed. One can also measure the γ relevant to the afterglow of a plasma (hundreds of μ s) by measuring the time scale for the atom density to decay, which is $\gamma_{\text{recom}}^{-1}$. The value of γ determined by the second method does not agree with the value determined by the other two methods, and the difference will

be discussed. The results are not necessarily in disagreement.

The actual quantity measured by the VUV system is the absorbance, which is an indicator of the atom density integrated along a path which passes through the discharge chamber, but which also passes through ~60 cm of vacuum plumbing. It is not immediately clear if the integrated density has a non-negligible contribution from the stray atoms in the differential pumping arms. First of all, we note that, for molecular flow, the contribution from the 'jet' just outside of an aperture exactly offsets the depletion inside of the aperture. Any correction necessary to the integrated density depends on the value of γ relevant to the atoms in the differential pumping arms, for which there are two limiting cases. The first is that all atoms are recombined on the first wall collision, in which case the correction factor is equal to unity. The second case is that the atoms don't recombine at all in the differential pumping arms and associated vacuum systems, in which case the correction is the same as for cold molecules, which has been experimentally determined to be 0.80 ($\pm 3\%$). The true value of γ in the differential pumping arms is unknown and cannot be measured presently, but we will estimate it at 0.05, a rather conservative estimate compared to the measured value of 0.14 for copper found by Woods and Wise.¹¹⁸ The atom loss rate γ_{recom} appropriate to the differential pumping arms will be given by $\sim v_{\text{th}}\gamma/(0.7\pi D)$, where D is the tube diameter, 10 cm, and v_{th} is the room temperature velocity of hydrogen atoms, $\sim 2.2 \times 10^5$ cm/s. This yields a value for γ_{recom} of $1.5 \times 10^{-3} \text{ s}^{-1}$, which means that the effective atom pumping speed in the arm is ~ 2000 l/s, as the volume of the arm is approximately 1.5 l (the diameter of each arm is 10 cm for ~20 cm of the length, but only 4 cm for the rest of the distance, which we ignore). The pumping speed of the other plumbing is negligible compared to that value. The density in the arm is then simply given by the density in the chamber

multiplied by the ratio of the pumping speed of the differential pumping aperture (0.38 cm diameter) to the above mentioned speed. The ratio is approximately $\sim (7 \text{ l/s}) / (2000 \text{ l/s}) = 0.0035$. The total path length in both arms is about 60 cm, whereas the path length in the plasma is 22.4 cm. Therefore the fractional line density outside the chamber is about 0.009 of the total, and this is much smaller than the estimated uncertainty of the raw data, so the correction, which is an overall multiplicative factor in any case, can be very safely neglected. The above numerical values apply to the data in which the VUV beam traversed the center of the discharge chamber. The data for which the VUV beam passed through only the filter region has an even smaller correction. Therefore the atom density presented, which is simply the line density measured divided by the distance between the differential pumping apertures, is very close to the true average along the path in the chamber.

The measured atom density and temperature in the discharge chamber are shown for various discharge currents, pressures, and voltages in Fig's 4-11 through 4-13. This data is an average based on a beam path which passes through the center of the discharge. For ease of writing, data of this type will be referred to as body data, and data derived from the path that traverse the filter region only is referred to as filter data. The geometry of the two different VUV beam paths is shown in Fig. 4-14. The qualitative trends are as one might expect: increasing the pressure, current, or voltage increases the atom density, and that increasing the power or decreasing the pressure increases the temperature. The measured profiles were almost always well fit by a single Gaussian, with very little evidence of superthermal wings. The atom densities tend to be rather low, in the range of 3% of the filling H_2 density, or ~5% of the actual molecule density when the discharge is on. The rather weak

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Fig. 4-11 Measured hydrogen atom density for various DC discharge parameters. Voltage was 90 V.

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Fig. 4-12 Measured hydrogen atom temperature for various DC discharge parameters. Voltage was 90 V. Note weak pressure dependence.

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Fig. 4-13 Measured hydrogen atom density (a) and temperature (b) as a function of voltage for several pressures. Discharge current was 25 A.

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Fig. 4-14 Diagram of discharge chamber illustrating the 'body' beam path and 'filter' beam path. Differential pumping apertures and associated plumbing are not shown. The distance between differential pumping apertures is 20 cm for the body (holes are slightly recessed from walls), and 7.6 cm for the filter.

dependence on current observed, particularly at higher pressures, is illusory: The atom temperature and hence the wall loss rate increases with current and the actual molecule density decreases, so the relative fraction of atoms is increasing more than it naively appears. It is clear from the data that discharge voltage has a weaker effect on the atom density than on the thermal plasma density, which increases by a factor of ~ 1.5 from 70 V to 150 V (see Fig. 4-1). The fact that the fractional increase with discharge voltage is the same at the three pressures measured in Fig. 4-13 indicates that the density of molecules is adequate to utilize the energy available from the primary electrons, even at the lowest pressure measured, 5 mTorr.

Filter data is shown in Fig.'s 4-15 and 4-16. The temperature data is very similar to the previous data, except that the temperatures are slightly lower in the filter, as might be expected, so it is not discussed further. However, the average atom density in the filter region is almost a factor of two less than that derived from the data in which the VUV beam passed through the center of the source. The difference was so striking as to indicate that possibly an error has been made in the data interpretation. All data was carefully rechecked and no trivial error had been made. In both cases the data was quite reproducible over weeks (or months in the case of the data for the discharge center) and after up-to-air events (after reconditioning described in chapter III, section A-3). Several points are worth noting. The data relevant to the center of the plasma was measured using Lyman- γ , while the data for the filter employed Lyman- β . The theoretical ratio of the oscillator strengths for Lyman- β and - γ was found to agree to the experimental ratio (unpublished data) to within 4% (which is smaller than our generally estimated uncertainty).⁹⁵ Also, it seems extremely unlikely that the theory calculations of a quantity this simple to calculate are incorrect, considering that the hydrogen atom has

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Fig. 4-15 Measured hydrogen atom density in magnetic filter region, as a function of discharge current (a) and pressure (b). Default parameters are 25 A, 90 V and 8 mTorr. The density inferred is less than the average over the chamber body.

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Fig. 4-16 Measured hydrogen atom temperature in magnetic filter region, as a function of discharge current (a) and pressure (b). Default parameters are 25 A, 90 V and 8 mTorr. This data agrees well with data appropriate to a path through the discharge center.

served as a virtual proving ground for quantum mechanics. It is known that the walls of the chamber were in the same condition for the two different measurements, namely, the 'low-power' state referred to in chapter III, section A-3, because the proportional reduction after operating at high-power was the same in both cases (this will be explained further in the next section). Therefore, we conclude that the density is, in fact, lower in the filter.

The most probable explanation for the two different measured densities is that the atoms are mostly created in the center of the discharge chamber and that as they travel outward towards the chamber wall, the density must decrease from flux conservation. This will be true whether or not diffusion through the molecules is important. If the atoms survived many wall bounces, the atom density would obviously become more uniform, but because it turns out that $\gamma \approx 0.6$, it is not inconsistent that there are gradients in the atom density. Diffusion involves momentum transfer collisions, which also cause the atoms to thermalize rapidly (translationally) with the much more numerous molecules, which have an average temperature of ~ 0.07 eV at most. Elementary mechanics shows that the energy excess of a hydrogen atom in a molecular gas is decreased by about a factor of two with each elastic collision, assuming isotropic scattering in the center of mass frame. Because the atom temperature in the filter is only slightly lower than the temperature inferred from the corresponding body data, it would appear that diffusion is not very important. Also, the ratio of the atom density in the filter to that averaged over the chamber has almost no pressure dependence, which again indicates that diffusion through molecules is not significant. If one assumes an momentum transfer cross section of 10^{-15} cm^2 , then the relevant mean free path is ~ 6 cm, which is close to the chamber radius. The actual beam path in the filter is recessed (see Fig. 4-14) and is shadowed slightly by the adjacent

pieces of the discharge chamber such as the filter rods, but the path has a clear view of most of the chamber, so it would seem unlikely that geometrical effects can explain the difference. In any case, one must take into account the density gradients when computing the average over the chamber. Because precise information is not available on the position dependent atom density, we will assume that the average density over the path through the center of the discharge is the same as the chamber average, as this path samples both the center and edge of the discharge chamber. This admittedly simple approximation probably slightly overestimates the true average over the chamber volume, but that depends on several factors, such as the effective volume of the atom-generating space and any possible diffusion taking place. Even if one knew the exact shape of the generating volume and assumed free space, isotropic, straight-line expansion, one would need to perform a Monte Carlo calculation in order to determine $n(\bar{x})$, from which the appropriate correction factor could be determined.

The comparison between the measured and calculated average atom density is shown in Fig. 4.17, as a function of various discharge parameters. The agreement is generally good, although the calculated voltage dependence is clearly incorrect, in a manner that is reminiscent of Fig. 4-1 (c). The measured atom temperature was used as an input to the model to calculate the wall bounce rate. The key assumption regarding the modeling is the assumed value of the wall recombination coefficient γ , which was measured directly by operating a typical low-power DC discharge with one of the filaments and pulsing a square-wave, low-duty-cycle perturbation discharge with the other filament. The actual parameters were 6 mTorr of filling pressure, 20 A and 120 V for the DC filament, and ~10 A at 120 V on the pulsed filament. The repetition rate was 10.5 Hz and the pulse length was

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Fig. 4-17 Measured versus calculated hydrogen atom density as a function of discharge current (a), pressure (b), and voltage (c). Default parameters are 25 A, 90 V and 8 mTorr. The qualitative disagreement for voltage variation is also observed in model vs. data comparisons of charged particle parameters.

1 ms. The second filament was kept hot and the bias was switched using the usual pulsed arc power supply. The atom density n_H was measured as a function of time relative to the start and end of the pulse. The laser pulse lasts only 20 ns, so the time resolution is clearly not a limitation. The density showed behavior close to a low-pass RC filter responding to a step function (the rise and fall time of the pulsed current was $\leq 1 \mu s$, which was effectively instantaneous). The time-dependent atom density is shown both for the rise and the fall in Fig. 4-18. The $1/e$ time scales observed are 43 and 40 μs , respectively, for data was measured in the filter region. A slightly longer figure (47 μs) for the rise was determined from the body data, but both figures have an estimated uncertainty of $\sim 10\%$. The measured time for equilibration is simply $(\gamma_{\text{recom}})^{-1}$, because the atom recombination rate is much faster than the effective molecule-to-atom rate, which is of order $200 s^{-1}$. The measured time scale is slightly longer for the rise than for the fall because the atom temperature also changes slightly with current, so the atoms are actually slightly cooler during the rise as compared to the fall. The atom thermal velocity corresponding to 25 A (~ 0.13 eV is best average) was used for the calculation of γ (see Eq. 2-21). The characteristic scale length is given by $2\sqrt{\pi} V/A$ and has the numerical value of ~ 12 cm, so the bounce time is $\sim 24 \mu s$ and therefore γ has the value of $(24 \mu s)/(41 \mu s) = 0.59 (\pm 10\%)$. This value was retained for the modeling at all DC discharge parameters modeled, effectively leaving no free parameters in the model other than the actual molecular density discussed previously in reference to the electron data.

One can also measure the decay of the atom population in the afterglow of a pulsed discharge in which there is no DC background. In this case, the atom temperature will quickly cool to a value near room temperature. One can correct for that effect easily, of course. The decay of the atom population

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Fig. 4-18 Measured rise (a) and fall (b) of the atom density as a function of time, for a 20 A, 120 V, 8 mTorr DC plasma with a low-duty-cycle, square-wave perturbation of ~ 10 A. $T_{\text{start}}, T_{\text{end}} = 10, 1030 \mu\text{s}$, respectively. Dotted lines have time scales of 43 and $40 \mu\text{s}$ for rise and fall, respectively. Walls are in their 'normal' state. See text.

measured in the filter is shown in Fig. 4-19. The plasma parameters were 8 mTorr, 20 A, and 120 V. The pulse length and repetition rate were 1 ms and 10.5 Hz, respectively. The time constant of the exponential decay is found to be 205 μs ($\pm 15\%$; the data is somewhat noisy). A small constant background density caused by filaments alone has been subtracted, but even if it had not been, the calculated time constant would have been only slightly different. Data measuring the atom density in the plasma body found 175 μs ; this data was also somewhat noisy for reasons not understood. The bounce time at the measured atom temperature of 0.033 eV (best average of many runs) is 48 μs , so the inferred value of γ is approximately 0.25 ($\pm 15\%$). Clearly, the disagreement between the value of γ derived with the afterglow method versus that derived from the perturbation method is larger than the associated uncertainties. We offer several possible explanations for the disparity, and they are related to each other. First of all, it may not be the case that the total proton density in the volume is constant in the afterglow of the pulse, that is, the walls may be evaporating hydrogen atoms. We speculate that during discharge operation, the walls of the discharge chamber have an excess of atoms very loosely bound to the surface and that the high surface density of atoms is maintained in a dynamic equilibrium by the large flux of atoms from the volume, $\sim 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$. When the discharge is terminated, the dynamic balance is changed and some of the atoms 'boil off'. Thus the atom data measured in the afterglow may not be described by the simple picture usually envisioned. Discharge pumping has been observed indirectly by a Russian group, for example.¹¹⁹ The effect is not directly observable for DC discharges because, once the wall has a steady-state population, it no longer acts as a source or sink for particles and thus flux conservation still holds. Another related explanation for the two different values of γ is that, even if the wall is in a

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Fig. 4-19 Measured atom density as a function of time, in the afterglow of a mild pulsed plasma (15 A, 120 V, 8 mTorr). $T_{\text{end}} = 1028 \mu\text{s}$. The temperature is approximately constant for $T_{\text{delay}} > 1200 \mu\text{s}$. The measured decay time is $\sim 205 \mu\text{s}$ ($\pm 10\%$). A small constant background caused by filament dissociation has been subtracted. Walls are in their 'normal' state. See text for further discussion.

quasi-steady state condition during the afterglow, the wall recombination coefficient applicable to the walls when only the filaments are operated may be different from that during the discharge, for precisely the reason that the steady-state of atoms on the surface is different. In order to test the theory of wall loading and unloading on a sub-millisecond time scale, one would have to measure the time histories of every neutral species in the discharge chamber in the afterglow of a pulse, that is, the atoms and all the significant $H_2(v'',J'')$ states. This experiment should be performed at a low pressure ideally so that there is no uncertainty about density gradients in the discharge, and one needs very good differential pumping so that the gas density outside the apertures is negligible, a condition that was not well satisfied for the present arrangement during relatively high-power discharge operation.

