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Fundamentals and application of an expanding hydrogen low-pressure plasma jet*

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The absolute density of atomic hydrogen excited states in two different regimes of a magnetized expanding plasma is determined using emission and absorption spectroscopy. First evidence has been found for the presence of high densities of negative ions in the "atomic" (recombining) regime of an expanding hydrogen plasma. Several clear observations of the presence of "hot" electrons have been made in the "molecular" (ionizing) regime of the expanding plasma. For both regimes the absolute density of atomic hydrogen in the ground state and the degree of plasma dissociation have been determined. Copyright © 1996 Elsevier Science Ltd.

Introduction

In the last decade hydrogen plasmas have been widely used in different research and application fields. Hydrogen containing plasmas have been utilized in various thin films deposition techniques,^{1,2} and for surface cleaning and passivation.³ For example, it has been established that high quality diamond films are grown in a hydrogen diluted plasma, and that the atomic hydrogen radicals are essential for the film quality. It is known that a key condition in fusion physics, required for controlled thermonuclear synthesis, is to heat the gas by injection of neutral hydrogen (deuterium) beams, produced by the neutralization of H⁻ (D⁻) from a negative ion source.⁴ Therefore, the kinetics of plasmas are of great interest in understanding the processes of H⁻ (D⁻) formation. As the hydrogen molecule and radicals are the simplest species among various atoms, molecules and ions, the investigation of the hydrogen plasma represents is fundamental for atomic, molecular and optical physics. For a better understanding of hydrogen plasmas a combined experimental and theoretical study of the plasma kinetics and plasma flow dynamics is required.

Experimental procedure

In the Department of Physics of the Eindhoven University of Technology a flowing cascaded arc is used as an effective source

of radicals and ions.⁵ In this type of arc a plasma is generated at subatmospheric pressures in a cylindrical channel consist of a number of plates. The arc is stabilized by water cooled walls. The power dissipation is relatively high, typically about 5 kW, and the carrier gas (argon, nitrogen, hydrogen) flows at a rate between 10 and 120 standard cm³ s⁻¹ (sccs).^{5,6} The arc expands into a low pressure background where monomers (SiH₄, C₂H₂, etc.) are injected. Experimental and theoretical investigation of the expanding cascaded arc show the source has a high efficiency for various technological applications.^{7,8} The important characteristics of the plasma source are the three functions (i) production, (ii) transport and (iii) deposition (etching), which are spatially separated, and optimization of these functions can occur more or less independently. Here we will concentrate on the characteristics of a strongly non-equilibrium expanding hydrogen low-pressure plasma jet.

The experiments were made in an expanding pure hydrogen plasma produced in a cascaded arc described in detail elsewhere.⁶⁻⁹ For the present studies a magnetic coil (diameter ≈ 0.5 m) is added at the location of the anode of the cascaded arc. This leads to a diverging magnetic field with a maximum induction between 8 and 40 mT on the axis. The motivation to apply a magnetic field is to extend the parameter range to lower pressure and thus to avoid the observed strong recombination in a freely expanding hydrogen plasma.¹⁰ A so-called 'molecular' regime of an expanding plasma has been realized for the low magnetic field induction $B_{\max} = 8$ mT, a so-called 'atomic' regime for $B_{\max} = 40$ mT. In comparison with previous experiments on the expanding hydrogen plasma jet, the hydrogen flow was 8 scc/s, and with that the pressure in the cascaded arc was low as well (about 20 mbar in the cathode region). This makes the assumption of a thermal

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plasma questionable.^{6,10} The pressure in the vessel and the arc current were kept constant at, respectively 5 Pa and 50 A ($V_{\text{arc}} = 130$ V).

The measurements of plasma characteristics were carried out using a movable Langmuir probe and spectroscopic system. The probe characteristics were interpreted using classical Langmuir theory, assuming a negligible sheath thickness. An Abel inversion was applied to derive local values of the emission coefficients and hydrogen excited state absolute densities. To measure the absolute density of the first excited states of H and H₂ a method of reabsorption with a mirror (which is identical to the method of two identical light sources^{11,12}) has been used. A concave mirror of reflectance r was placed behind the plasma beam, and the line intensity was measured with a mirror covered, or not covered. The mirror reflectance coefficient $r = r(\lambda)$ has been measured using a spectral line for which the plasma was optically thin.

