Anomalous fast recombination in hydrogen plasmas involving rovibrational excitation

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Langmuir-probe measurements in a hydrogen-containing plasma jet show anomalous fast recombination that cannot be attributed to atomic processes such as radiative or three-particle recombination. In this paper a molecular mechanism, based on the charge transfer between the atomic hydrogen ions and the rovibrationally excited hydrogen molecules ($H_2^{v,J}+H^+ \rightarrow H_2^+ + H$), is presented that explains the observed fast recombination.

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INTRODUCTION

Rotational and vibrational excitation of hydrogen molecules is known to be essential in negative-ion formation, as the dissociative attachment reaction is endothermic. In this paper it is argued, on the basis of ion-density measurements in a hydrogen plasma jet, that rovibrational excitation can also cause an anomalous fast recombination loss of protons. The mechanism involved is a charge transfer from a proton with a rovibrationally excited molecule, followed by a molecular dissociative recombination. The rovibrational excitation is needed as the charge transfer is also endothermic. The experiments discussed in this paper concern the jet of a thermal plasma expanding into a low-background pressure (50 Pa). The source, a cascaded arc, is a hot thermal plasma (1 eV) and produces predominantly atomic ions. The resulting plasma jet is cooled by expansion down to temperatures of 0.2 eV both for the heavy particles and for the electrons. The plasma is freely expanding, i.e., the walls of the reactor are far from the plasma. There is no important negative-ion formation expected under the experimental conditions. Yet a strong decrease in the ion density is observed in the hydrogen plasma jet, which can be explained only by the above-mentioned charge-transfer mechanism. This mechanism can be important in any plasma where hydrogen atomic ions and rovibrationally excited molecules are present. Examples are volume negative-ion sources [1–3], interstellar shock waves [4], plasma deposition [5,6], and hydrogen atom and ion sources [7].

EXPERIMENT

The experimental arrangement under research (cf. Fig. 1) can be divided into a source part, where the plasma is generated, and a low-pressure chamber, where the plasma expands to a recombining jet. The source is a cascaded arc. For a detailed description of the cascaded-arc plasma, we refer to other publications [8,9]. Here it will be described in a condensed manner. It consists of three tungsten cathodes at one end, a stack of eight water-cooled copper plates insulated electrically from each other by polyvinyl chloride (PVC) spacers and vacuum sealed by O rings, and an anode plate at the other end. Through the copper plates there is a central bore diverging from 3 to 4 mm, forming a central channel of approximately 50 mm length. The center of the anode plate is a 4-mm nozzle, connecting the cascaded arc to the vacuum chamber. The discharge is created between the cathodes and the anode plate. The pressure in the arc is subatmospheric (0.1–0.5 mbar).

The vacuum chamber is a vessel with a diameter and a length of 400 mm. A set of two rotary pumps and a roots blower keeps the pressure at 50 Pa in the described experiments. At the given flows the residence time of a particle in the vessel is in the order of 0.1 s. The ion-density measurements are performed using a Langmuir double probe. The Langmuir probe could be positioned at 200 to 310 mm from the exit of the cascaded arc. A radial scan from −50 to +50 mm from the plasma axis could be made. The probe characteristics were interpreted using the classical Langmuir theory, assuming a negligible sheath thickness. The probe dimensions were chosen such that the probe diameter is much smaller than all relevant mean-free-path lengths and much larger than the Debye length in all experiments. The tungsten probe wires have a diameter of 400 μm and a length of 7 mm, and the distance between the two wires is 2 mm.

In what follows we will first discuss the plasma source and then the plasma expansion. Three plasma compositions have been studied: pure argon, 10% hydrogen in argon, and 95% hydrogen in argon, hereafter referred to

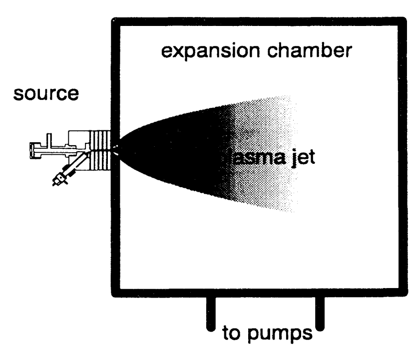

FIG. 1. The experimental setup.

as the pure-argon, low-hydrogen, and high-hydrogen cases, respectively. The latter case is very close to a full hydrogen operated source; 5% argon was added near the cathodes to protect them from erosion.