The atom density and temperature for the selected high-power pulsed parameters, 250 A, 120 V, and 8 mTorr, were measured to be $1.8 \times 10^{13} \text{ cm}^{-3}$ and 0.35 eV, respectively. The temperature and density inferred from the body data and filter data agreed well this time, in contrast to the low power data. Generally, the atom density was found to increase with increasing power, but one unusual effect was observed: when the discharge voltage was low enough so that the space-charge effect had a strong limiting effect on the discharge current obtainable, the atom density saturated or even decreased. For instance, Fig. 4-20 shows the atom density as a function of discharge current for 8 mTorr and 100 V. The atom density decreases from 150 A to 200 A, in contrast to the behavior at lower currents and to what one would expect. The filament heater current necessary to obtain the 200 A data was extremely high (270 A), and the filaments will burn out in a short period of time at this power. Data measured with 150 V instead of 100 V of discharge voltage (which is enough of an increase to eliminate the space-charge current limitation problem) did not

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Fig. 4-20 Measured atom density as a function of current. Discharge is pulsed; other parameters are 8 mTorr and 100 V. Severe space-charge current limitation starts at same current where atom density turns over.

have the turnover, at least up to 250 A. The reason for this effect is unknown, but an obvious possibility is that the tungsten evaporation rate is so high as to bury some of the atoms. The true filament temperature could not be measured, but it must be higher than the minimum temperature necessary (~ 3100 K) to supply the emission current density from the filaments (~ 25 A/cm²). The time necessary to coat the walls of the discharge chamber with a monolayer of tungsten is close to 100 seconds at that temperature, and even if the temperature were 400 K higher, which is almost to the melting point of tungsten, the time would still be at least one second, thus it would appear that the tungsten flux should not be able to bury the atoms. No loss in pressure could be observed on a downstream ion gauge, but this may be because the atom density is a small fraction of the molecule density, even at these high-power levels. The effect is not a hysteresis effect, that is, reducing the discharge current from the turnover point will increase the atom density again. The explanation for the turnover is thus still unresolved.

C. Hysteresis Effect

The atom density during DC discharge operation is generally a single-valued function of the discharge parameters. Once the conditioning procedure following an up-to-air event is performed and after about 10 minutes of operation each morning, the values for the atom density and also of the vibrationally-excited molecules are very reproducible ($\pm 10\%$ at worst), even on the time scale of months. However, if a high-power (≥ 250 A) discharge is performed for approximately 30 minutes or more, the atom density during subsequent DC discharges will be reduced by almost a factor of two. Interestingly enough, the same factor of reduction is observed for the vibrationally-excited H₂. This hysteresis effect is clearly related to the

condition of the walls and not an ion pumping effect. The walls can be recovered to their normal state by either bringing the source up to atmosphere pressure (and reconditioning) or simply by waiting some period of time without operating a discharge. The recovery time varies, but is at least several hours and usually overnight. The wall condition also apparently recovers during low-power DC discharge operation, although it was never possible to observe the complete recovery with continuous discharge operation for practical reasons of time. The two states of the wall are simply referred to as 'normal' (or 'low-power') walls, and 'high-power' walls. The cause of this hysteresis effect is not understood. A discussion of some of the possible fundamental causes is found in chapter III, section A-3. The present section is restricted to the raw data. One very important fact is that the procedures to effect the change and the recovery of the walls are very reproducible. The behavior was observed perhaps 20 or 30 times over the course of these experiments.

The wall recombination coefficient for atoms was directly measured to have been altered by the process of operating a high-power discharge for the prerequisite amount of time. Fig. 4-21 shows the response of the atom density to the same discharge conditions used to measure the data shown in Fig. 4-18 (actually, the pulsed current was accidentally slightly larger in magnitude by about 10%, but this will not change the fundamental results). The time scale for the rise of the atom population has decreased from 43 to 27 μ s, yielding an increase of 1.6 in the atom recombination rate. The bounce time for atoms is only 24 μ s for the condition measured, so the value of γ is almost unity! This value means that every atom that impacts the wall returns as part of a molecule. Surprisingly, the temperature of the atoms is not measurably different for the two different wall conditions during DC discharge operation,

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Fig. 4-21 Measured atom density as a function of time, for a 20 A, 120 V, 8 mTorr DC plasma with a low-duty cycle, square-wave perturbation of ~ 10 A. $T_{\text{start}} = 10 \mu\text{s}$. Dotted line has time scale of 27 μs . Walls are in their 'high-power' state. See text.

although it may be very slightly smaller for the high-power wall conditions. The best value of the fractional reduction of the atoms for DC discharge parameters of 35 A, 90 V, and 8 mTorr is about 0.55. The reduction was not systematically explored as a function of DC discharge parameters, but various data indicate that the reduction is always about the same proportionally. The afterglow decay of the atoms could not be measured for the 'high-power' walls because the atoms decayed away so quickly that the plasma was not completely gone yet; also the atom temperature was still changing.

D. Discussion

The measured values of the ion density, ion species ratio, and atom density are in good agreement with the model in most cases. The discrepancy between the measured and calculated values, as a function of discharge voltage, is clearly caused by some error in the measurement of the primary electron parameters, which is unexplained. However, the same behavior was observed by Eenshuistra, et al., so the explanation is not simply experimental error.¹¹⁷ It seems that the most likely explanation is simply a larger effective volume of primaries for high discharge voltages. In order to perform a clean test of that hypothesis, one would have to measure the EEDF at a variety of points along a chamber radius. But because moving the probe (and its associated shield) causes the plasma to be perturbed in an uncontrollable manner, one would ideally use an array of fixed probes at different radii. The wall recombination coefficient γ has been demonstrated to have a value of ~ 0.6 , much larger than previously observed.^{1,8,87} However, the evidence is quite compelling that this value is correct, particularly the response of the atom density to a perturbation of the discharge. We will only discuss data in the literature applicable to a true discharge. The value published in Ref. 1, 0.05, is actually in error, due to a

mistake in the data analysis, and should be ~ 0.14 .¹²⁰ That value was arrived at by varying the value of γ in the model in order to fit the calculated species ratio to the observed values; however, the discharge power was very high in that application, so considering the poor performance of the model presently for the high power data, this may be not be completely valid. Secondly, the cross section for dissociation of H_2 assumed in Ref. 1 is much higher than more recent, calculated values. Finally, the species ratio is not very sensitive to the value of γ when the power density and the scale length are relatively high, so the method of determining γ is not very accurate.

Eenshuistra found a value for γ of 0.12 for discharge conditions and chamber similar to those employed here. However, the calibration of the absolute H-atom density inferred from the REMPI signal in that experiment was based on the assumption that the loss of density in the lower v'' and J'' states was caused by dissociation into atoms (after taking flux conservation and increased temperatures into account). However, we observe that in the present work, the decrease in density of the lower rovibrational states is not caused by dissociation, but rather displacement into states of high rotational quantum number, and that the equivalent molecule flux of the atoms passing through the differential pumping holes can only account for a small fraction of the observed reduction in density of molecular states with low values of v'' and J'' . If the atom density of Ref. 87 is actually lower than is stated, then the value of γ found in that work would have to be increased by the inverse factor. Therefore, it is possible that this may explain some of the discrepancy. It must be noted that both the thermal and primary electron densities were smaller in that experiment by about a factor of three, which would make the high J'' populations less important. In any case, it is not necessarily true that a direct comparison is possible because it is not known if the condition of the walls in

that experiment was similar to that in the present experiment. For instance, it may be that the impurities in the tungsten filaments are different and that these impurities have a strong effect on the wall reaction rate. The conclusion is that the two results are not necessarily in disagreement. We suggest that any future experiments use the perturbation-response method in addition to other data, because we believe that that technique is a more direct way to measure γ .

There is no mention of a hysteresis effect regarding the atoms in the references, at least not that has behavior similar to that found presently. At this time, the effect is not understood, although the processes of grossly increased surface roughness and/or some change in the chemical nature of the surface have been discussed. The density of excited molecules was also observed to decrease when the walls were in the high-power state. If these effects are common to most experiments, then it might explain why the high power H^- extraction results found in Ref.'s 85, 89, and 90 do not seem to be as large as might be expected based on results of experiments conducted at much lower power. It would be most gratifying to see the behavior reproduced in an independent laboratory.

Chapter V

Experimental Results - II

The results of the measurements of the H_2 rovibrational distributions are presented in this chapter, as are the measured H^- data. In each case, the data are compared to model calculations in which most or all of the inputs to the model were measured rather than calculated. It is found that the measured vibrational distribution can be characterized by a temperature and that it agrees well with a model that employed measured quantities for almost all input parameters. The relaxation probabilities per wall collision of quasi-rotationless states of $v''=1-5$ were measured in a relatively direct manner and found to be in the range of 0.025 to 0.09. The corresponding relaxation rates are smaller than the calculated rates for unit changes of the vibrational quantum number, which leads to the conclusion that cascade pumping by thermal electrons is the dominant mechanism of vibrational excitation. Model calculations indicate that the direct influence of the primary electrons on the vibrational distribution is weak. The H^- density has been measured and is consistent with the measured rovibrational population distribution, assuming moderate extrapolations of the rotational distribution for $v''=5-8$ (which could not be measured for sensitivity reasons). However, the data is not conclusive. In particular, it appears that the 'tail' of the rotational distributions for almost *all* of the vibrational levels could play a significant role in H^- production.

A. Rovibrational Distributions -Preliminary

The ideal goal of this thesis would be to measure the population and temperature of each individual $H_2(v'',J'')$ state as a function of the various

discharge parameters and then to compare that data to a complete model of the rovibrational distribution and also to use the data to calculate the H^- density expected as a result of those measurements. However, the large number of bound $H_2(v'',J'')$ states (~ 294) forces one to make various approximations and simplifications in order for the problem to be tractable, both for the measurements and the model calculations. In particular, the subdivision of the vibrational levels into rotational levels enormously increases the effort required for the analysis. Conventionally, rotational substates have been completely ignored in the modeling^{49,53,54} and have been treated only as an effective degeneracy factor for measurements.⁸ There is some justification for these assumptions. First of all, it is sometimes true in a discharge that most of the molecules within a given vibrational level are concentrated in the first few rotational states at low discharge power.⁸ Also, the dissociative attachment cross sections do not increase as much with rotational energy as with vibrational energy, according to several theoretical works and one experiment, although the rotational enhancement from the various papers do not agree exactly.^{23,26,44} However, as was first observed by Péalat, et al. and is confirmed presently, the rotational distribution within a given vibrational level is strongly superthermal for states with $J'' \geq 7$.^{57,58} Péalat, et al. did not measure how the tail of the distribution was affected by changing the discharge parameters, in particular, by increasing the discharge current. The data presented here illustrates that the superthermal tail of the distribution can have a significant part of the population within a vibrational level and can contribute most of the dissociative attachment rate from a given vibrational level. At very high powers (i.e., 250 A, 120 V), even most of the raw population within a vibrational level will be contained in the high rotational states.

The influence of the superthermal tail of the rotational distributions complicates matters because 1) it is not always sufficient to simply measure the population of the $J''=1$ state in order to determine the total population of a vibrational level, as is sometimes assumed, and 2) one must account for the fact that high J'' states have substantially different dissociative attachment rates than low J'' states within the same vibrational level. Thus it is imperative to derive approximate scaling laws from the data so that one does not have to measure all $H_2(v'',J'')$ states at all discharge parameters. As will be seen, it was possible to do just that and still be reasonably accurate, up to the highest rotational state measured for each vibrational level. However, it was not possible to measure all of the 'tail' of the rotational distributions, even for $v''=0$, for various technical reasons. First of all, the relatively small population within a particular high J'' state made detection difficult because the signal-to-noise ratio became too small, particularly for $v''\geq 3$. Secondly, the wavelengths of most of the higher J'' transitions (for bands that have a good Franck-Condon factor) are in a spectral region in which the present VUV generating scheme does not function well (λ_{max} is ~ 125 nm, also there are several 'dead' VUV-generation regions at smaller wavelengths caused by resonant Hg photoabsorption in the Hg vapor oven). Third, the wavelengths of most high J'' transitions are not even known. And last but certainly not least, one must remember that it has been assumed that the oscillator strength for a particular transition is simply the product of an electronic-vibrational band factor multiplied by the usual Hönl-London rotational factor. However, this approximation must break down at high J'' , because the vibrational wavefunctions and therefore the effective Franck-Condon factors are altered by the centrifugal distortion of the potential wells. In fact, it is possible that the approximation is not completely accurate even for the moderately high J''

states observed ($J_{\max}=15$). As discussed in chapter III, section B-2, it should be possible to calculate correction factors (for each rotational transition within each band!), but to our knowledge this task has not been performed. To repeat, the reasons that complete rotational distributions were not measured for the various vibrational levels are 1) lack of sufficient detection sensitivity needed to measure the small populations in high J'' states, 2) lack of VUV generation capability for many high J'' transitions, 3) lack of wavelength data for many other high J'' transitions, and 4) loss of confidence in oscillator strengths determined using the assumption that the rotational factors are separable from the electronic and vibrational factors.

This section and the next presents the results on the measured populations and temperatures of various rovibrational states of the ground electronic state of the hydrogen molecule. The key topics of interest are 1) the nature of the rovibrational distribution for 'typical' discharge parameters, and 2) the scaling laws for discharge current and pressure variation. Because preliminary data indicated that the change of the various populations with varying voltage was considerably smaller than the change with current, it was decided to best utilize the available resources and time by only measuring the variation with current. More simply put, current is apparently more effective than voltage at converting electrical energy into internal energy of the the discharge constituents. The default discharge parameters used for the DC data presented in this chapter were 35 A, 90 V, and 8 mTorr.

The densities presented are simply the total line density measured divided by the distance defined by the differential pumping apertures. All data presented is that inferred from absorption of the VUV beam traveling through the center of the discharge chamber, unless otherwise stated (see chapter IV, section B). An estimation of the contribution from rovibrationally-excited H_2

in the differential pumping arms depends on the assumed wall collision relaxation probability for rovibrationally-excited molecules. Actually, the wall relaxation probability depends on v and J ; also, it is unlikely that a rovibrationally-excited molecule loses all of its energy during a single wall collision. A more realistic model for the stray gas would include the effect of cascading. However, neither the total loss probability from a given state (per wall collision) or the branching ratios to the energetically-accessible states are known in general, so a sophisticated treatment is not warranted. A correction factor was derived for the simpler case of the hydrogen atom measurements (see chapter IV, section B) and it was very small ($\sim 1\%$), even for an atom recombination probability of only 0.05 per wall collision. Therefore, in the absence of better information, it is simply assumed that the contribution to the line density from the differential pumping arms is negligible, for any $H_2(v, J)$ state with $v \geq 1$ or $J \geq 4$. In any case, the correction factor is between 0.80 and 1 and probably is very insensitive to discharge conditions, so the results presented would not be qualitatively changed. However, cascade relaxation from high J and/or v to low (but not zero) v and J in the differential pumping arms could possibly lead to a higher fractional population of $H_2(1, \text{low } J)$ outside the chamber than inside the chamber, and there is some indirect evidence for this, which is discussed in the next paragraph.

