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ATOMIC HYDROGEN LEVEL POPULATIONS AND HYDROGEN DISSOCIATION DEGREE IN AN EXPANDING THERMAL PLASMA

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ABSTRACT. Optical absorption spectroscopy has been applied to measure the absolute population densities of the first excited levels of atomic hydrogen $H^*(n=2)$ and argon $Ar^*(4s)$ in an expanding cascaded arc plasma in a hydrogen-argon mixture. It is demonstrated that the method allows us to determine both $H^*(n=2)$ and $Ar^*(4s)$ absolute density radial profiles for H_2 admixtures in Ar ranging from 0.7 to 10 % with good accuracy. It has been shown, that the density of hydrogen excited atoms $H^*(n=2)$ serves as an indicator of the presence of argon ions and hydrogen molecules in the expanding plasma. A kinetic model is used to understand evolution of $H^*(n=2)$ density in the expansion, and to estimate the total atomic hydrogen population density and hydrogen dissociation degree in sub- and supersonic regions of the plasma.

1. INTRODUCTION

Hydrogen plasmas have important applications in many areas of modern science and technology, in particular in surface modification techniques. Therefore a special interest arises in the development and characterization of high intensity sources of reactive hvdrogen atoms. The hydrogen atoms population density is difficult to model as it requires accurate knowledge of all the relevant kinetic processes, including heterogeneous phenomena on the walls [1]. On the other hand, experimental methods can be employed to determine the density of H atoms. The analysis of the literature shows, that mainly the VUV absorption methods (including laser absorption techniques) have been used for the direct measurements of the ground state atomic hydrogen population density in a low-temperature plasmas. The attempts on determining the $H(n=1)$ atom density from hydrogen excited level populations $H(n \geq 2)$ in ionizing plasmas are usually not accurate enough, since detailed information of the electron energy distribution function (EEDF) behavior near the excitation thresholds of the excited states is required.

The aim of this paper is to determine the population density of atomic hydrogen in the first excited state $H^*(n=2)$ in a freely expanding recombining hydrogen-argon plasma jet. This is achieved by direct measurement of atomic hydrogen Balmer-α spectral line absorption. A quantitative model of the relevant atomic and molecular processes, which does not require information on the EEDF has been used to derive the absolute density of atomic hydrogen in the ground state and an estimate of the plasma dissociation degree from the experimental data. Other reliable data on expanding cascaded arc plasmas [2] have been used to obtain the $H(n=1)$ density.

2. EXPERIMENT

The experiments are carried out in the expanding thermal plasma produced by a cascaded arc, described in detail elsewhere [2, 3, 4]. The mixture of hydrogen and argon is injected at flow rates adjustable over a range from 10 to 400 standard cm^3s^{-1} (scc/s) to the beginning of the cylindrical arc. The pressure in the arc channel with the diameter of 4 mm is about 0.5 bar ($0.5 \cdot 10^5$ Pa). The total current can be adjusted from 30 to 90 A, with the voltage in the range of 50-150 V. The plasma generated is close to partial local thermal equilibrium (PLTE) conditions with temperatures of the order of 1 eV, an electron density of the order of 10^{22} m^3, and an ionization degree of about 10 % [2]. The thermal plasma flows through the channel, is accelerated and expands supersonically into a low background pressure (p = 10-100 Pa) vessel. Three regions can be distinguished in the expanding plasma: a region with supersonic expansion, a shock region and a subsonic expansion region.

The argon and hydrogen absolute densities in the first excited states $Ar^*(3p^54s)$ and H^*(n=2) have been measured by the absorption of eight argon spectral lines, belonging to the transition of argon $Ar(3p^54p \rightarrow 3p^54s)$, and atomic hydrogen H_α line, respectively. A highly sensitive spectroscopic set up, using the principle of optical absorption [5], has been developed. The system [6] uses a high resolution monochromator for wavelength selection and a stagnant high pressure cascaded arc as a bright external continuum light source [7].