The plasma source

The source is characterized by a high-particle and -power density. This results in a plasma that is strongly collision dominated and the excited states are in equilibrium, the so-called partial-local-thermodynamic-equilibrium (PLTE) state [10]. The ionization degree is high and the temperature is in the 1-eV range. As a consequence, the excitation from the ground state to the first exited level, which is the largest energy step, invariably leads to ionization due to ladder excitation. Furthermore, in this type of collision-dominated plasma, the ions will preferably be from the species with the lowest ionization energy, as charge exchange is very effective. The source is operated on 3 slm (standard liter per minute) at a power input of 3 kW in the pure-argon case, and up to three times more if hydrogen is admixed. This yields a plasma with an ionization degree of 10% at the exit (anode side) of the source [9].

Now consider the situation in the plasma if hydrogen is added. Relating measurements on stationary cascaded-arc plasmas to the presented situation, the same arc current gives the same axial temperatures for hydrogen and argon within 10% [11,12]. The first excited level of hydrogen is somewhat lower for hydrogen than for argon, which facilitates the ionization through ladder excitation in hydrogen.

Furthermore, if the ionization degree is more than 1%, the plasma conductivity is determined by Coulomb collisions, independent of the electron density and proportional to $T_e^{-3/2}$ [8]. As the electron temperature is equal within 10% for the two cases, the plasma resistance is inversely proportional to the effective plasma channel cross section. In the low-hydrogen case the plasma resistance is found to be almost two times higher than in argon, indicating a two-times-smaller plasma channel cross section. Combining this with the foregoing, we conclude that the plasma-cross-section averaged electron density in the low-hydrogen case will be less than a factor of 2 lower than that in argon. This is experimentally confirmed for low admixtures up to 1.4% hydrogen [13], showing no difference with the full argon case at the arc exit up to the gasdynamical shock. As mentioned above, the ionized particles in the source plasma will preferably be from the species with the lowest ionization energy, in the case of hydrogen. If the percentage of atomic hydrogen admixed is below the ionization degree in pure argon, the plasma ionizes the added hydrogen by means of the charge transfer between argon ions and hydrogen atoms. This process is very effective until the full amount of argon ions is consumed; at above roughly 5% molecular hydrogen gas flow in argon, the ions will mainly be H^+. Experimental support for this is found in emission spectroscopy in the expansion close to the exist of the same plasma source [7]. In a situation where 10% hydrogen was added in the plasma source, the only spectral lines measured in the expansion section were the atomic hydrogen Balmer series. Since the temperature in the expansion is decreasing fast to values of about 0.3 eV [14], the light emission in the argon case can only originate from dielectronic recombination. The absence of argon lines, therefore, implies the absence of a significant argon ion density.

The plasma jet

The outflowing plasma jet in pure argon was studied thoroughly by Van de Sanden [14] by means of accurate Thomson-Rayleigh scattering measurements. The main characteristics are listed here. Directly after the source, the plasma expands supersonically and cools down to 0.3 eV. The plasma composition is frozen in as a result of the high velocity and low density. After a few centimeters, when the stagnation pressure in the plasma jet becomes equal to the background pressure, a shock occurs. After the shock, the flow is subsonic and only slightly decelerates over the studied region (200 to 310 mm downstream from the source). The plasma jet in pure argon does not recombine significantly, in accordance with theoretical expectations: Radiative and three-particle recombination are too slow. The absence of recombination is confirmed by Langmuir double-probe measurements, which show good agreement with Thomson-Rayleigh scattering results [15]. Figure 2 shows three radial ion-density profiles at 200, 255, and 310 mm from the source, which can be described by Gaussian profiles. The surface under these Gaussian profiles remains approximately constant for the three different axial profiles. This indicates that the ion line density N_i, i.e., the ion density integrated over the cross section of the jet, is constant. As the flow velocity w_{plasma} is approximately constant, this implies that the ion flux is approximately constant for the three axial positions, confirming that no significant recombination occurs for argon.