If all the gas in the differential pumping arms is essentially at 300 K with respect to internal energy and translation, then the $H_2(0, J)$ line density measured when the discharge is operated must be corrected downwards by 0.20 of the total line density measured for cold gas at the same pressure. During DC operation at least, the gas density in the differential pumping arms is only a function of the gas flow rate (i.e., the pressure measured with the discharge off), but not the discharge conditions, because of flux conservation. This result

assumes only translation equilibration with the walls. The correction is substantial, even at moderate powers. For instance, at 35 A, 90 V, and 8 mTorr, the correction to $\Pi(0,1)$ is $\sim 3/4$ of the measured line density! If $n(0,1)$ is plotted on a semi-log graph along with the other $n(v'',1)$, $n(0,1)$ falls below the line applicable to the $v'' \geq 1$ points (see Fig. 5-13), which is the opposite behavior of what one expects, therefore it is probably true that the gas outside the arms does have some mild internal excitation. Although we have no data regarding this issue, the 'best estimate' is that almost all of the stray gas is in the lower four J'' states of $v''=0$ and 1. Some justification for this is derived from the measured translational temperatures: the $J''=0-3$ states of $v''=0$ and 1 are cooler than the other states of either high J'' ($J'' \geq 5$) or high v' ($v' \geq 2$), which are generally in the range of 0.08 eV for the aforementioned discharge conditions. It may be true that the average translational temperature of the molecules in the discharge that are in the low J'' states of $v''=0$ and 1 is less than the temperature of the other states, but it is certainly true that the temperature inferred from the absorption data must be contaminated by cold gas outside the discharge chamber. Unfortunately, the measured absorption profiles are not accurate enough in order to determine the profile due to the gas inside the chamber by subtracting the calculated absorbance profile of the background gas from the measured absorption profile.

Fig. 5-1 shows the population of the lowest four rotational states of the $v''=0$ state for room-temperature gas divided by the appropriate degeneracy factors measured using the $B \leftarrow X \ 0 \leftarrow 0$ band. The gas was flowing through the discharge chamber at a pressure of 3.05 mTorr ($\pm 2\%$), while the discharge and filaments were completely off. In this case, the line density correction factor of 0.80 was applied to the data to account for the non-negligible gas density in the differential pumping arms. The inferred densities are all $\sim 15\%$ lower than that

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Fig. 5-1 Measured density of first four rotational states of hydrogen ($J''=0-3$), for room temperature gas at 3.05 mTorr. The data is uniformly 15% lower than the values inferred from true Boltzmann equilibrium and the ideal gas law. Data has been corrected for cold gas outside the discharge chamber.

densities calculated based on the ideal gas law and the usual partition function calculation. We believe that the discrepancy is *possibly* due to an error in the calculated band factor,⁹⁴ although we do not claim this absolutely. The capacitance manometer was very well calibrated (~2% accuracy) and has very good zero drift behavior; also, the uncertainty in the total integral of pressure over the path was only ~4% because the pressure in the differential pumping arms was measured, not calculated (the lengths are accurately known, of course). The error is not related to incorrectness of Hönl–London factors because the least-squares-fit rotational temperature (289 K) is in very good agreement with the wall temperature (291±0.5 K). The statistical uncertainties were only a few percent at most. An error of 15% is certainly consistent with the experimental data to date on the oscillator strength, although the present data is admittedly on the outside of the spread.¹²¹ The B←X 0←0 band factor is relatively weak, and transitions that have more cancellation (in the vibrational wavefunction overlap integral) are more subject to error, as is stated in Ref. 94. On the other hand, one might expect that the calculated 0←0 Franck–Condon factor would be the most accurate because the shapes of potential wells are generally most accurately known at the bottom of the well. Measurements comparing the transitions from the B←X 0←0 and 3←0 bands agree very well (~5%), so it appears that there may be a quasi-universal scaling error. If the electric dipole moment of the B←X transition calculated by Wolniewicz is low by only 8%, the discrepancy would be explained.¹²² All other $v''=0$ data was shifted upwards by the factor $(0.85)^{-1}$ independent of any other corrections, but there is no easy method to check the band factors for $v'' \geq 1$, as calibrated sources of $H_2(v'', J'')$ do not exist. Possibly, one could build an oven that has VUV windows and that could be heated enough to generate a detectable amount of $v''=1, 2, \dots$ ($n(v''=1)/n(v''=0) \approx 10^{-9}$ at room temperature),

but this was not done for obvious reasons of practical difficulty.

If one believes that the calculation of the band factor for $v''=0$ is incorrect by 15%, then one must immediately assume that the other band factors could have similar errors, so the uncertainty of the data is increased. This uncertainty is comparable to the generally estimated uncertainty from other sources (10%), for states where the absorption is strong enough ($\geq 10\%$) to perform a measurement with statistical uncertainty of 5% or less. For measurements in which the peak absorption is smaller than ~ 0.1 , statistical errors often become more significant, although usually the data was averaged over more laser pulses to attempt to compensate for that fact. The estimated total absolute uncertainty is then $\sim 18\%$ for states where the statistical uncertainty is small, but the relative uncertainty, at least for measurements using the same transition, is estimated to be $\leq 5\%$.

Generally, only the odd J'' states (ortho-hydrogen) were measured because they are three times more numerous than even J'' states due to the well-known correlation between total angular momentum and nuclear spin imposed by quantum mechanics. Many different data of the present work, including that presented in the preceding paragraph and other data not shown, indicate that the '3 to 1 rule' is completely reliable, not only for cold gas, but when the discharge is on. One might believe that the discreteness of the various rotational energy levels would cause the actual ratio of ortho- to para-hydrogen to deviate slightly from 3 for true Boltzmann equilibrium, and that is true, but the error in estimating the total population as $4/3 \times$ the population of only the odd J'' states is less than 1%, even at room temperature. Because the even J'' states are interwoven between the odd J'' states, we are effectively only increasing the density of rotational states per unit energy by $4/3$.

B. Rovibrational Populations – Data

The density of various rovibrational states is shown in Fig. 5–2 for DC discharge parameters of 35 A, 90 V, and 8 mTorr. The abscissa is the rotational energy of the state, defined as $E_{\text{rot}} = E(v'', J'') - E(v'', 0)$. The $v''=0$ data were corrected as discussed on p. 171. Also, $n(5,3)$, $n(7,1)$ and $n(8,3)$ were estimated based on $n(5,1)$, $n(7,3)$, and $n(8,1)$. The distinctive feature that seems to be universal about the data is that the normalized rotational distribution plots have a second derivative that is positive or at least zero for all values of E_{rot} . The populations in the high J'' states of the first two vibrational levels decrease slowly with J'' (neglecting nuclear spin factors) for $J'' \geq 10$. We assume that the same is true for the higher vibrational levels, although the sensitivity is not sufficient to truly reach the 'plateau' region of the rotational distribution for $v'' \geq 2$. Similar behavior was observed by Péalat, et al.^{57,58} In previous work by the author, the rotational distributions in a discharge with similar parameters (but with a LaB_6 cathode and therefore with very different wall conditions) were measured and a rotational quasi-temperature was assigned to each vibrational level based on the population of the $J''=0-3$ states.¹²³ The basis for using the concept of temperature at all is that the data points should fall on a straight line for a graph of $\ln(n_i)$ vs. E_i , where i is a generic subscript. However, for the present data, even $J''=3$ was found to be off the line formed by $J''=0-2$ (for $v''=1$), so the concept of rotational temperature is not very useful presently. The temperature inferred from the $J''=0-2$ data, ~ 0.04 eV, is very similar to that found from the previous work, as is the general shape of the distribution. However, the rotational temperature derived from the low J'' states cannot be used to predict the total population of the vibrational level with any accuracy, so the measured distributions must be used without approximation for calculations of densities and rates. The vibrational distribution is well

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Fig. 5-2 Measured density of various rovibrational states of hydrogen. Discharge parameters were 35 A, 90 V, and 8 mTorr. $v''=0$ data was corrected (see text). $n(5,3)$, $n(7,1)$, and $n(8,3)$ were estimated based on $n(5,1)$, $n(7,3)$, and $n(8,1)$, respectively.

described by a temperature of ~ 4650 K ($\pm 5\%$), based on the $J''=1$ state populations only. However, the vibrational temperature determined using the total population within each vibrational level is undoubtedly somewhat higher, because the $J''=1$ fraction of the population decreases with v'' . For instance, $(\sum n(v'', J''))/n(v'', 1)$ changes by a factor of 2 from $v''=1$ to 4 (arbitrarily taking $J_{\max}=9$), so the temperature determined using the summed population is ~ 5450 K, while the temperature based on $n(v'', 1)$ for $1 \leq v'' \leq 4$ is ~ 4450 K. Actually, the total population for each vibrational level is not known because the populations of the high J'' states are not known, especially for $v'' \geq 5$. The vibrational temperature and the high J'' state populations are discussed further in section D.

Table 5-1 lists the transitions used to measure the data of Fig. 5-2. In some cases, the population of a given $J''=1$ state was measured using transitions from two different bands, and the agreement was better than 10% in all cases. No comparisons are available for $v'' \geq 4$ because the only bands (besides those actually used) which have large enough Franck-Condon factors to be useful are not accessible because of wavelength restrictions on the VUV that can be produced. The combined facts that many different vibrational levels of the B state were used as the final state while measuring the various J'' states of $v''=0-2$, and that the high J'' populations in Fig. 5-2 have no glaring structure is somewhat reassuring, in that apparently any relative errors of different band factors are not enormous.

The effect of varying the discharge current on the rotational distributions and the populations of specific (v'', J'') states is shown in Fig.'s 5-3 through 5-8. The $v''=0$ data have been corrected based on the assumption that the gas outside the discharge chamber is completely equilibrated with the walls (300 K); even if the correction is not 100% accurate, the qualitative results found

Table 5-1

Molecular Hydrogen Transitions Used for Absorption Measurements

v''	J''	Transition	Alternate*
0	0	B $\leftarrow$ X 0 $\leftarrow$ 0 R(0)	
	1	" " P(1)	B $\leftarrow$ X 3 $\leftarrow$ 0 P(1)
	2	" " R(2)	
	3	" " R(3)	
	5	" 1 $\leftarrow$ 0 P(5)	
	7	" " R(7)	
	9	" 3 $\leftarrow$ 0 P(9)	
	11	" 4 $\leftarrow$ 0 P(11)	
	13	" 5 $\leftarrow$ 0 R(13)	
1	0	B $\leftarrow$ X 0 $\leftarrow$ 1 R(0)	
	1	" " R(1)	
	2	" " R(2)	
	3	" " R(3)	
	5	" 1 $\leftarrow$ 1 P(5)	
	7	" " R(7)	
	9	" 2 $\leftarrow$ 1 R(9)	
	11	" 3 $\leftarrow$ 1 R(11)	
	13	" 4 $\leftarrow$ 1 R(13)	
	15	" 6 $\leftarrow$ 1 R(15)	
2	1	B $\leftarrow$ X 0 $\leftarrow$ 2 R(1)	B $\leftarrow$ X 3 $\leftarrow$ 2 R(1)
	3	" " P(3)	
	5	" " R(5)	
	7	" 1 $\leftarrow$ 2 R(7)	
	9	" 2 $\leftarrow$ 2 P(9)	
	11	" 2 $\leftarrow$ 2 R(11)	
3	1	C $\leftarrow$ X 0 $\leftarrow$ 3 Q(1)	B $\leftarrow$ X 6 $\leftarrow$ 3 R(1)
	3	" " Q(3)	
	5	" " Q(5)	
	7	" " R(7)	
	11	" " Q(11)	
4	1	C $\leftarrow$ X 1 $\leftarrow$ 4 Q(1)	B $\leftarrow$ X 9 $\leftarrow$ 4 R(1)
	3	" " Q(3)	
	5	" " Q(5)	
	7	" " Q(7)	
	9	" " Q(9)	
5	1	C $\leftarrow$ X 2 $\leftarrow$ 5 R(1)	
6	1	C $\leftarrow$ X 2 $\leftarrow$ 6 Q(1)	
	3	" " Q(3)	
7	3	C $\leftarrow$ X 3 $\leftarrow$ 7 R(3)	
8	1	C $\leftarrow$ X 4 $\leftarrow$ 8 Q(1)	

*Densities inferred using $J''=1$ transitions from different bands agree to 10% or less in all cases.

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Fig. 5-3 Measured rotational population distribution for $v''=0$ (a) and $v''=1$ (b), at several currents. Other discharge parameters were 90 V and 8 mTorr. The 200 A data for $v''=1$ cannot be directly compared to the other data because the voltage was higher and the condition of the walls was different.

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Fig. 5-4 Measured rotational population distribution for $v''=0$ (a) and $v''=1$ (b), at several currents. Other discharge parameters were 90 V and 8 mTorr.

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Fig. 5-5 Measured rotational population distribution for $v''=4$ at several currents. Other discharge parameters were 90 V and 8 mTorr. The 200 A data cannot be compared directly with the other data because the voltage and the wall conditions were different.

XBL 908-2643

Fig. 5-6 Measured effect of discharge current on the populations of several rotational states of $v''=0$ (a), 1 (b), and 2 (c). Low J'' states show no increase with current past threshold, but states of higher J'' do. Other discharge parameters were 90 V and 8 mTorr.

XBL 908-2644

Fig. 5-7 Measured effect of discharge current on the populations of several rotational states of $v''=3$ (a) and 4 (b). Low J'' states show no increase with current past threshold, but states of higher J'' do. Other discharge parameters were 90 V and 8 mTorr.

XBL 908-2645

Fig. 5-8 Measured effect of discharge current on the populations of several rotational states of $v''=5$ & 6 (a) and 7 & 8 (b). Note weak scaling with current. Other discharge parameters were 90 V and 8 mTorr.

presently will not change. The observed behavior is clearly that increasing the discharge current beyond ~10 A decreases the population of the low J'' states and increases the population of the high J'' states, for $v''=1$. The same general trends were observed for all of the vibrational levels in which a spread of rotational levels could be observed ($v''=0-4$). For higher vibrational levels, the current corresponding to maximum density of the $J''=1$ state can be somewhat higher, but in all cases it is clear that the dependence of $n(v'',1)$ on current is characterized by an (unobserved) sharp rise at low current followed by an almost flat region which eventually turns over. All rotational states of the $v''=0$ level with $J'' \geq 9$ apparently have the same relative scaling with current, at least from 5 to 35 A. In other words, the rotational temperature of the very high J'' states by themselves seems to be invariant with respect to discharge current over the range measured. The same behavior also seems to be observed for $v''=1$, although the data is a little more ambiguous in that case. It is assumed that similar behavior would be observed for high J'' states ($J'' \geq 10$) of the higher vibrational levels, although we do not have the sensitivity to measure it. The rotational distribution for high-power (200 A, 120 V), pulsed operation was obtained for $v''=1$ and 4 (see Fig.'s 5-3 (b) and 5-5). The walls were in the 'high-power' state for this data, however, so the 200 A data cannot be compared directly to the 35 and 5 A data. The trend of increased discharge current increasingly shifting the population within a vibrational level to the higher J'' states is clear, though. Surprisingly, it turns out that the vibrational temperature is only slightly different at 250 A than at 35 A, based on the $J''=3$ state populations (which are generally the most populated rotational state for high power).