Results and discussion

'Atomic' regime. The lateral scans of the hydrogen Balmer spectral lines emissivities were performed at different axial positions in the expansion. As has been shown, the radiation from up to $p = 18$ is detected.¹³ Also an inversion is observed for large distances from the anode nozzle. In general the inversion is more pronounced downstream in the plasma jet and the maximum of n_p/g_p vs I_p occurs for the higher quantum numbers. In Figure 1 the absolute population densities on the plasma beam axis at a position $x = 24$ cm from the nozzle as derived from emission and absorption spectroscopy measurements are shown as a function of the ionization potential I_p of the level p .

Atomic hydrogen density in the first excited state $H^*(p = 2)$ has been determined by $H\alpha$ ($\lambda = 656.3$ nm) spectral line absorption. To the same spectral range as $H\alpha$ belongs the spectral line of argon: $\lambda = 660.5$ nm (radiative transition $Ar(3p^5 4d \rightarrow 3p^5 4p)$). It has been shown, that the plasma was optically transparent for this line, and this line can be used to determine the reflectance coefficient of the mirror. In Figure 1 the absolute population density $H^*(p = 2)$ per statistical weight is shown as well.

Comparing the measured population densities (Figure 1) with the densities calculated on basis of the measured n_e and T_e (see later), using a purely atomic collisional-radiative model, leads to the conclusion that purely atomic recombination processes can not account for the large population densities observed. It is

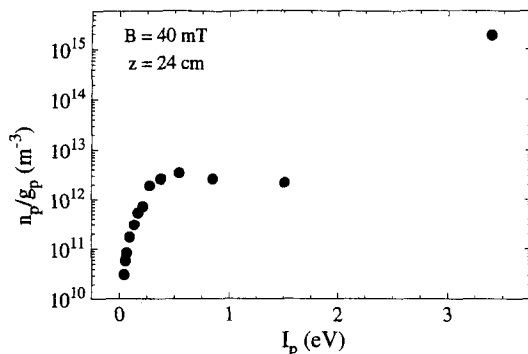
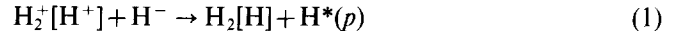


Figure 1. The atomic hydrogen absolute population densities per statistical weight n_p/g_p vs the ionization potential I_p on the plasma beam axis at a position $x = 24$ cm from the nozzle of the arc as derived from emission and absorption spectroscopy measurements. Experimental conditions: $I_{\text{arc}} = 50$ A, $Q = 8$ sccm/s, $P = 5$ Pa, $I_b = 250$ A.

argued that molecular induced recombination reactions in which the negative ion participates should be taken into account.^{14,15}



Note that the reaction of mutual neutralization of H^+ and H^- can only lead to the excitation of the quantum states $H(p \leq 3)$. Hydrogen negative ions H^- and positive molecular ions H_2^+ are either generated by the arc or formed in the reactions with the participation of Rydberg H_2^R molecules¹⁶ or rovibrationally excited H_2^v molecules:



Kinetic analysis of the rates of various processes in the expanding plasma show, that in the discussed regime of an expanding magnetized hydrogen plasma only spontaneous radiative processes are controlling the density of $H^*(p = 2)$ state; namely, radiative decay from the high-lying atomic states, and partially trapped resonance radiation to the ground state. Therefore the general balance equation for $H^*(p = 2)$ can be transformed to the following:

$$\sum_{n=3}^{\infty} \Phi_{n \rightarrow 2} = \Phi_{2 \rightarrow 1} = n_2 A_{21} \Lambda_{21} \quad (4)$$

where $\Phi_{k \rightarrow i}$ are the radiation fluxes between the quantum states k and i , n_2 is the absolute density of $H^*(p = 2)$ state, A_{21} is the absolute transition probability of the resonance Lyman- α spectral line, and Λ_{21} is the escape factor for resonance radiation. Another important conclusion can be derived from the kinetic analysis. Namely, in the plasma it should be a strong production source of highly excited hydrogen atoms $H^*(p \geq 3)$, which then radiatively decay to $H^*(p = 2)$ state. This statement is confirming the conclusion made earlier about the excitation mechanism of the highly excited hydrogen states.