If hydrogen is added to the plasma, the situation changes drastically in the plasma jet. The plasma tem-

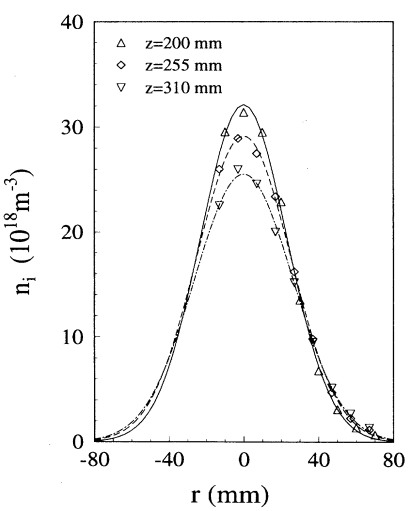

FIG. 2. Radial ion densities in the plasma jet for pure argon at 200, 255, and 310 mm downstream from the plasma source. The arc current is 45 A; the reactor pressure is 0.5 mbar.

perature is lower, 0.2 eV in the low-hydrogen case and somewhat more than 0.1 eV in the high-hydrogen case. Figure 3 gives the radial density profiles as measured with a Langmuir double probe at 200, 255, and 310 mm downstream from the source for the three studied plasma compositions. Apparently, the presence of hydrogen can lead to a decrease in the ion density of three to four orders of magnitude.

The low-hydrogen-case plasma has almost the same acoustic properties and can therefore be directly related to the argon plasma. The acoustic properties of the high-hydrogen-case plasma will be closer to the full hydrogen case. In this case the velocities can be up to a factor of $\sqrt{(m_H/m_{Ar})}$ larger, where m_H and m_{Ar} are the mass of the hydrogen and argon atoms. In the following we will concentrate on the low-hydrogen case in comparison with the pure-argon case. The radial density profiles measured in the hydrogen mixtures are not significantly broader than in a pure-argon plasma (cf. Fig. 3), confirming similar transport behavior. As the ion density at the source and the flow behavior are similar for the first two cases, the addition of hydrogen must cause a new and strong recombination channel in the bulk plasma. To establish the cause of this decrease, several items have to be addressed. As mainly atomic hydrogen ions leave the source, the responsible mechanism must start with these ions. It can easily be shown that two- and three-particle recombinations are not effective at the given time scale and plasma densities, as is also evident from the pure-argon case. The same thing accounts for the formation of negative ions in combination with mutual annihilation. Here we present a mechanism based on charge exchange and dissociative recombination that explains the observed electron-density decay. The first step in this reaction mechanism is the charge transfer between a proton and a rovibrationally excited molecule,

$$H_2^{v,J} + H^+ \rightarrow H_2^+ + H \ . \tag{1}$$

The molecular ion formed by the charge-transfer reaction

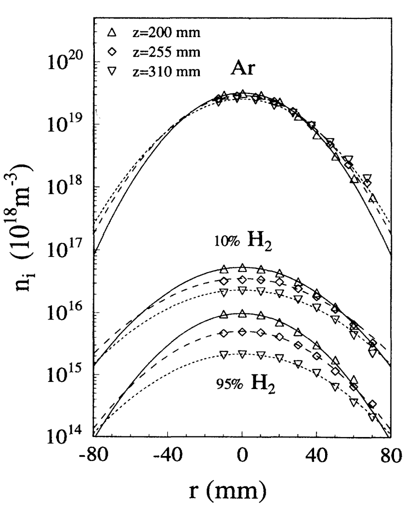

FIG. 3. Radial ion-density profiles for Ar and Ar-H_2 mixtures. The arc current is 45 A and reactor pressure is 0.5 mbar in all cases. The *y* scale is now logarithmic.

can directly recombine dissociatively,

$$H_2^+ + e \rightarrow H + H \tag{2}$$

or by formation of H_3^+,

$$H_2^+ + H_2 \rightarrow H_3^+ + H \ , \tag{3}$$

again followed by dissociative recombination:

$$H_3^+ + e \rightarrow H + H + H \tag{4}$$

or

$$H_3^+ + e \rightarrow H_2^{v,J} + H \ . \tag{5}$$

Reaction 2 is very fast. Under the plasma conditions as presented in this paper, due to the low ionization degree, reactions 3 to 5 will be dominant, as was confirmed by the presence of a significant amount of H_3^+ in mass spectroscopy measurements and the total absence of H_2^+ [7]. The rate coefficient for reaction 5 has been subject to discussion in several publications over the years [16–20]. It is likely to be very large. Therefore, in the molecular recombination channel the charge-transfer reaction is an essential step. For ground-state molecules this is an endothermic reaction. Niedner, Noll, and Toennies [21] have shown that this charge transfer is a two-step mechanism: a vibrational excitation to $v \geq 4$ followed by a resonant, exothermic charge transfer. In a plasma, a fraction of the molecules will already be in the vibrational states $v \geq 4$. Cross sections for the second step, the exothermic charge transfer, are not available. However, in an exothermic charge-transfer reaction, the Langevin limit [22] usually is a good estimate for the charge-transfer cross section σ_{CT}. The corresponding charge-transfer rate k_{CT} has a value of approximately 2.5×10^{-15} m^{3}s^{-1}. Now the time-dependent behavior of the atomic ion density is given by

$$\frac{dn_{H^+}(t)}{dt} = -k_{CT} n_H + n_{H_2^{v,J}} \ , \tag{6}$$

which has the solution

$$n_{H^+}(t) = n_{H^+}(0) \exp(-n_{H_2^{v,J}} k_{CT} t) \ . \tag{7}$$

The evolution of $n_{H^+}(t)$ in time due to the charge-exchange channel now depends on $n_{H_2^{v,j}}$ and k_{CT}. At the position of the measurements the ion density has decreased by almost three orders of magnitude, so $n_{H_2^{v,J}} k_{CT} \approx \ln(1000)$. At a typical temperature of 2000 K and a time of flight of 0.4, a population density for $H_2^{v,J}$ of $\approx 10^{19}$m^{-3} is required. It has been measured that in the vessel and in the plasma jet the abundance of H_2 is much larger than that of H atoms, even though the source delivers mainly atoms and atomic ions. The reason for the dominance of molecular hydrogen is the wall association of atoms to molecules and the finite residence time of ~ 0.1 s. The molecular-hydrogen density is approximately 2.5×10^{21}m^{-3} at a pressure of 50 Pa and a temperature of 2000 K. A vibrational temperature of approximately 3000 K yields a sufficient thermal population of the higher vibrational levels. The vibrational temperature can be "frozen" in the expanding plasma jet [23]. Upstream, the temperature is higher, so there may be an overpopulation of higher vibrational levels. Another source of vibrational excited molecules can be the Eley-Rideal associative desorption of hydrogen atoms at the walls. It is suggested [24] that up to 40% of the thus-formed molecules reenter the plasma in a vibrational excited state $v \geq 4$. As the reentering molecules form the main part of the residual H_2 abundance, this again makes a significant vibrational population plausible.

So far, we have followed the two-step reaction, *vibrational* excitation followed by charge transfer. However, as the gas temperature is close to the electron temperature in the presented experiments, the internal energy of the molecules in reaction (1) may well originate from rotational excitation. The increasing statistical weights of the higher rotational levels $(2J+1)$ will enhance their importance. In this sense the experimental situation presented here is different from the usual low-pressure gas discharges where the rotational excitation is negligible. To reiterate, the main points of the above are (1) charge exchange followed by dissociative recombination are the dominant ion loss processes; (2) both are fast, and (3) vibrational and/or rotational excitation are essential to have a fast exchange.

A last point will be addressed here. The charge transfer is assumed to be the rate-limiting step in the above-described recombination process. This is certainly true in the first part of the plasma jet, as the electron density is high and $n_e k_{\mathrm{DR}} > n_{\mathrm{H}_2^{v,J}} k_{\mathrm{CT}}$, where k_{DR} is the dissociative recombination rate coefficient, k_{CT} the charge-transfer rate coefficient, and $n_{\mathrm{H}_2^{v,J}}$ the density of rotationally and vibrationally sufficiently excited molecules. However, under the assumption that the density of excited molecules is not decreasing very fast, the observed efficient molecular recombination process decreases the ion and electron density decrease fast to such low values that the dissociative recombination becomes the rate-limiting process. This actually is the case between $z=200$ and 310 mm, where the electron density is a few times $10^{16}\mathrm{m}^{-3}$ in the low-hydrogen case and even lower in the high-hydrogen case (see Fig. 3). The ratio $[\mathrm{H}^+]$:$[\mathrm{H}_3{}^+]$ can be estimated by balancing the production and destruction of the molecular ion. The production is governed by reaction 1 and the destruction by 4 and 5. Balancing destruction and production, we obtain

$$n_e n_{\mathrm{H}_3{}^+} k_{\mathrm{DR}} = n_{\mathrm{H}^+} n_{\mathrm{H}_2(v,J)} k_{\mathrm{CT}} \ . \tag{8}$$