A very important question is, how does discharge current affect the source term for H^- , $n_{H_2} \langle \sigma v \rangle_{AD}$, or alternatively, $\sum n(v'', J'') \langle \sigma v \rangle_{DA; (v'', J'')}$. The

calculation is not trivial because the different J'' states have different responses to varying the discharge current. In addition, the contribution of the superthermal tail of the various rotational distributions will be significant. Actually, most of the states observed have a negligible rate constant for dissociative attachment.²⁶ In particular, all of the rovibrational states that could be detected for $v'' \leq 4$ make an insignificant contribution to the total H^- creation rate, although the $J''=7$ and 9 states of $v''=4$ probably contribute a few percent of the total. The only $H_2(v'', J'')$ states observed that have a large enough dissociative attachment rate constant to possibly contribute significantly to the overall dissociative attachment rate are (5,1), (6,1), (6,3), (7,3), and (8,1). The dependence of those populations on discharge current is shown in Fig. 5-8. Even the relative uncertainties are significant for the $v''=7$ and 8 data, but it is clear that the scaling with current is weak, past some threshold region. The populations of all of these states apparently saturate at ~ 15 A, which implies that they are not the dominant source terms for H^- in the discharge, because H^- increases strongly with current (an increase in electron density alone will not increase n^- , see Eq.'s 2-31 and 2-32). The conclusion is, unfortunately, that no rovibrational states which contribute significantly to the total dissociative attachment rate have been observed! This important conclusion will be discussed in further detail in section E.

The scaling with pressure of various $H_2(v'', J'')$ states is shown in Fig.'s 5-9 through 5-11. Pressure had no measurable effect on the relative rotational distributions; that is, the fraction of the population of a vibrational level within a given J'' state was apparently independent of pressure. This conclusion was based on the simple observation that, for a given vibrational level, the ratio of the population of the $J''=1$ state population versus that of the highest accessible J'' state (for that vibrational level) was independent of

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Fig. 5-9 Measured effect of pressure on the populations of several rotational states of $v''=0$ (a), 1 (b), and 2 (c). Note that different J'' states within a vibrational level apparently scale proportionally. Other discharge parameters were 90 V and 35 A.

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Fig. 5-10 Measured effect of pressure on the populations of several rotational states of $v''=3$ (a) and 4 (b). Note that different J'' states within a vibrational level apparently scale proportionally. Other discharge parameters were 90 V and 35 A.

XBL 908-2648

Fig. 5-11 Measured effect of pressure on $n(5,1)$ (a) and $n(6,3)$ (b). The two sets of data in (a) were taken a few months apart. The turnover seen in (b) is probably statistical noise, based on other data. Other discharge parameters were 90 V and 35 A.

pressure, within the experimental uncertainties. The highest vibrational level in which a spread of rotational states could be measured was $v''=4$, therefore we do not claim that the relative rotational distribution of the $v''\geq 5$ levels is also invariant with pressure. The baseline noise would have to be considerably reduced in order to answer that question. There was a difference of the pressure scaling between the low vibrational levels and the higher levels. The populations of the $v''=0$ and 1 vibrational levels was observed to scale linearly with pressure, up to 20 mTorr at least. For higher vibrational levels, the scaling was less than linear, although the density was monotonically increasing with pressure up to 20 mTorr for all v'' measured. Interestingly, the relative increase with pressure was not significantly weaker for the higher v'' levels. No pressure dependence data was measured for $v''\geq 7$.

Collisions with cold gas molecules can relax molecules with internal energy, but the rate constants for these processes are apparently small enough to be unimportant in the pressure range of interest. The rate constant for relaxation of vibrational excitation has been calculated for various vibrational levels and gas temperatures, and the results agreed with the experimental data available (for $v''=1$).⁷⁹ However, these rate constants are no more than $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for the highest gas temperature and vibrational level of interest here, $v''=8$, so the relaxation rates are at most a few times 10^2 s^{-1} , which is small compared to other rates. The rate constant for rotational relaxation of $v''=1$ in room temperature H_2 was measured to be in the $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ range for $J''=1 \leftrightarrow J''=3$, which still yields actual rates that are probably negligible compared to wall relaxation rates.¹²⁴ To our knowledge, no data exists regarding relaxation of highly rotationally-excited states of H_2 by H_2 . However, the fact that the relative rotational distributions are apparently not affected by pressure over the range measured is strong evidence against gas

relaxation being an important factor in determining the relative rotational distributions.

It is apparent from the measured data that there is missing gas. In steady state, the conserved quantity is the total flux of protons in whatever form, so the densities and temperatures with the discharge on and off are related by

$$n_{\text{H}_2, \text{off}} \sqrt{kT_{\text{H}_2, \text{off}}} = n_{\text{H}_2, \text{on}} \sqrt{kT_{\text{H}_2, \text{on}}} + n_{\text{H}, \text{on}} \sqrt{kT_{\text{H}_2, \text{on}}/2} \quad (5.1)$$

where the symbols have obvious meanings. The factor of two in the last square root is due to the fact that an atom contributes only half of a molecule, but an atom at the same temperature as a molecule moves $\sqrt{2}$ times faster. In practice, it is actually a good approximation that $T_{\text{H}} = 2T_{\text{H}_2}$ over a wide variety of conditions. When the total proton flux from the atoms and all measured molecular states is summed, the total is less than the flux inferred from the measurements when the discharge is off. Also, the discrepancy increases with power. The missing flux is definitely not due to any uncertainty in the atom flux, which is only about ~4% of the total and is accurately known in any case. We conclude that a significant portion of the missing flux is in the form of undetected states of high rotational excitation. This conclusion is also based on the smooth extrapolations of the measured rotational distributions for $v''=0-4$, shown in Fig. 5-12. That figure is similar to Fig. 5-2, except that the estimated populations in the high J'' states are also shown. Because the extrapolation extends far beyond the region where data is available, the uncertainty is large for these populations, particularly at very high values of J'' , and no claim is made as to the accuracy of these extrapolations, but it is necessary to make some estimate of the contribution from the tails of the rotational distributions, both

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Fig. 5-12 Measured density of various rovibrational states of hydrogen, plus estimated extrapolations (by 'eye') to the dissociation limit. Measured and estimated densities have different symbols. The uncertainty of the extrapolations is unknown, but must increase with J'' . It is believed that the extrapolations up to $J''=9$ for $v''=5-8$ are less uncertain, based on the trends for $J'' \leq 10$ for $v'' \leq 4$. Discharge parameters were 35 A, 90 V, and 8 mTorr.

to the total population and to the dissociative attachment rates.

Table 5-2 lists the total population of each vibrational level for discharge parameters of 35 A, 90 V, and 8 mTorr, both with and without the estimated contributions of the rotational distributions. The flux equivalent densities (at 300 K) and the ratio of the measured population to the total estimated population within each vibrational level have also been shown. The same data is shown graphically in Fig. 5-13. Several facts are immediately apparent from the table and the graph: 1) there is a deficit of particles, even for the flux equivalent data, and 2) the fraction of measured population to estimated population within a given vibrational level decreases significantly with v'' , and thus the uncertainty of the extrapolation is increasing with v'' . The +15% correction to the $v''=0$ data has already been applied, so this is not the cause of the discrepancy. Several possibilities that would tend to explain the observed particle deficit are 1) the corrections to the $v''=0$ data caused by gas in the differential pumping arms may be overestimated because the gas is not completely relaxed translationally or rovibrationally, 2) there may be a systematic decrease of the true oscillator strengths as J'' increases (particularly for the $v''=0$ data) caused by centrifugal distortion of the potential wells which would cause the inferred populations of the high J'' states to be artificially low; this would also probably cause the estimated populations of the high J'' states to be too low, 3) the oscillator strengths for the $v''\geq 1$ transitions may be also be low by 15%, and 4) the extrapolations of the rotational distributions might be too conservative.

These possibilities are discussed in order. First of all, if the gas in the differential pumping arms did not translationally equilibrate at all, the discrepancy would be almost completely explained. However, each molecule experiences ~100 wall bounces (10 ms) on the average before it is pumped away.

Table 5-2

Total Population of each Vibrational Level

v"	Measured States Only		Estimated Totals		Measured/ Est. Total
	n(v")	n(v") (Flux Equiv.)	n(v")	n(v") (Flux Equiv.)	
0	6.40(13)*	1.15(14)	7.75(13)	1.39(14)	0.83
1	1.97(13)	3.54(13)	2.27(13)	4.08(13)	0.87
2	5.37(12)	9.66(12)	7.33(12)	1.32(13)	0.73
3	2.44(12)	4.40(12)	3.63(12)	6.52(12)	0.67
4	9.53(11)	1.72(12)	1.49(12)	2.70(12)	0.64
5	1.87(11)	3.36(11)	7.88(11)	1.42(12)	0.24
6	8.44(10)	1.52(11)	4.73(11)	8.52(11)	0.18
7	5.15(10)	9.26(10)	2.77(11)	4.98(11)	0.19
8	2.69(10)	4.85(10)	1.48(11)	2.67(11)	0.18
9-∞	2.69(10)	4.85(10)	1.48(11)	2.67(11)	0.18
Atoms	-	7.50(12)	-	7.50(12)	-
Totals	9.27(13)	1.75(14)	1.14(14)	2.14(14)	
Expected	1.46(14)	2.62(14)	1.46(14)	2.62(14)	
Ratio		0.67		0.82	

*1.23(13) = $1.23 \times 10^{13} \text{ cm}^{-3}$.

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Fig. 5-13 Population of $J''=1$ state for $v''=0-8$ and estimated total population in each vibrational level (see text). Data shows clear evidence that vibrational temperature corresponding to $n(v'')$ is higher than that for $n(v'', 1)$. Least-squares fit yields 6200 K and 4850 K, respectively. Discharge parameters were 35 A, 90 V, and 8 mTorr.

It seems very unlikely that the molecules would not equilibrate with the wall in this amount of time. If the molecules are relaxed translationally, but not completely rovibrationally, then the measured total density in the discharge would still be accurate if all the oscillator strengths are correct and the dominant $H_2(v'', J'')$ states of the stray gas are observed states. Essentially, we would only be counting the molecules in the wrong category. Secondly, if there is a systematic decrease of the transition oscillator strengths from the assumed values for increasing J'' , then part of the missing gas would be explained. The multiplicative correction factor would have to be at least a factor of three for $J'' \geq 10$ (we include the estimated high J'' tails of $v''=0$ and 1) to completely explain the anomaly; it seems unlikely that the error could be so strong. Third, if all $v'' \geq 1$ oscillator strengths are low by 15%, then approximately 1/4 of the deficit would be explained, even including the estimated high J'' tails of all $v'' \geq 1$ vibrational levels. Fourth, it is possible that the extrapolations are too low, however, the assumed population distributions have little decrease with increasing J'' up to the dissociation limit, so one could easily argue that the extrapolations are already unreasonably high. Barring a gross population inversion caused by some unknown mechanism, the estimations of Fig. 5-13 are probably somewhat optimistic.

The disturbing result of this data is that the total H_2 population in the discharge is not accurately known. If the translational temperature of all the low v'' and J'' states was known, we could calculate the missing density from flux conservation, but the uncertainty of the temperature of the molecules in those states is too large to make a reliable determination. The minimum density that can be inferred from the data is that deduced by assuming that all of the gas is at the temperature observed for the J'' states of high v'' or J'' , ~ 0.08 eV. The atoms must be taken into account, and the end result is

$\sim 1.4 \times 10^{14} \text{ cm}^{-3}$. Even including the estimated tails of the rotational distributions, we find only $1.14 \times 10^{14} \text{ cm}^{-3}$, or 81% of the expected value. In order to attempt to resolve the problem, it is imperative to measure the rotational distributions of the first few vibrational levels up to very high values of J'' , and to perform calculations for the oscillator strengths that take centrifugal distortion accurately into account. There is no question that flux conservation must be valid; also, the translational temperatures have a well-defined average of $\sim 0.08 \text{ eV}$, therefore, the molecule density must be higher than the value inferred presently.

The mechanism of rotational heating is not immediately apparent. There are several possibilities, all of which may contribute. First of all, the cross section for electron impact rotational (de-)excitation has values in the mid 10^{-16} cm^2 range at a few eV for $|\Delta J|=2$:⁵

The cross sections decrease rapidly with increasing $|\Delta J|$,¹²⁵ so it would appear that the populations at high J'' would have to be formed by cascade pumping, but if that were true, it seems unlikely that the tail of the distributions would decrease as slowly with J'' as they are observed to, or that the high J'' state rotational temperature would not depend on power. Therefore, we conclude that collisions with electrons do not directly heat the molecules rotationally.

There is another possible channel of production of molecules with high rotational excitation: associative detachment of hydrogen atoms to H^- yielding $\text{H}_2(v'', J'')$ and electrons:

The cross section for the individual rovibrational channels have been calculated at several discrete energies. For the purposes of this discussion, we will refer to the results for a collision energy of 0.129 eV, given in Table 2 of Ref. 69. The equilibrium density of molecules in any given $H_2(v'', J'')$ state, assuming that associative detachment is the only source term and ignoring cascading, is given by

$$n(v'', J'') = n^- n_H \sigma_{AD} v_{th} / \gamma_{destroy} \quad (5.4)$$

where $\gamma_{destroy}$ refers to the total destruction rate of $H_2(v'', J'')$ due to all destruction processes and is estimated to be 10^4 s^{-1} , which is accurate enough for our present purposes. The H^- density n^- is estimated to have a chamber average of 10^{10} cm^{-3} at most and n_H is about $7 \times 10^{12} \text{ cm}^{-3}$ for typical parameters. The thermal velocity is $\sim 3 \times 10^5 \text{ cm/s}$ and the cross section into any single $H_2(v'', J'')$ state is no more than 10^{-16} cm^2 , so the equilibrium density due to this process only is $\sim 2 \times 10^8 \text{ cm}^{-3}$, which is roughly 3 orders of magnitude smaller than the observed high J'' state populations for $v''=0-4$. We conclude that recycling of $H_2(v'', J'')$ through the channel of associative attachment is a very weak process and that this mechanism cannot explain the superthermal high J'' populations observed.