The experimental information on the population density of hydrogen atoms in the excited states $H^*(p \geq 2)$ (cf. Figure 1), and known radiative transition probabilities, allows one to determine from (4) the escape factor Λ_{21} for resonance Lyman- α radiation. For the conditions mentioned of an expanding hydrogen plasma at a distance of $x = 24$ cm from the nozzle of the arc the escape factor was equal to $\Lambda \approx 7 \times 10^{-4}$. So, in other words the plasma under investigation can be described as an optically thick medium for the resonance Lyman- α radiation. The escape factor is related to the optical depth $\bar{k}R$ of the absorbing medium¹⁷. Assuming that the effective radius for the absorbed atoms, i.e. for the $n_{H(p=1)}$, is known one can estimate an over the line of sight average of the absolute population density of $H(p = 1)$ state. Here we want to underline that because of the fast diffusion phenomenon, the hydrogen atoms have to be present not only inside the plasma beam, but in a more broader area. The determined ground state density will be therefore an upper side estimate for the real density. In the 'atomic' regime of an expanding plasma at the position $x = 24$ cm from the arc nozzle, the averaged atomic hydrogen ground state density will be $n_{H(p=1)} \approx 4.8 \times 10^{20} m^{-3}$. The corresponding upper side estimate for the dissociation degree of hydrogen plasma is then approximately $\beta \approx 26\%$. It is essential that an accuracy of the discussed procedure is determined only by the experimental accuracy, but not by the uncertainties in the kinetic coefficients, since the radiative transition probabilities,

which were used in the kinetic scheme are known with high accuracy.

The correctness of the Langmuir probe diagnostic has been checked by comparison with the results of the Thomson scattering measurements, which is a non-intrusive optical diagnostic to determine simultaneously the electron density and temperature.⁹ The mean ion energy was approximately 0.3 eV, whereas the ion density was in the range $(1.4\text{--}2.4) \times 10^{17} \text{ m}^{-3}$.

'Molecular' regime. The measurements show that the electron temperature in the expansion as determined by Langmuir probe diagnostics in the 'molecular' regime is rather high, and for all positions in the expansion exceed 10^4 K , i.e. 1 eV. In the emission spectrum in this regime the strong emission of the Fulcher- α band of $\text{H}_2(d^3\Pi_u \rightarrow a^3\Sigma_g^+)$ transition (excitation potential is $\Delta E_1 = 13.87 \text{ eV}$) can be observed. Rotational (excitation) temperature and neutral particle (gas) temperature of an expanding plasma can be derived from the analysis of rotational spectra of Fulcher- α system of H_2 .¹⁸ Typical results are presented in Figure 2. The Boltzmann plot of the rotational lines intensities clearly shows that all three curves, corresponding to (0-0), (1-1) and (2-2) bands of Fulcher- α system can be considered as linear with approximately the same slope. The rotational temperature of $\text{H}_2(d^3\Pi_u)$ state, derived from slope of the lines (Figure 2), is in the range of 245–280 K, therefore the gas temperature in the plasma should be very low and in the range of 490–560 K (see Ref. 18).

It is crucial to mention the experiments with a local excitation of the Ar and He spectral lines. In this case the transport of Ar and He to the particular local points in the plasma active zone have been made through a thin cylindrical ceramic tube. In the 'atomic' regime of an expanding plasma and within the detection limit of the optical system, any presence of argon and helium spectral lines was not observed. However, in the 'molecular' regime one could see an appearance of the spectral line both of neutral argon Ar I ($7d \rightarrow 4p$) $\lambda = 4876.26 \text{ \AA}$ and $\lambda = 4887.95 \text{ \AA}$, and of ion argon Ar II ($4p^2D \rightarrow 4s^2D$) $\lambda = 4879.86 \text{ \AA}$. The excitation potential of these lines was $\Delta E_2 = 15.45 \text{ eV}$, and $\Delta E_3 = 19.68 \text{ eV}$, respectively. An appearance of the spectral lines with even higher excitation potentials has been observed in the case of helium, namely the spectral lines of He I ($3d \rightarrow 2p$) $\lambda = 5875.70 \text{ \AA}$ ($\Delta E_4 = 23.07 \text{ eV}$), and He I ($5d \rightarrow 2p$) $\lambda = 4026.20 \text{ \AA}$

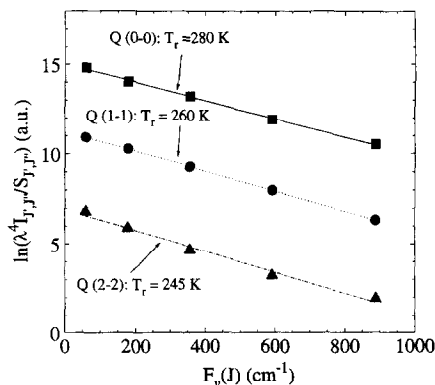


Figure 2. Boltzmann plot of the first five lines of Q -branch for the first three vibrational bands of the Fulcher- α system of molecular hydrogen $\text{H}_2(d^3\Pi_u, v' = 0, j' \rightarrow a^3\Sigma_g^+, v'' = 0, j'')$. Experimental conditions: $I_{\text{arc}} = 50 \text{ A}$, $Q = 8 \text{ sccm/s}$, $P = 5 \text{ Pa}$, $I_B = 50 \text{ A}$; \blacksquare —(0,0) band, \bullet —(1-1) band, \blacktriangle —(2-2) band.