For $n_e = 5\times10^{16}$, the maximum value in the low-hydrogen case, this yields a ratio $[\mathrm{H}^+]$:$[\mathrm{H}_3{}^+]$ of 1:10. As a consequence, the dominant ion at these positions will be $\mathrm{H}_3{}^+$ rather than H^+. Therefore, for the Langmuir-probe measurements the $\mathrm{H}_3{}^+$ ion mass is used in both the low- and the high-hydrogen cases. This implies that almost all atomic ions emanating from the source already have been transferred to molecular ions, confirming that reaction 1 is very fast. In Fig. 4 the radial profiles from Fig. 3 are integrated to line ion densities N_i, i.e., the ion densities

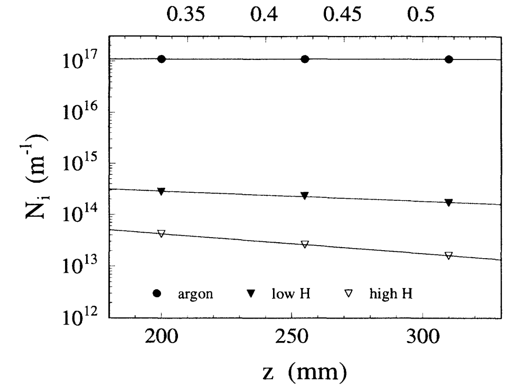

FIG. 4. Axial line ion densities for the three plasma compositions. The numbers along the top denote time in msec as discussed in the text.

are integrated over the cross section of the plasma jet. At the top of this figure a time scale is added. The time scale along the plasma axis is given by $t = z/w_{\mathrm{plasma}}$, where w_{plasma} is the plasma flow velocity. After the shock, the plasma is only slightly decelerating. The magnitude of the velocity depends on the pressure in the expansion chamber, and has a value between 500 and 1000 $\mathrm{m\,s^{-1}}$ [8]. Under the given conditions it is estimated to be 600 $\mathrm{m\,s^{-1}}$. The addition of a time axis allows us to estimate the rate for dissociative recombination for $\mathrm{H}_3{}^+$ ions. Using the molecular-ion mass for the probe measurements and the decrease in ion density observed from Fig. 4, k_{DR} is estimated at a value of 6×10^{-14} $\mathrm{m^3s^{-1}}$ at a plasma temperature of 2000 K. The accuracy of this value is estimated to be 50%. If we assume that the T_e^{-1} dependence of the dissociative recombination cross section on the electron temperature as found in the literature [19] is still valid around 2000 K, the agreement is good: We find $2\times10^{-13}\mathrm{m^3s^{-1}}$, extrapolated to 300 K, whereas in the literature values from

$$(1.7-2.3)\times10^{-13}\ \mathrm{m^3s^{-1}}$$

are reported [17–20].

CONCLUSIONS

The presented experiments show that expansion leads to an electron density of as low as 10^{19} m^{-3} in a pure-argon plasma jet, with a marginal influence of recombinative atomic processes. In a hydrogen-containing plasma jet, ion densities three to four orders of magnitude lower are found. The anomalous fast recombination in hydrogen cannot be explained with two- or three-particle recombination in the pure-hydrogen and argon-hydrogen mixtures. It is shown that the observed ionization loss can be described by the molecular dissociative recombination process. However, the cascaded-arc source is known to contain only atomic ions. In this paper a molecular channel is proposed that is based on the conversion of atomic to molecular ions by charge transfer.

This charge-transfer reaction is endothermic if the molecules do not have an important internal energy, vibrational and/or rotational. However, if the internal energy of the ion is sufficient, the reaction becomes exothermic and can become very fast. It is shown that with the charge-transfer cross section according to the Langevin limit and with reasonable assumptions on the rovibrational population, the charge-transfer reaction is fast enough to explain the observed time-scale behavior of the recombination process in the plasma jet, whereas no reasonable alternative explanations seem to be available. This implies that in any hydrogen-dominated plasma that contains a sufficient rovibrational population and atomic ions, charge exchange can be an important source of molecular-hydrogen ions.

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