Another production term for high J'' molecules is the wall relaxation of molecules that initially have more internal energy which is in the form of vibrational energy. Generally, electron-impact electronic excitation of molecules does not impart much angular momentum to the molecule directly,¹²⁵ and radiative decay cannot change J'' by more than one unit of angular momentum, so one does not expect that the vibrationally-excited

molecules created by reaction 2.25 to have much angular momentum *ab initio*. The process of internal energy relaxation via collisions with the walls of the discharge chamber provides a mechanism for conversion of vibrational into rotational energy. Karo, et al. performed calculations that determined the rovibrational distribution of molecules that were initially in states of high v'' and low J'' after they collided with an iron wall:¹²⁶

It was found that the rebounding molecules had broad vibrational and rotational distributions after only a few bounces, and that some of the internal energy was converted into translational energy. However, molecules can only lose internal energy from wall collisions, therefore this mechanism does not explain how molecules are originally formed with high internal energy. Molecules of low v'' but very high J'' , such as 25, must have originally had a vibrational quantum of at least 8 or 9. If this process is indeed the source of highly rotationally-excited molecules, and the cross sections for reaction 2.25 are correct,⁵⁶ and if the extrapolations of Fig. 5-12 are close to being correct, then the molecules of high rotational excitation must survive on the order of 10 wall bounces; also, the conversion from almost pure vibrational energy into an admixture weighted in the form of rotation must take place in only one or two bounces. We are not in a position to evaluate whether the above scenario is reasonable; certainly, the dynamics of internal energy conversion by surface collisions is a complicated and interesting subject that deserves further attention.

In the present experiment, rovibrationally-excited molecules experience collisions with hydrogen atoms at a rate of about 10^3 s^{-1} , and it is possible that

this process generates molecules of rotational excitation:⁴⁹

However, no information about rotation (de-)excitation is given in the Ref. 49, therefore it is not possible to make even a qualitative conclusion regarding this process. The rotational distributions do 'heat up' with increasing discharge power, which also increases the atom density and temperature, but it is not at all clear that the two processes are related in any manner.

Upon reflection, it is apparent that there are many forms of internal energy present in the particles of the discharge, including that of ionization, dissociation, translational energy (of heavy particles), and rovibrational energy. As long as the energy is only transferred from particle to particle, there is no loss from the system as a whole. Therefore, it is worthwhile to recount the mechanisms (and the corresponding rates) that can transfer the raw energy of the fast electrons to the heavy particles and also those mechanisms that can transfer energy from the heavy particles to the walls, which eventually absorb all of the discharge energy (the energy of ionization can be thought of as existing in the ions for this purpose). Fast electron energy can be directly converted into all forms of internal energy in roughly equal magnitudes. Internal energy of the discharge constituents in the form of dissociation, ionization, translation, and rovibrational excitation can be lost by wall recombination of atoms, of charged particles, and wall relaxation (twice), respectively. The rates of energy loss per proton equivalent are probably highest for the ions and lowest for the translationally and rovibrationally excited molecules, with atom recombination somewhere in the middle.

The various forms of internal energy can be converted into the others,

although the efficiencies vary considerably. For instance, once a molecule has been converted into two atoms, the only mechanism that prevents the complete loss of the energy of dissociation to the walls is recombinative desorption. In this process, recently discovered by Hall, et al. and Eenshuistra, et al., atoms recombining at the walls form molecules with rovibrational distributions that are strongly superthermal with respect to the wall temperature.^{45,88} Molecules in vibrational levels as high as $v''=11$ have been observed in one experiment.¹²⁷ However, the data indicates that the contributions to the rovibrational populations via this process are probably small compared to those other sources, although the data is somewhat ambiguous (this will be discussed in detail in the next section). Therefore, H_2 dissociation is mostly wasted energy with regard to the H^- creation. A substantial fraction of the energy of ionization lost by the primary electrons can be converted to the other forms of internal energy by recombination, either with H^- or electrons. In the latter case, the process can happen at the wall. Free space recombination of any of the positive hydrogen ions with either an electron or an H^- ion is discussed first. In this process, the energy made available by the ion gaining an electron must be converted into dissociation energy (because of the necessity of conserving energy and momentum simultaneously), translational energy, and possibly electronic and/or rovibrational energy. The latter forms are applicable only if the total number of protons involved is three or more, so that H_2 can be one of the resultants. Any electronic energy created will be mostly lost in the form of a photon(s), but some may remain in the form of rovibrational excitation. It is not clear at the present time how efficient free space recombination of H_2^+ or H_3^+ with electrons or H^- is at generating rovibrational excited molecules. Wall recombination of any of the positive hydrogen ions can also form $H_2(v'',J'')$. Hiskes has created a

model which predicts that H_2^+ and H_3^+ will form a broad spectrum of $\text{H}_2(v'')$ states upon wall neutralization and that this mechanism could be the largest source term of $\text{H}_2(v'')$ in typical low- and medium-power discharges, but there is no experimental confirmation as yet.¹²⁸ Translational energy is generally not converted into other forms of energy before being lost to the walls and thus is wasted energy.

Until the atomic and molecular processes discussed are better understood with regards to vibration and rotation, it may be difficult to arrive at a realistic physical description of the physics taking place in these discharges. We therefore urge that detailed experimental and theoretical work be performed on the individual reactions, particularly those involving H_3^+ , in order to determine the (v'',J'') specific cross sections.

C. Wall, Gradient, and Hysteresis Effects

The wall of the discharge chamber plays an important role in determining the rovibrational distributions. Collisions with the wall can alter the form of the internal energy and will generally decrease the total internal energy, albeit at an unknown rate. The wall also may serve to catalyze production of rovibrational molecules via recombinative desorption or ion recombination. Data on the recombinative desorption efficiencies and wall relaxation of $\text{H}_2(v'',1)$ for $v''=1-5$ is presented in this section. No data regarding ion recombination at the walls creating rovibrational H_2 is presented because the current experimental arrangement does not allow an unambiguous measurement.

Recombinative desorption may be a moderate source of $\text{H}_2(v'',J'')$ during discharge operation. The populations of the $(v'',1)$ states for $v''=1-4$ were measured for conditions of 30 mTorr of H_2 with no discharge but the filaments

operated at ~ 2600 K. Other data indicated the dependence on filament temperature was not strong in this range. The temperature estimate was based on the current density that could be drawn from the filaments at high discharge voltage (i.e., no space-charge effects) and the known filament surface area ($\sim 10 \text{ cm}^2$). The measured densities are shown in Fig. 5-14. Note that $n(1,1)/n(0,1) \approx 0.003$, in contrast to the value of ~ 0.3 during typical discharge operation. The $v'' \geq 1$ populations are described by a temperature of 4750 K ($\pm 5\%$). No data for higher vibrational levels could be obtained because of lack of sensitivity. The rotational distributions were not measured because previous work has shown that the molecules produced in this fashion are cool rotationally.^{45,88,127} It was not possible to measure the atom density simultaneously because the wavelength required was much different, but based on data from other days, the estimated atom density was $\sim 5 \times 10^{12} \text{ cm}^{-3}$, with an uncertainty of 30%; the filament-induced atom density showed more day-to-day variation than most other data. It is impossible to directly determine the magnitude of the effect during discharge operation, but if the rovibrational populations found presently scale as the flux of the atoms arriving at the wall divided by the total loss rate due to fast electron processes and wall relaxation, then the densities of Fig. 5-14 would be multiplied by a factor of ~ 1 for discharge conditions of 35 A, 90 V, and 8 mTorr. The densities inferred are about a factor of 3 less than observed but the $n(v'',1)$ vibrational temperature is almost identical in the two cases. However, this mechanism could explain *almost all* of the low J'' populations observed at low power, such as 5 A, because the atom flux is much lower but the rovibrational populations are actually larger in some cases. However, one cannot simply assume that data applicable to hot filaments only is relevant to discharge operation. For instance, Eenshuistra measured the density of atoms "immediately" after

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Fig. 5-14 Population of $J''=1$ state for $v''=1-4$. Pressure was 30 mTorr. The filaments were heated to ~ 2600 K, but there was no discharge. Vibrational temperature for $v''=1-4$ is 4750 K. Note that $n(0,1)$ is 300 times larger than $n(1,1)$ and is not visible on graph. Atom density is estimated at $\sim 5 \times 10^{12} \text{ cm}^{-3}$.

the termination of a DC discharge that had been operated for some time and found that the density was less than the atom density after the discharge had been off for 10 minutes or more.¹²⁹ We believe "immediately" means about 30 seconds or less. The present apparatus needed at least 5 minutes to scan over an absorption feature, so we could not see the effect. The fact that the vibrational temperature inferred from the $J''=1$ states is almost the same with and without a discharge is suspicious, in fact, the implication is that recombinative desorption dominates the production of at least some $H_2(v'',J'')$ states! It would be worthwhile to perform a detailed study in order to assess the relative importance of this effect for typical discharge parameters. If this mechanism is indeed a significant source of $H_2(v'',J'')$, then the question remains, why does this process decrease its apparent efficiency when the discharge power is increased beyond approximately 5–10 A?

The decrease in the density of several rovibrational states in the afterglow of a mild, pulsed discharge was measured and the time constants observed were all in the range of a millisecond or more. Because the bounce time for a molecule is $(v_{th}/0.6D)^{-1} \approx 75 \mu s$, the inferred bounce parameters are in the range of 10 and above, which is significantly higher than calculated by Karo, et al.¹²⁶ The decay of $n(v'',1)$ for $v''=1-5$ is shown in Fig.'s 5-15 and 5-16, and the associated wall bounce survival coefficients, $b(v'')$, are listed in Table 5-3. In all cases, the measurements did not start until at least 400 μs past the discharge termination. The higher vibrational levels apparently decay faster than the lower levels, confirming a trend calculated in Ref. 126. It is not clear if the coefficients measured in the afterglow are applicable during the discharge operation or if these coefficients depend on discharge parameters in a continuous manner. The decay of $H_2(1,1)$ during the condition of high-power walls was measured and found to be significantly faster than under normal

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Fig 5-15 Measured decay of $J''=1$ population of $v''=1$ & 2 (a) and 3 (b) after termination of a mild pulsed plasma (≤ 20 A). Data starts at least 400 μ s after discharge termination, so plasma is all gone. The $1/e$ time scales inferred are in Table 5-3. Pressure was 8 mTorr, so diffusion cannot explain the long time scales. Walls are in the normal state.

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Fig. 5-16 Measured decay of $J''=1$ population of $v''=4&5$ after termination of a mild pulsed plasma (≤ 20 A). Data starts at least $400 \mu s$ after discharge termination, so plasma is all gone. The time scales inferred are in Table 5-3. Pressure was 8 mTorr, so diffusion cannot explain the long time scales. Walls are in normal state.

Table 5-3

Wall Collision Survival Probabilities for $v''=1-5$

v''	T_{decay} (1/e time, ms)	$b(v'')$ *
1	2.0	27
2	3.2	43
3	0.85	11
4	0.94	13
5	1.4	19

* $b(v'')$ is average number of bounces before loss, and is given by $T_{\text{decay}} / T_{\text{bounce}}$, where $T_{\text{bounce}} \approx 0.075$ ms.

conditions; in that case, the time constant was reduced to 450 μ s or approximately 6 bounces. However, that data was performed only once, so the reproducibility on a long-term basis is not known.

The hysteresis effect described in chapter III, section A-3 and chapter IV, section C also has an effect on the rovibrational populations. In particular, it seems to decrease the population of most $H_2(v'', J'')$ states for $v'' \geq 1$ by a factor of ~ 2 , which is very close to the reduction in the atom density observed when this effect was operational. The fact that the $H_2(v'', J'')$ populations, the atom density and the H^- density are all decreased by the same factor is very surprising. One might expect that the vibrational or rotational temperature would change strongly, however, that does not seem to be the case. Fig. 5-17 shows the rotational distribution of $v''=1$, for normal and high-power walls. The decrease is not exactly the same for each rotational state. There is some scatter in the data, but it is clear that states of $J'' \approx 7$ have been affected less than states of either very low or very high J'' . This effect is not understood. The same transitions were used for the two measurements, so the difference is not an experimental error. However, the total population within a vibrational level will scale very similarly to the low J'' state populations, as they contribute most of the absolute population. Also, the high J'' states are reduced by the same factor as the very low J'' states apparently. The $n(v'', 1)$ populations for $1 \leq v'' \leq 5$ are shown in Fig. 5-18 for the two wall conditions. The vibrational temperature of the $J''=1$ states only were determined by least-squares fit and found to be similar, 4340 K and 4620 K, with estimated uncertainties of 5% and 10%, respectively, which implies that they do not necessarily disagree. The data as a whole is *consistent* with the basic idea that dissociative attachment to rovibrational molecules is the only significant creation term of H^- and that H^- is predominantly destroyed by ion-ion mutual neutralization (the ion density

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Fig. 5-17 Measured rotational distribution for $v''=1$ for normal wall conditions and 'high-power' wall conditions. It is not known why the behavior for $J''=7$ is different than for lower or higher J'' , but the difference is definitely not statistical noise. Discharge parameters were 35 A, 90 V, and 8 mTorr.

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Fig. 5-18 Measured vibrational distribution for $J''=1$ states for normal wall conditions and 'high-power' wall conditions. The vibrational temperatures for normal and 'high-power' walls are 4340 and 4620 K, with estimated uncertainties of 10% and 5%, respectively. Discharge conditions were 35 A, 90 V, and 8 mTorr.

is only very slightly affected by the wall conditions). However, it is not clear what is the cause and what is the effect, so this data does not prove the hypothesis.

Absorption data taken in the filter region yielded results that were very similar to the chamber average data, however, there were some mild, but clear differences. The densities inferred for $v''=1$ and also $v''=2$ somewhat were enhanced relative to the body data, causing the effective vibrational temperature to be lower in the filter. Fig. 5-19 shows the rotational distribution of $v''=1$ inferred from the body data and the filter data. Fig. 5-20 shows the measured $J''=1$ populations for $v''=1-5$ in the filter and from the averaged data. Most of the rotational populations inferred from the filter region data are higher by ~ 1.5 (of $v''=1$ only). However, the states of intermediate J'' are much less enhanced. The reason for this behavior is not understood. The same set of transitions was used in each case, so the effect is not caused by a systematic error in the oscillator strengths. The quasi-universal factor observed is not caused by incorrect pressure calibration; the capacitance manometer was periodically rechecked and was never found to need any adjustment (other than the zero, which was calibrated against an ion gauge at low pressure at least daily). Also, simultaneously measured $v''=3$ and 4 data agreed very well with the body data. Thus, the higher $v''=1$ density in the filter remains unexplained. In any case, the absolute populations for $v''=5-8$ inferred if one fits a line to the filter data are not more than a factor of ~ 1.5 lower than inferred from the body data. The scaling laws for various states ($v_{\max}=4$ for this data), as a function of pressure and discharge current, were measured and found to be identical in all cases, except for the quasi-universal enhancement of $v''=1$ and 2. This is what one would expect because the mean-free paths of the molecules are long compared to a chamber length, as

Fig. 5-19 Measured rotational distribution for $v''=1$, averaged over the chamber (body data) and in the magnetic filter region. Filter data is higher by ~ 1.5 except for $J''=5$. It is not clear why the different rotational states are affected differently. Discharge parameters were 35 A, 90 V, and 8 mTorr.