The optical system allows us to scan the complete plasma beam. Afterwards an Abel inversion procedure has been applied to obtain experimental parameters as a function of axial and radial position. The system was calibrated by positioning a tungten ribbon lamp in the vessel, and recording the spectrum at a known true temperature of the ribbon. The detection section consist of high resolution monochromator with a focal length of 1 m, and a Peltier cooled photodiode array. After AD conversion the signal of the photodiode array is recorded by a personal computer.

2. RESULTS

The standard condition under which the experiments have been performed is the following: background pressure 40 Pa, particle source arc current 45 A, arc voltage 80 - 115 V. The gas mixture of argon and hydrogen in various proportions can be introduced directly into the beginning of the cascaded arc at a flow rate of 58 scc/s. The hydrogen percentage in the total gas flow is varied: 0.7, 1.4, 2, 3, 5 and 10 %. In some of the experiments hydrogen was introduced in various concentrations not into the cascaded arc itself, but directly into the vacuum vessel. In the latter situation a pure argon plasmas is expanding from the cascaded arc into the vessel, where it interacts with the background hydrogen.

By using the absolute calibration of the atomic hydrogen Balmer line intensities, the absolute densities of the quantum states H(n $\geq$ 3) have been determined. The measured atomic hydrogen excited states densities are in the range of $(1 - 3) \cdot 10^{13}$ m^{-3} for the H^*(n=3), $(0.7 - 2) \cdot 10^{13}$ m^{-3} for the H^*(n=4), and $(0.5 - 1.5) \cdot 10^{13}$ m^{-3} for the H^*(n=5). Besides, these measurements were used in order to make a direct comparison possible with similar experiment in which the plasma parameters n_e, T_e and n_0 have been measured by Thomson-Rayleigh scattering, quoted in [2, 4]. The absolute densities of the quantum states $H(n = 3 - 5)$, which have been measured in both experiments for identical plasma conditions were the same within $\simeq$ 30 %.

For the examination of the absorption method three spectral lines with the same lower level of radiative transitions of argon - $3p^54s(^3P_1)$, but with different (up to factor of six) radiative transition probabilities have been chosen. In earlier analyses the heavy particles temperature was set as a parameter in an Abel integration fit procedure; the results were

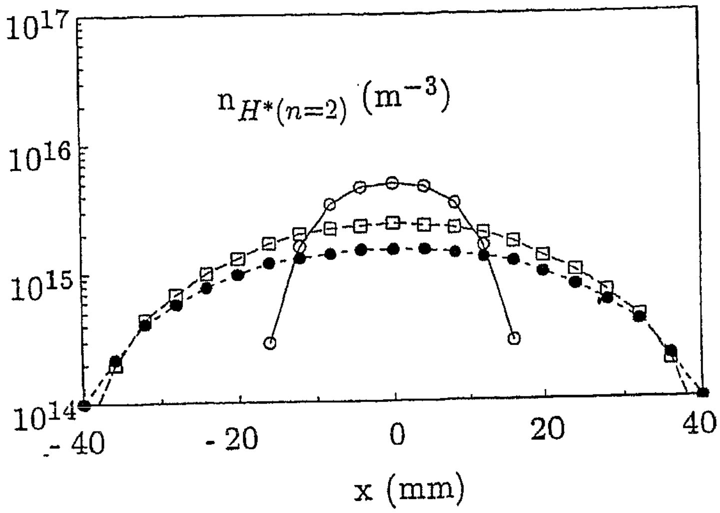

Figure. 1. The radial dependencies of the hydrogen H*(n=2) absolute density for the different axial positions in the expansion of argon-hydrogen arc and 2 % of H_2 in the gas flow: ○ - z = 20 mm, ● - z = 40 mm, □ - z = 70 mm.