($\Delta E_5 = 24.04 \text{ eV}$) can be seen in the emission spectra of an expanding plasma.

Optical actinometry has been applied to measure the absolute density of hydrogen atoms and hydrogen plasma dissociation degree. It has been shown that the atomic $\text{H}^*(n = 3, 4, 5)$, and molecular $\text{H}_2 d^3\Pi_u$ radiative quantum states are excited mainly by a direct electron impact from the ground states $\text{H}(n = 1)$ and $\text{H}_2 X^1\Sigma_g^+$, respectively, and depopulated via spontaneous radiative decay (corona balance). The method of reabsorption with a concave mirror was used to determine the population density of the first excited states of H and H_2 , and thus to estimate the influence of the stepwise electron excitation. The densities were lower than 10^{15} m^{-3} , and it can easily be shown, that here the stepwise electron excitation was inefficient.

The results of determining the dissociation degree on the axis of an expanding hydrogen plasma are shown in Figure 3. It is essential to mention that the dissociation degree does not strongly depend on the atomic spectral lines selected, i.e. H_α , H_β or H_γ . We believe that the results presented provide strong support for the corona balance approximation, and to the optical actinometry method as a whole. The measured absolute density of hydrogen atoms are in the $(1\text{--}1.4) \times 10^{20} \text{ m}^{-3}$ range. The dissociation degree of the hydrogen plasma is in the range of 8–13% and within experimental accuracy does not depend on axial position. This probably indicates that for given experimental conditions the recirculation gas flows in the vessel are ineffective, and both processes of H_2 dissociation, and of H recombination are slow, and do not influence the kinetics of hydrogen atoms in the plasma.

Emission spectra of OH. Besides of the spectral lines of Balmer series of H, the emission spectra of an expanding hydrogen plasma in the 'atomic' regime contain the strong bands of so-called violet system of OH ($A^2\Sigma \rightarrow X^2\Pi$ transition), and the weaker bands of so-called 3360 Å system of NH ($A^3\Pi \rightarrow X^3\Sigma$ transition).¹⁹ At the same time in the 'molecular' regime of an expanding plasma the intensity of the same bands were at least two orders of magnitude lower. It is interesting to make an analysis of these differences.

Appearance of mentioned molecular species can be caused in principle by two reasons: (i) desorption from the vessel walls and following dissociation of the water vapours and (ii) leakage into the vacuum system. Typical leakage rate was very low $\approx 10^{-3} \text{ slm}$, which is 2–3 orders of magnitude lower, than the gas flow

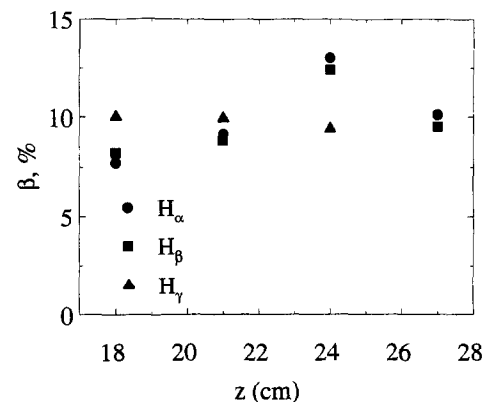


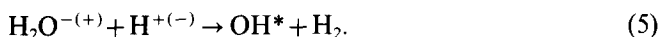
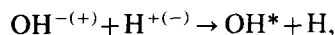
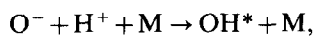
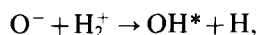
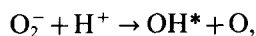
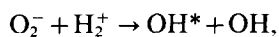
Figure 3. Dissociation degree in the 'molecular' regime of an expanding hydrogen plasma; \bullet —experiments with H_α , \blacksquare — H_β , \blacktriangle — H_γ . Experimental conditions are the same as in Figure 2.

rate through the arc. Nevertheless, even such small leakage can be a reason for the appearance of molecular bands of OH and NH in the emission spectra.