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Fig. 5-20 Measured vibrational distribution for $J''=1$ states. Body data is average over chamber; filter data means in magnetic filter. The vibrational temperatures are 4620 and 4000 K respectively, with estimated uncertainties of 5%. Discharge conditions were 35 A, 90 V, and 8 mTorr.

discussed in chapter II, section A. The important point of the comparison is that the discrepancies between the present data and the results of Eenshuistra, et al. are definitely not related to any gradient effects.⁸

D. Vibrational Distributions – Model vs. Data

In this section, the experimental results on the vibrational distribution are compared to the calculations of the model described in chapter II, section C. The model does not take rotation into account at all and thus cannot really be an accurate picture of the physics taking place in the discharge. Nevertheless, the agreement can be made quite good by adjusting the set of wall relaxation coefficients in the model, which is essentially the only free parameter in the model. There are at least two sets of wall relaxation coefficients to try: the first choice is the set of $b(v'')$ given by Hiskes and Karo,⁸² the other choice is the set determined experimentally in the previous section (see Table 5-3). The latter set has values for $v''=1-5$ only. The set was completed by selecting the value of 10 for $6 \leq v'' \leq 9$. That choice was, of course, arbitrary; the values selected were influenced by the fact that the $b(v'')$ was decreasing somewhat with v'' . The choice turns out to be fairly unimportant for a completely different reason: the matrix of rate constants for the reaction 2.23, changes of the vibrational quantum number by (low-energy) electron impact, is empty for v'' or $v' > 6$, except for $|v' - v''| = 1$, simply because no values are given in Ref. 80. The calculated populations for $v''=7-9$ are clearly artificially low as a result; $v''=6$ seems to be affected slightly also (see Fig. 5-21). As a result of this problem, the model results always have a distinct kink from $v''=6$ to $v''=7$ when the density of thermal electrons is high enough to be important. Therefore, one should really only compare the model results to the data for $v''=0-6$.

Fig. 5-21 shows the measured vibrational distribution plus the model

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Fig. 5-21 Measured vibrational population distribution (including extrapolated states) and model calculation for three different sets of wall relaxation coefficients $b(v'')$. Wall A uses values determined in present work. Wall B uses those values scaled down by a factor of $2/3$. Wall C uses values from Ref. 82. See text for further explanation. The wall B results can be duplicated using wall A and scaling the volume-averaged electron down by a $2/3$ factor.

results for three different sets of $b(v)$. The discharge parameters were 35 A, 90 V, and 8 mTorr. All input parameters to the model were *measured* quantities for these parameters. The set of points labeled wall A corresponds to the set of $b(v)$ experimentally determined in the section C of this chapter. The set of points labeled wall B uses the same values scaled downwards by a factor of 2/3 (which *increases* the actual rates). These results are clearly in the best agreement with the data for $v=0-6$. The third set of points, labeled wall C, uses the set of $b(v)$ given in Ref. 82. These results are clearly in disagreement with the data by an order of magnitude. The characteristic shape of the usual model results is seen in that curve, namely, an initial sharp decrease followed by a much flatter region. If those results were extended to higher v (i.e., 14), the plateau region would become much more evident. Another calculated vibrational distribution is not shown in the figure. For that case, the true measured wall coefficients were used (wall A), but the thermal electron density was reduced by a factor of 3/2. The results were almost identical to the wall B results and will be referred to as set D for future reference.

It is not exactly clear why the model agreed more favorably with the data when the empirically determined wall relaxation coefficients were arbitrarily reduced by a factor of 3/2. The rates for relaxation of vibrational energy via collisions with atoms are given for 1000 K and 4000 K in Ref. 49, but the true atom temperature is ~ 1750 K and it is not obvious how to interpolate these rates. The above calculations all used the 1000 K rates, however, use of the 4000 K rates yielded good agreement for wall A with the data. The dependence on electron temperature is much weaker; 1.4 eV and 2.6 eV gave almost the same results. The true electron temperature was ~ 2.1 eV. The data regarding the molecular translational temperature was quite accurate ($\leq 10\%$) for both the discharge data and the afterglow data used to measure the relaxation

coefficients, therefore the inferred wall bounce rates should be quite accurate ($\sim 2 \times 10^4 \text{ s}^{-1}$ during discharge operation). It is possible that rotational energy is lost more easily via wall collisions than vibrational energy and that the molecules have a greater degree of rotational energy during discharge operation than the post-discharge period, and that as a consequence, the effective wall relaxation coefficients during discharge operation are higher than those measured without a discharge. This idea is only conjecture; no wall relaxation data for rotationally-excited molecules was obtained. It is also conceivable that the decay measurements of the previous section were contaminated by downwards cascading from states of higher internal energy to the state being measured; in other words, the implicit assumption that there was no production of the $\text{H}_2(v'', J'')$ state of interest during the period of the measurement may have been incorrect. That effect would increase the measured loss time scale, and the inferred value of $b(v'')$ proportionally. The calculated results of set D as well as the wall B results (see above paragraph) agree very well with the data. That indicates that the volume-averaged electron density may be incorrect. It is possible that we have overestimated that quantity by 50%. The similarity of the calculated results for wall B and set D is interesting. In one case, the electron pumping rate was reduced by a factor of 3/2, and in the other case, the wall relaxation rate was increased by a factor of 3/2. The agreement between the two calculations indicates that the competition between thermal electron effects and wall relaxation must be the key determining ingredient for the vibrational distribution. Evidence will be presented in subsequent paragraphs that bolsters this argument.

The scaling with pressure and current will be discussed only qualitatively. The fact that the dependence of the $v''=0$ population is not accurately known makes a quantitative discussion of the effect of discharge current on the

vibrational distribution difficult, but some conclusions can still be derived from the data. The following processes take place as the current is increased: the density and temperature of the atoms and thermal electrons increase (although less than linearly), and the primary electron density increases linearly. All of these effects will naturally lead to an increase of the calculated vibrational temperature. Experimentally, the $v''=0$ population must decrease, although exactly how much is not certain, because of increased gas temperature and because of displacement to other vibrational levels and atoms. Except for $v''=1$ and maybe 2, the total population within an excited vibrational level increases mildly with discharge current, because although the $J''=1$ states may be decreasing slightly, the higher J'' states will compensate. In order to be quantitative, one has to measure the dependence on current for each rotational level of each vibrational state, or at least a large subset thereof, and that is not practical with the present level of baseline noise in the measurements. However, it is clear that the vibrational temperature must be increasing with current. This leads to the conclusion that the electrons are more effective at 'pumping up' the molecules than the atoms are at relaxing them, a result which is to be expected because the rate constants for electron impact are larger than those for atom impact by the ratio of the characteristic thermal velocities, which is approximately one hundred. Both processes have cross sections in the 10^{-16} cm^2 range.

The quantities that change with pressure are the atom density and the primary electron density. The atom density increases almost linearly with pressure, while the primary electron density decreases somewhat. The change in the thermal electron density is weak over the range of pressures considered (see Fig. 4-1 (b)), and the same is true for the atom temperature. The electron temperature decreases with increasing pressure, and the effect may be

important. All of these trends will decrease the rates that push molecules upwards in vibrational energy and increase the relaxation rates. The experimentally-determined scaling of the low v'' populations, in particular $v''=0$, is linear with pressure, but the scaling of higher v'' populations is less than linear with pressure. Therefore, the experimentally-determined vibrational temperature must also decrease with increasing pressure. Using only the data for $v''=0$ and $v''=5$ and 6, we can roughly estimate the decrease of the vibrational temperature as the pressure is increased from 8 to 20 mTorr. The $v''=0$ population increases by a factor of 2.5, but the $v''=6$ population increases by a factor of only ~ 1.5 (estimated uncertainty of 25%). Combining that data with the information in Table 5-2, we find that the 20 mTorr vibrational temperature is ~ 5400 K, compared to the value of ~ 5950 K for 8 mTorr. The model predicts that the $n(v''=6)/n(v''=0)$ will decrease by a factor of 1.3, in fair agreement with the measured quantity.

The favorable comparison of the model with the data implies that the model should give an accurate description of the vibrational distribution if various physical processes could be artificially 'turned off', that is, if some cross section or rate could be set to zero. Fig. 5-22 shows the distribution calculated by the model for the standard discharge conditions, but in each case, one of the input parameters has been altered. The highest vibrational level shown in the figure is $v''=6$, because of the kink in the model results at the $v''=6$ to 7 transition discussed previously. Specifically, the process that has been 'turned off' in the model was 1) wall relaxation, 2) atom relaxation, 3) nothing, 4) the primary electrons, and 5) the thermal electrons. The most important point is that, the primary electrons apparently do almost nothing! This is in stark contradiction to the usual picture, in which fast electrons provide most of the production rate for high v'' states. The results clearly show that the

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Fig. 5-22 Calculated vibrational distribution for 5 sets of input parameters. The third case is normal (same as wall B) of previous graph; others have a certain process 'turned off'. Clearly, thermal electrons, not primary electrons are the chief vibrational excitation agent. The qualitative reason for this is $|\Delta v| = 1$ transition rate is faster than wall relaxation rate.

thermal electrons are the active agent of vibrational excitation in this discharge. If one examines the contributions to the production rate (via this process only) of some higher vibrational level, $v''=6$ for example, the dominant term corresponds to the $\Delta v = +1$ transition. In other words, cascade pumping apparently is the dominant source of high vibrational levels. This result will only be true when the wall relaxation rates are small enough so that the volume-averaged rates of $\Delta v = +1$ transitions can exceed the wall relaxation rates. Other qualitative results are 1) the walls are fairly unimportant already; their removal does not cause too much further increase in the $H_2(v'')$ populations, and 2) the atoms relax the high v'' state populations with moderate efficiency.

E. H^- results – Data and Theory

Two different sets of measurements have been performed regarding H^- , in addition to the modeling calculations. One set of data measured the H^- density in the magnetic filter region of the discharge using the photodetachment method,⁶² and the other set of data measured the H^- current extracted at high voltage from a small (2 mm) aperture. The drift velocity of the extracted H^- could be calculated easily using the relation $I_{\text{extract}}^- = n^- e A_{\text{hole}} v_{\text{drift}}$, where the symbols have obvious meanings,¹³⁰ however, the results yield implausibly large values, corresponding to electron temperatures approximate 10 times larger than the measured value. The explanation for this effect is seen in Fig. 3-21, which shows the extracted H^- and electron current, as a function of extraction voltage. At the extraction voltage employed (15 kV), the scaling is clearly beyond the Child–Langmuir $v^{3/2}$ regime, but there is a moderate linear increase with voltage. This behavior indicates that there is no space charge limitation of the current, and

that in fact, the H^- was probably 'funneling' through the extraction hole because the extraction electric field is penetrating through the hole and into the plasma. Thus, the true extraction area is probably larger than the physical hole size by a considerable factor.

The measured H^- density in the filter region is shown for various DC discharge parameters in Fig.'s 5-23 through 5-25. The dependencies are similar to those observed by others;^{85,89,90} the density increases with increasing discharge current or pressure, but will eventually saturate with either parameter. The H^- density will actually decrease if the pressure is increased past the optimum value; there is no apparent turnover with current in the range of measured parameters. The optimum pressure increases with current and vice versa. Also, the relative increase with either quantity is enhanced by using a higher base value of the other quantity. The dependence on discharge voltage is monotonically increasing over the range measured, although the fractional increase is small. The relative increase of n^- as the discharge voltage is increased from 70 V to 150 V is only about 20% for the three different pressures measured: 5, 8, and 15 mTorr. This data reinforces the conclusion inferred from other data, which is that increasing the discharge current is a more effective means of depositing electrical energy into the discharge constituents than increasing the voltage. The absolute densities are in the range of 10-30% of the electron density for most parameters studied. The densities are also what would be expected for a current density of 10 mA/cm² and a drift velocity corresponding to an electron temperature of ~1 eV, values that roughly characterize the large-volume, large-extraction-area ion sources under development at LBL and elsewhere.^{85,89,90} The general conclusion regarding this data is, unfortunately, that H^- ion sources utilizing volume production of H^- need a

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Fig. 5-23 H⁻ density in the filter region of the discharge, measured using the photodetachment method, as a function of discharge current, for several pressures. Voltage was 90 V.

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Fig. 5-24 H⁻ density in the filter region of the discharge, measured using the photodetachment method, as a function of pressure. Discharge current was 25 A and voltage was 90 V. Also see previous figure.

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Fig. 5-25 H⁻ density in the filter region of the discharge, measured using the photodetachment method, as a function of discharge voltage for several pressures. Current was 35 A.

fairly high operating pressure (10–20 mTorr) to produce reasonably high current densities. The high pressures involved greatly increase the practical problems of pumping away stray gas at a large enough rate so that stripping of fast H^- in the accelerator will not be too large.

The data for extracted H^- current is presented in Fig.'s 5-26 and 5-27. The data has not been corrected for stripping because a crude estimate shows that the correction is small because the extraction hole size is small (2 mm diameter). For example, the estimated loss at 20 mTorr is only about 4%. Also, the extracted H^- current decreases almost linearly and by only a factor of 2 as the pressure is increased from 15 to 50 mtorr, therefore the attenuation factor, which increases exponentially with pressure, must be small. The data is presented in units of current density rather than current because that quantity should be less device specific. The trends observed are similar to those seen in the previous set of figures, specifically, that the optimum current increases with optimum pressure and that the fractional increase with current (pressure) is greater at high pressure(current). The optimum pressure for a given current was slightly lower for extraction than for the density measurements. This may be caused by a decrease of the electron temperature (and therefore drift velocity) with pressure. The fractional increase with current, for a given pressure, was almost identical for the two sets of data. One would have expected that the extracted current increased faster, because the electron temperature increases significantly with current, however, that behavior was not observed. The dependence on voltage was slightly different for the two sets of data. For the extraction data, increasing the pressure does increase the fractional change with voltage. For instance, the increase of n^- from 70 V to 150 V is ~25% at 5 mTorr, in agreement with the photodetachment data, but is ~45% at 15 mTorr. The difference is not understood, but it may be a systematic error of

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Fig. 5-26 Extracted H⁻ current density, for various currents and pressures. Voltage was 90 V. Hole diameter was 2 mm; extraction voltage was 15 kV. Compare to Fig. 5-23 and 5-24.

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Fig. 5-27 Extracted H⁻ current density as a function of voltage for several pressures. Current was 35 A. Hole diameter was 2 mm; extraction voltage was 15 kV. Compare to Fig. 5-25.

unknown origin.