Analysis of rotational and vibrational structures of OH and NH molecular spectra in atomic regime of an expanding hydrogen plasma enables a determination of the rotational and vibrational excitation temperatures of those species. It was shown, that the rotational temperature of OH molecules in the excited state OH ($A^2\Sigma$, $v' = 0$) was $T_{rot}^* = 7300$ K, whereas the vibrational temperature of NH ($A^3\Pi$) excited molecules was $T_{vib}^* = 3300$ K (the molecular constants for the corresponding molecular states have been taken from Ref. 19). It can clearly be seen that the measured excitation temperatures are significantly higher, than the translational temperature of the heavy particles (gas temperature) in the plasma (see earlier). The only possible explanation of high excitation temperatures of OH* and NH* radicals in our experimental conditions is that the corresponding excited states are populated in the processes of non-resonant interaction between the heavy particles.^{18,20,21}

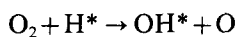
Since the 'atomic' regime of an expanding hydrogen plasma is a purely recombining plasma (see earlier), the following reaction can be responsible for appearance of the 'hot' OH* molecules.

1. Ion-ion recombination (where M can be any component of the plasma):



The reactions with participation of negative oxygen ions must be very effective, since free electrons with the high probability can be attached by the oxygen atoms and molecules²².

2. Excitation exchange:



3. Direct electron impact (in this case to explain high rotational temperature of excited OH* molecules, we should assume high rotational temperature of OH molecules in the ground electronic state):



It was shown earlier, that in the 'molecular' regime of an expanding hydrogen plasma the main reason of excitation of the plasma components is the direct electron impact from the ground state. Much weaker intensity of OH spectra in the molecular regime can mean only that either the non-resonant heavy particle collisions are more efficient than the direct electron impact, or that the ground state density of OH ($X^2\Pi$) radicals are much smaller than the corresponding density of the excited state OH*($A^2\Sigma$). In the latter case perhaps the situation is somewhat similar to those, when the inversion of the populations between the quantum states of C and C₂ radicals has been observed in an expanding hydrocarbon plasma.¹² As was shown in Ref. 12 both C and C₂ showed a significant population inversion.

Production of the negative oxygen ions can be a reason for reduction of H⁻ density in the plasma, since the attachment of electrons to the oxygen is a much faster process for oxygen, than for hydrogen.²² Therefore, to have a higher density of hydrogen negative ions one should try to minimize the oxygen concentration in the plasma, i.e. to decrease the leakage rate.

Conclusions

The absolute density of atomic hydrogen in the first excited state H*($p = 2$) has been determined in the 'atomic' regime of an expanding hydrogen magnetized plasma by using the reabsorption method with a concave mirror. A kinetic model is used to understand the H*($p = 2$) density in the plasma. It was shown that in the 'atomic' regime of an expanding hydrogen plasma a rather unusual situation is observed: not collisional, but only the spontaneous radiative processes are controlling the density of H*($p = 2$) state. Namely, there are the radiative decay from the high-lying atomic states, and partially trapped resonance radiation to the ground state. Strong flux of radiation from the highly excited states H*($p \geq 3$) to H*($p = 2$) state clearly shows, that in the atomic regime of an expanding hydrogen plasma we have a situation with the strong production source of highly excited hydrogen atoms H*($p \geq 3$). This experimental observation confirms the previously made conclusion about the excitation mechanism of highly excited hydrogen states. Since the escape factor for resonance radiation appears to be the determining factor of the H*($p = 2$) population density, it has been calculated from the kinetic balance equation. Finally, the escape factor has been used to determine the effective optical depth for the resonance radiation, the absolute density of atomic hydrogen in the ground state, and hydrogen plasma dissociation degree.

Several clear observations of the presence of 'hot' electrons have been measured for the 'molecular' (ionizing) regime of an expanding plasma. Optical actinometry has been applied to determine the absolute density of hydrogen atoms and hydrogen plasma dissociation degree. It has been shown, that in this regime the atomic H*($p = 3, 4, 5$), and molecular H₂($d_3\Pi_u$) radiative quantum states are excited by a direct electron impact from the ground states H($p = 1$) and H₂($X^1\Sigma_g^+$), respectively, and depopulated via spontaneous radiative decay. The neutral particle (gas) temperature of the expanding hydrogen plasma has been derived from the analysis of rotational spectra of the Fulcher- α system of H₂. It has been shown that the 'molecular' regime can be treated as optically thick media for the resonance atomic radiation. Method of reabsorption with a concave mirror has been used in order to determine the population density of the first excited states of H and H₂. The densities were lower than 10^{15} m⁻³, and for the same reasons an expanding plasma will be optically transparent for the radiative transitions between the excited states. It is demonstrated that the results do not strongly depend on the atomic spectral lines H $_{\alpha}$, H $_{\beta}$ or H $_{\gamma}$, which have been used for diagnostics. This is strong support for the corona balance approximation and for the optical actinometry method as a whole.

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