The relation between the rovibrationally-excited molecule density and the averaged dissociative attachment rate constant, and the H^- density is

$$n_{H_2} \langle \sigma v \rangle_{DA} = \sum_{v'', J''} n(v'', J'') \langle \sigma v \rangle_{DA, (v'', J'')} = n^- \langle \sigma v \rangle_{MN} \quad (5.7)$$

where the subscripts DA and MN refer to dissociative attachment and ion-ion mutual neutralization respectively. Loss via associative detachment is only about 10% of the mutual neutralization loss and is ignored for the present discussion. For typical discharge parameters, the numerical value of the right-hand side is $6 \times 10^{10} \text{ cm}^{-3}$ times $10^{-7} \text{ cm}^3 \text{ s}^{-1}$, which is $6 \times 10^3 \text{ s}^{-1}$.

Therefore, the total density of rovibrational states that have dissociative attachment rate constants close to the optimum value, $10^{-8} \text{ cm}^3 \text{ s}^{-1}$, must be approximately $6 \times 10^{11} \text{ cm}^{-3}$, which is simply the ratio of the appropriate rate constants multiplied by the H^- density. Considering the uncertainties of all the rate constants for the various processes, particularly the value for ion-ion mutual neutralization, the uncertainty is at least a factor of three either way.

The sum in the middle of Eq. 5-7 is tedious, but trivial to perform. The rate constants for individual rovibrational states were taken from Ref. 26. Some values were interpolated; the uncertainty involved is of order 30%. As stated in chapter II, the values given assume an electron temperature of 1 eV, however, the dependence of the rate constants on electron temperature in the range of 0.5 eV (the present value) to 1.5 eV is small for those states which have enough internal energy to contribute significantly to the sum. Nevertheless, one would expect some increase of the H^- production rate as kT_e was increased from 0.5 to 1 eV. Unfortunately, data is not available to calculate

that effect, so it must be ignored for the present work. However, the fact that H^- scales well with increasing pressure (and decreasing electron temperature) indicates that the effect is probably small. The sum depends critically on the fraction of molecules in 'good' (v'', J'') states. In particular, the H^- density is very sensitive to the extrapolations of the rotational distributions shown in Fig. 5-12. The minimum J'' necessary to be an important contributor to the total dissociative attachment rate (i.e., a rate constant of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ or more) is, for $v''=0-4$ respectively: 25, 21, 17, 13, and 9. All rotational levels of $v''=5-12$ satisfy the above requirement, which is admittedly a somewhat arbitrary definition. Of course, if the density of a given state is large enough, it could dominate the total rate, even if the corresponding rate constant was not optimum, but the data indicate that this is not a likely scenario because the populations decrease with v'' or J'' slower than the rate constants increase, so the product increases with J'' . This trend is only necessarily true for the portion of the rotational distributions that have been observed!

The moment of truth has arrived: can the *measured* rovibrational distribution explain the measured H^- density for our typical discharge parameters of 35 A, 90 V, and 8 mTorr??? NO! The value of the left-hand side of Eq. 5-7 calculated using only the measured states shown in Fig. 5-2 is $\sim 1.6 \times 10^3 \text{ s}^{-1}$, which is too low by a factor of four. In fact, this total actually includes the contributions from the estimated populations of the (5,3), (7,1), and (8,3) states (these small extrapolations have little uncertainty). The 4/3 factor caused by the contributions from states of even J'' has also been included. A disagreement of this size is not absolutely excluded considering the uncertainties of the rate constants. However, the scaling is also in disagreement, in particular, the relative changes observed as the current is decreased from 35 to 10 A. The H^- production clearly decreases strongly, but

the populations of the rovibrational states that contribute more than 90% of the sum relevant to 35 A, ($J'' \geq 5$ of $v''=4$ and all states of $v'' \geq 5$) remain constant or even increase! The decrease of the electron temperature in the filter region may explain a small part of H^- decrease, but not the bulk of it. The only states whose population increases with current are the high J'' states of the various vibrational levels. Therefore, we tentatively conclude that the high J'' state populations of unknown vibrational level(s) contribute most of the total dissociative attachment rate. In order for this result to hold, we must assume that the high J'' state populations for $v'' \geq 5$ also increase significantly with current. Although there is no direct data to that effect, the trends observed in the rotational distributions of $v''=0-4$ are all very similar, so the assumption seems entirely reasonable. The data shows that the population of the $J'' \leq 3$ states saturate at ~ 15 A for $v'' \leq 8$, so these states cannot be the dominant sources of H^- in the discharge. The scaling with pressure, is somewhat less than linear for both the H^- and all $v'' \geq 2$ rovibrational populations. Thus, very high J'' states of $v''=0$ and 1 are not the sources of H^- , if the linear scaling of high J'' populations with pressure for $v''=0$ and 1, observed for (0,9) and (1,9), continues to hold for higher J'' states.

If unobserved populations of high J'' are the source for the H^- in the discharge, it remains to be determined what vibrational level(s) yield the dominant contribution. Unfortunately, that question cannot be definitely answered until data is in hand regarding the tails of all the rotational distributions, at least for $v'' \leq 6$. The central result of the H^- modeling is that, as the maximum J'' considered for the rotational distributions is increased, the quantum number of the most important vibrational level decreases. The reason is that the fractional enhancement caused by the rotational excitation is a monotonically decreasing function of v'' . Table 5-4 demonstrates the

Table 5-4

Total DA Rate for Different Subsets of Estimated Rovibrational Distribution¹

	Measured ² data	Partial Extrapolation #1	Partial Extrapolation #2	Full Extrapolation ³
Rate [s ⁻¹]	1.67(3)*	4.89(3)	1.24(4)	9.86(4)
<u>J_{max}</u>				
(v''=0)	13	13	19	31
1	15	15	19	29
2	11	11	19	27
3	11	11	17	25
4	9	9	15	23
5	3	9	13	23
6	3	9	13	21
7	3	9	13	19
8	3	9	11	17

¹estimated populations are shown in Fig. 5-12.²includes estimated values of n(5,3), n(7,1), and n(8,3)³includes all bound states*1.67(3) = 1.67 × 10³

sensitivity to the tails of the rotational distributions conclusively. Four subsets of the estimated $H_2(v'', J'')$ distribution are evaluated for the total dissociative attachment rate. Each set is a subset of the next one. The first set is only the measured data, the second set is measured data only for $v'' \leq 4$ and extrapolations up to $J''=9$ for $5 \leq v'' \leq 8$, the third set has extrapolations to the value of J'' that is halfway between the $J''=0$ state of the given vibrational level and the dissociation limit (in energy), and the last set is the complete (estimated) distribution, up to the dissociation limit. The two intermediate extrapolations will be referred to as the first and second partial extrapolation, respectively. The calculated dissociative attachment rate varies over a range of 60, while the total absolute population has changed by only 20%! The total rates are $1.67 \times 10^3 s^{-1}$, $4.89 \times 10^3 s^{-1}$, $1.24 \times 10^4 s^{-1}$, and $9.86 \times 10^4 s^{-1}$ respectively. The value corresponding to measured states only is low, but not impossibly so, as discussed. The values corresponding to the two partial extrapolations are both in good agreement with the value inferred from the H^- density, $6 \times 10^3 s^{-1}$, considering the stated uncertainties. The last value is too high by a factor of 20 and can definitely be ruled out. The calculations show that the most important vibrational level for each case is $v''=4$, $v''=6$, $v''=4$, and $v''=0$, respectively. However, the measured data is not really a fair test, because the different fractions of the rotational distributions were measured for different vibrational levels. The total dissociative attachment rate from each vibrational level is shown in Fig. 5-28. In addition, the effect of not including rotational enhancement is shown for the first partial extrapolation in Fig. 5-29.

There are at least four ways to explain the widely ranging results. First and most likely, the estimations of the very high J'' state populations may be overestimated, particularly for $v'' \leq 2$. However, the trends are very clear in the measured data up to $J''=15$ (for $v''=1$). Secondly, the rotational enhancement of

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Fig. 5-28 Calculated dissociative attachment rate $n(v'') \langle \sigma v \rangle (v'')$ for each vibrational level, but using different subsets of the extrapolated rovibrational distribution. See Table 5-4 for subset definitions. Data for full extrapolation is not shown because it is off scale. The 'noise' is probably due to inaccurately interpolated values of the state-specific rate constant data of Ref. 26.

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Fig. 5-29 Effect of including rotational enhancement in calculation of dissociative attachment rate. Upper curve uses separate rate constants for each individual (v'', J'') state, lower curve employs the rotationless rate constant for all the population in a vibrational level. This data is based on the first partial extrapolation (see text). The relative enhancement is largest at lower vibrational levels and that trend is accentuated as the extrapolations are extended.

the dissociative attachment rate constants may not be as large as calculated in Ref. 26; there has been some controversy on this subject. Wadehra used the 'local potential approximation' in his calculations. Gauyacq used a very different formalism in his calculations, but unfortunately, he did not give any results for ultra high J'' (i.e., $j' \approx 25$), so no comparison can be made.²³ Berman, et al.¹³¹ used a non-local treatment, but results were given for only a very limited range of rovibrational states. We do not mean to imply that Wadehra is incorrect, just that this subject is an important topic for theorists to address. The third possibility is that the values for associative detachment or ion-ion mutual neutralization are significantly underestimated. The former case is unlikely because experimental confirmation exists.⁶⁹ The latter case is certainly possible, but it is not clear what a reasonable upper limit for the rate constant is; $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ is a large value already. It would clearly be of interest to measure the $\text{H}^- - \text{H}_3^+$ recombination rate constant. The fourth possibility is that we have made a significant mistake by ignoring the loss of H^- by transport. The calculated time scale for H^- loss by binary processes is $\sim 20 \mu\text{s}$ for our standard parameters. The loss rate to the wall $\gamma_{\text{wall loss}}$ can be estimated by $\bar{v}_{\text{drift}}/L$, where L is a scale length of about 3 cm. If the H^- velocity distribution is isotropic and described by a temperature of $\sim 0.13 \text{ eV}$, then we obtain a value for $(\gamma_{\text{wall loss}})^{-1}$ of $\sim 20 \mu\text{s}$, and the effect of this additional loss term would decrease the inferred H^- density by a factor of two. However, the plasma potential is about +2 V in the filter region and the ions have only a few tenths of an eV of energy. Therefore, the H^- should be able to reach the wall only by repeated collisions, probably with other charged particles rather than the cool neutrals. There may also be anomalous transport via instabilities or turbulence.

Summarizing, in brief, we must unfortunately conclude that the situation

regarding rovibrationally-excited hydrogen and H^- production is still an open subject. We have shown that, although the measured rovibrational distribution probably cannot explain the measured H^- density, modest extrapolations of the rotational distributions for $v''=5-8$, up to $J''=9$, will bring the total dissociative attachment rate up to the value inferred from the H^- measurements. These extrapolations are based upon well-defined trends in the measured data and we believe that they are close to the true quantities. When the rotational distributions of the lower vibrational levels, $0 \leq v'' \leq 3$, were extrapolated to the dissociation limit, the inferred dissociative attachment rate was far too large, from which we conclude that the extrapolations are probably overestimated and that there, in fact, is a dramatic fall-off of the rotational populations at some value of J'' . The inferred corrections to the absolute populations of the various vibrational levels are small ($\leq 10\%$), so that the vibrational distribution can be almost unchanged while the total dissociative attachment rate has changed enormously. This emphasizes the fact that simply categorizing rovibrational states by the vibrational quantum number only is an oversimplification of the true physical situation. It is also possible that the rate constants for the states of very high J'' (i.e. 25) are overestimated and that the populations are in agreement with the extrapolations; however, we have no direct evidence and only admittedly weak inferences to support this hypothesis. In order to answer this question, the rotational distributions of the lower vibrational levels must be measured out to the dissociation limit, and to do that, new calculations of the centrifugally-distorted band factors must be carried out. Assuming the calculated values are correct and that the extrapolations of the rotational distributions must be corrected downwards by a factor of 10, it could still be true that the populations of the very high J'' states of the first few vibrational levels are the major source of H^- . Because

experiments to determine rate constants applicable to specific quantum states of H_2 are difficult (if not impossible) at the present time, we believe that the emphasis must be on theory in the immediate future.

Chapter VI

Conclusion

This thesis has examined many aspects of low-pressure hydrogen discharges employed as volume-production H^- ion sources. The density and temperature of the thermal electrons, the primary electrons, the hydrogen atoms, and a large subset of the molecular rovibrational distribution were measured. In addition, the positive ion species ratio, the absolute H^- density and the extracted H^- current were also measured. The novel feature of this study is the thorough and direct absolute measurement of the neutral species, the atoms and the rovibrationally-excited molecules, using single-photon absorption in the VUV, which offers a very direct and reliable interpretation. The many different types of measurements were performed over a variety of discharge parameters and compared to three separate, staged models of the discharge. In this manner, any disagreement between calculated and experimental results could be isolated and modeling errors would not propagate.

In the first phase of this study, the balance between molecules, atoms, and positive hydrogen ions was examined experimentally and the results were found to agree well with a slightly modified version of the model originally created by Chan, et al.¹ The wall recombination coefficient γ was measured directly and indirectly (by comparison with the model) and found to have the value of ~ 0.6 under normal conditions and a value close to unity under certain conditions which could be produced and also terminated in a well-defined, repeatable manner.

In the second phase of the study, the density and translational temperature of many rovibrational states of H_2 were measured and the results were

compared to a model. This is of much practical interest because theory predicts that the H^- density will be directly proportional to the total population of highly-excited rovibrational molecules. The rotational population distributions of each vibration level observed were completely non-thermal, in particular, the population in the states of high rotational quantum number J'' showed almost no decrease with J'' . One of the key questions raised by this work is the nature of the rotational distribution for values of J'' greater than ~ 15 . If the distributions do not 'fall off' dramatically at higher values of J'' , conventional theory predicts that the highly-rotationally molecules of the few vibrational levels should dominate H^- production. Although there were some unexplained and novel effects, the measured vibrational distribution agreed surprisingly well with a model which incorporates essentially the same reactions as the models found in the literature. The model did not take rotation into account at all, a feature which is shared by those in the literature. The wall-collision destruction rates for rotationless molecules were measured in a very direct manner and were found to correspond to time scales of 10 to 30 bounces, as opposed to the theory values, which range from 1.5 to 2.5 bounces. In order to obtain optimum agreement between the data and the model, it was necessary to scale the directly-measured values of the relaxation probability per wall collision upwards by a factor of $3/2$. However, the agreement could also be optimized by reducing the estimated value of the volume-averaged electron density by the same factor or by using the next higher atom temperature for which de-excitation rates were available. Calculations showed that the dominant source term for excited molecules under the present conditions studied was unit-step cascade pumping by the thermal electrons, not electron-impact-induced electronic excitation from the ground vibrational

level and subsequent radiative decay. There is some evidence which indicates that the process of recombinative desorption is a significant source term of excited H_2 at low discharge power.

For the final stage of the study, the absolute H^- density was measured with the photodetachment method in the magnetic filter region of the discharge and compared to models relating it and the population of highly-excited molecules. The H^- current extracted at high voltage was also measured, which does not yield an absolute density in itself. The results of the two methods agreed very well in a relative sense. The conclusions regarding rovibrationally-excited H_2 and H^- were somewhat open-ended, as the sensitivity and scope of the experiment were not sufficient to measure all of the rovibrationally-excited H_2 states that potentially have enough population to play a role in H^- production. Agreement between the model and the various populations can be obtained by moderate extrapolations of the rotational distribution (to $J''=9$) of $v''=5-8$. However, the importance of contribution from highly rotationally-excited states of the lower vibrational levels remains an open question.

Appendix 1

It was recently suggested that the H_2 vibrational distribution observed in the present study might be perturbed by mercury migration from the mercury vapor oven used in the experiment to the discharge chamber itself, changing the physics of the discharge. This issue was investigated and it was concluded that mercury migration is not a problem. This conclusion is supported by several observations. First, a careful examination of the visible and near UV emission from the discharge yields a conservative upper limit on the mercury atom density in the discharge of $\sim 10^{10} \text{ cm}^{-3}$, and therefore the rates for any free-space binary reactions involving mercury atoms must be very low and can be neglected. The details of that spectroscopy is given below.

Secondly, two sets of data were taken on H^- in the filter region of the discharge chamber. The first data set used high-voltage extraction and was performed before the discharge chamber had a chance to be contaminated by mercury. The second data set was measured a year later using the photodetachment technique, and the discharge chamber was and had been in the same vacuum arrangement as that used to measure the neutral species by VUV absorption, leading the author to the conclusion that any contamination present for the VUV data was also present for this data. These two data sets compared very well in a relative sense (and, as far as could be estimated, in an absolute sense; the extraction data does not yield absolute populations without some assumptions about drift velocities). Therefore, it would appear that the H^- was not measurably perturbed by the presence of any mercury, and the standard model of H^- formation leads to the conclusion that the vibrationally-excited hydrogen molecules were also not perturbed.

Lastly, the VUV data did not show any variations or hysteresis (other than

that related to cleaning the chamber of water after being at atmospheric pressure or the hysteresis effect described in chapter III, section A-3). In particular, the measured $H_2(v'',J'')$ densities did not change depending on how long the gate valves between the mercury oven and the discharge chamber had been open or how long the discharge had been operated since those gate valves were opened.

Emission spectroscopy on the discharge was performed using the same monochromator, an Acton 502, which is usually on the VUV system but with a phototube which has a relatively flat sensitivity from ~300 nm to ~600 nm (to within a factor of two). The monochromator efficiency should also be flat and fairly high in this region. The line of sight used passes through the center of the discharge (see Fig. A1-1). An X-Y recorder plotted the detected photon intensity as a function of wavelength. Frequency calibration was performed by comparing to the Balmer series (beta through epsilon were observed clearly) and to the spectrum of a sealed mercury discharge lamp hung inside the discharge chamber (when it was open to the air). The FWHM width of observed lines was ~3 Å with slits of ~20 μ. The spectroscopy was always performed with the discharge on, at discharge parameters of 8 mTorr, 25 A, and 120 V. Several different time histories were used however. For case 1, the VUV system and the discharge were turned on roughly simultaneously, then operated for 1 hour before the emission data was taken. For case 2, the discharge had been on 1 hour and the VUV system was off and isolated from the discharge chamber before and during the emission spectroscopy. For case 3, the VUV system was left on all day (8 hours) with all valves open but with the discharge off, in order to permit accumulation of Hg in the discharge chamber. The discharge was then turned on and the emission spectroscopy performed in 3 minutes. A preliminary scan showed only hydrogen atom lines (molecular

lines are at least a factor of 200 weaker). Then careful scans were carried out at the five brightest mercury lines in this spectral region (see Table 1). The phototube voltage was set so that the Balmer- γ peak was ~ 200 mm high and so that the phototube was kept far from saturation at all times. The minimum detectable peak height was ~ 0.5 mm.

No discernible Hg peaks were observed in the 3 cases. For analysis we will concentrate on the Hg line at $4358 \text{ \AA}$, which is very close to Balmer- γ , thus the detection efficiencies for these two wavelengths can be taken as equal. A similar coincidence happens for the Hg line at $4047 \text{ \AA}$ and Balmer- δ . Therefore one can determine limits of the ratio of the mercury atom density to that of hydrogen atoms if the cross sections and the electron energy distribution function (EEDF) are known. Two factors complicate this analysis. First, hydrogen molecules also have a significant cross section for electron impact leading to Balmer line emission from dissociated excited atoms. This can be accounted for, as the cross sections are known.^{132,133} Secondly, $\sigma_{\text{Hg},4358\text{\AA} \text{ emission}}$ is not well known. This problem is more serious. However, the mercury lines under study are all of the strongest emission lines in the region, but the Balmer- γ excitation cross section for hydrogen atoms has a relatively small peak value of $\sim 3 \times 10^{-19} \text{ cm}^2$ at an incident electron energy of $\sim 40 \text{ eV}$ (actually this is the calculated $1\text{S} \rightarrow 5\text{P}$ excitation cross section times the appropriate branching ratio).⁹⁵ Formally

$$n_{\text{Hg}} = R(n_{\text{H}^0} \langle \sigma v \rangle_{\text{H}^0, \beta-\gamma} + n_{\text{H}_2} \langle \sigma v \rangle_{\text{H}_2, \beta-\gamma}) / \langle \sigma v \rangle_{\text{Hg}, 4358 \text{ \AA}} \quad (\text{A1.1})$$

where R the ratio of the Hg $4358 \text{ \AA}$ peak height to the Balmer- γ peak height and the other symbols are obvious, all referring to electron impact processes. The hydrogen atom density has been measured to be $\sim 7 \times 10^{12} \text{ cm}^{-3}$

at these parameters. The molecule density summed over all v'', J'' states is $\sim 2 \times 10^{14} \text{ cm}^{-3}$ when the discharge is on. The molecular dissociative excitation cross section for Balmer- γ has a peak value of $\sim 5.5 \times 10^{-20} \text{ cm}^2$ at an energy of $\sim 75 \text{ eV}$, and therefore the molecular contribution will dominate somewhat. The peak height ratio R has been experimentally determined to be less than 0.0025. We will assume that the mercury excitation cross section has a peak value of 10^{-17} cm^2 and that the energy dependence is similar to that of the dissociative excitation cross section. We believe that this is being conservative, because the actual mercury excitation cross section is probably larger and probably has a peak value at lower energy, which would increase the rate (and decrease the inferred mercury density) significantly. The numerical result for the upper limit on the mercury atom density is $3 \times 10^9 \text{ cm}^{-3}$, which we round up to 10^{10} cm^{-3} for simplicity. Even assuming a very large cross section of 10^{-14} cm^2 for vibrational relaxation of H_2 by mercury atom impact the relaxation rate, given by $n_{\text{Hg}} \sigma_{\text{relax}} v_{\text{H}_2}$, is only $\sim 25 \text{ s}^{-1}$. This estimate uses the measured H_2 temperature of 0.06 eV. This rate is very small compared to other rates for destruction of $\text{H}_2(v'')$. For instance, wall relaxation has measured times scales of order 10^3 s^{-1} and the volume averaged dissociative attachment loss rates are of order 10^4 s^{-1} .²⁶ We therefore believe that relaxation of $\text{H}_2(v'')$ by collisions with mercury atoms is negligible.

Mercury could be on the walls of the discharge chamber, however, and we have no method to detect it. However, surface effects are known to be very sensitive to vacuum conditions and difficult to reproduce, and that description does not apply to the present data. In particular, the fact that the measured density shows no dependence on the history of the gate valves between the discharge chamber and the other vacuum systems strongly suggests that there

is no anomalous surface effect taking place. Also, one would expect that the extreme environment of a discharge would be efficient at driving mercury atoms off the surface into the volume where they would be detectable by their electron impact induced emission.

We thus conclude that mercury atoms are not responsible for any significant vibrational relaxation in the volume, and that it is possible that some mercury could be on the surfaces of the discharge chamber, but considerable indirect evidence indicates that this is unlikely.

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Fig. A1-1 Schematic of vacuum system relevant for possible mercury contamination and discharge emission spectroscopy.

Table A1

Mercury Emission Lines Examined

Wavelength [$\text{\AA}$]	Transition [N.B.S. Identification]
3650.2	$6s6d\ ^3D_3 \rightarrow 6s6p\ ^3P_2$
3654.8	$6s6d\ ^3D_2 \rightarrow 6s6p\ ^3P_2$
4046.6	$6s7s\ ^3S_1 \rightarrow 6s6p\ ^3P_0$
4358.4	$6s7s\ ^3S_1 \rightarrow 6s6p\ ^3P_1$
5460.7	$6s7s\ ^3S_1 \rightarrow 6s6p\ ^3P_2$

Appendix 2

We derive formulas pertaining to the correction of raw absorption data, necessitated by the finite VUV bandwidth $\Delta\omega_{\text{VUV}}$. All calculations are performed in ω space, although the results do not depend on this fact. We assume that the true absorbance $a_{\text{true}}(\omega)$ is Gaussian, with the center being at ω_0 , the maximum absorbance A_0 , and the $1/e$ half-width given by $\Delta\omega_0$. The integral of $a_{\text{true}}(\omega)$ is simply $\sqrt{\pi} A_0 \Delta\omega_0$. The spectral power profile of the VUV probe beam $f_{\text{VUV}}(\omega)$ is also assumed to be Gaussian, with corresponding parameters of ω_a , $(\sqrt{\pi} \Delta\omega_p)^{-1}$, and $\Delta\omega_p$. Note that f_{VUV} is parametrically dependent on ω_a and $\Delta\omega_p$, and that $\int f_{\text{VUV}}(\omega) d\omega$ equals 1. Because the final results and even the intermediate results depend only on the quantity $(\omega_a - \omega_0)$, we will henceforth assume that ω_0 is zero, in order to simplify the algebra. This assumption, although clearly unphysical, does not change anything. The measured absorbance profile $a_{\text{exp}}(\omega_a)$ is exactly given by

$$a_{\text{exp}}(\omega_a) = -\ln \left[\int f_{\text{VUV}}(\omega') e^{-A_{\text{true}}(\omega')} d\omega' \right] \quad (\text{A2.1})$$

This expression cannot be analytically integrated. Therefore we must make one or more approximations.

We first examine the case of $A_0 \ll 1$, because this case is simplest.

We first expand the exponential inside the integral to first order:

$$e^{-A_{\text{true}}(\omega')} = 1 - A_{\text{true}}(\omega') + \dots \quad (\text{A2.2})$$

The integral in Eq. A2.1 then has two terms, one of which trivially integrates to 1. The other term is the convolution of two Gaussians, which itself is a Gaussian:

$$\int f_{vu}(\omega') A_{\exp}(\omega') d\omega' = \sqrt{\pi} A_0 \Delta\omega_0 \left[\frac{e^{-\left(\frac{\omega_a}{\Delta\omega_m}\right)^2}}{\sqrt{\pi} \Delta\omega_m} \right] \quad (\text{A2.3})$$

where $\Delta\omega_m$ is the measured 1/e half-width and is given by

$$\Delta\omega_m = \sqrt{\Delta\omega_0^2 + \Delta\omega_p^2} \quad (\text{A2.4})$$

The natural logarithm in Eq. A2.1 is expanded to first order in the usual way, and the result for $A_{\exp}(\omega_a)$ is the right hand side of Eq. A2.3. Note that the term in brackets is a normalized Gaussian that has a characteristic width of $\Delta\omega_m$. Also, note that $\int A_{\exp}(\omega_a) d\omega_a$, given by the right-hand pre-factor in Eq. A2.3, is the same as $\int A_{\text{true}}(\omega) d\omega$. Thus, the conclusions are that the inferred line density is correct as it stands, and that the true linewidth is the quadrature difference of the the measured linewidth and the probe beam bandwidth.

If A_0 is not assumed to be small, then we must assume that the probe beam bandwidth $\Delta\omega_p$ is small compared to the absorption linewidth $\Delta\omega_0$. We then can approximate $A_{\text{true}}(\omega')$ as a Taylor expansion about (fixed) ω_a ,

specifically,

$$A_{\text{true}}(\omega) = A_{\text{true}}(\omega_a) + (\omega - \omega_a) A'_{\text{true}}(\omega_a) \quad (\text{A2.5})$$

The integral of Eq. A2.1 is then easily evaluated and the result is

$$A_{\text{exp}}(\omega_a) = A_{\text{true}}(\omega_a) - \left[\frac{\Delta\omega_p A'_{\text{true}}(\omega_a)}{2} \right]^2 \quad (\text{A2.6})$$

We are now in a position to determine $\int A_{\text{exp}}(\omega_a) d\omega_a$, using the Gaussian $A_{\text{true}}(\omega_a)$. The algebra is unpleasant but straightforward and the result is

$$\int A_{\text{exp}}(\omega_a) d\omega_a = \sqrt{\pi} A_o \Delta\omega_o \left(1 - \frac{A_o}{4\sqrt{2}} \left[\frac{\Delta\omega_p}{\Delta\omega_o} \right]^2 \right) \quad (\text{A2.7})$$

The inverse of the term in parantheses is the correction factor. Note that the measured line density will also be less than the true line density. The fractional error scales as the peak absorbance divided by the square of the width ratio. Roughly speaking, the sides of the measured absorbance profile will be depressed from their true values. Thus the area under the curve is decreased and the effective width is also decreased. Because $A_{\text{exp}}(\omega_a)$ is not a Gaussian we cannot trivially define the width. However, we note that, for the true absorbance profile $A_{\text{true}}(\omega)$, the relation between the variance $\langle \omega^2 \rangle$ and the characteristic width $\Delta\omega_o$ is given by

$$(\Delta\omega_0)^2 = 2\langle\omega^2\rangle = \frac{\int A_{\text{true}}(\omega) \omega^2 d\omega}{\int A_{\text{true}}(\omega) d\omega} \quad (\text{A2.8})$$

We generalize this relation in an obvious way to define a characteristic measured width $\Delta\omega_m$ based on $A_{\text{exp}}(\omega_a)$. Here, $\Delta\omega_m$ has a slightly different meaning than for the earlier section. The calculation is straightforward and the result is, after some work

$$\Delta\omega_m = \Delta\omega_0 \left(1 - \frac{A_0}{16\sqrt{2}} \left[\frac{\Delta\omega_p}{\Delta\omega_0} \right]^2 \right) \quad (\text{A2.9})$$

The only new assumption used is that the quantity to the right of the minus sign is small compared to 1. Using the above formula, one can iteratively correct data, although in practice only one iteration is needed. Note that the measured variance is always smaller than the true variance, even when A_0 is small. Thus the above width does not reduce to that obtained in Eq. A2.4. However, because we assumed that $\Delta\omega_p$ was small compared to $\Delta\omega_0$, the error is small, scaling as $[\Delta\omega_p/\Delta\omega_0]^2$.

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