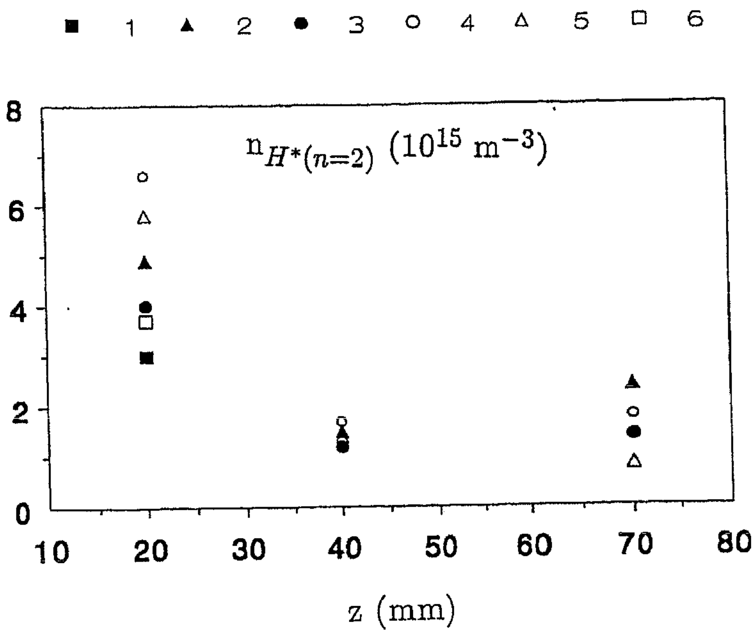

Figure 2. The axial dependences of the hydrogen H*(n=2) absolute density on the axis of the plasmas as function of various molecular hydrogen percentage in the gas flow: 1) 0.7 % H_2, 2) 1.4 %, 3) 2 %, 4) 3 %, 5) 5 %, 6) 10 %.

compared with the earlier obtained values and it was shown that average values can be chosen for the final fit [6]. The difference in radiative transition probabilities of the argon spectral lines provides us with an excellent check for testing the accuracy of the fit procedure and validity of the results (cf. Ref. [6]).

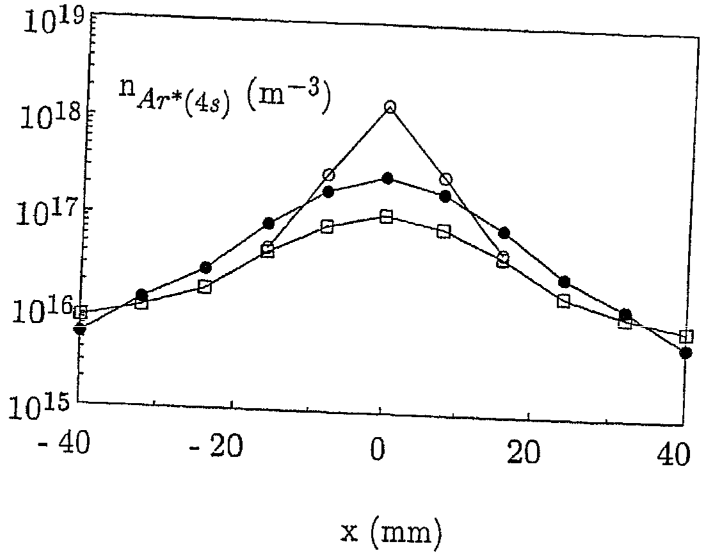

Figure 3. The radial dependences of the argon $Ar^*(3p^5 4s, {}^3P_2)$ absolute density for the different axial positions in the expansion of argon-hydrogen arc and 2 % H_2 in the gas flow: o - z = 20 mm, • - z = 40 mm, □ - z = 70 mm.

In Fig. 1 the radial dependencies of the hydrogen H*(n=2) density obtained for the different axial positions in the expansion are shown. In Fig. 2 the dependences of the hydrogen H* (n=2) axial density are given as a function of various hydrogen percentages in the gas flow. Fig. 3 illustrates the radial distribution of the argon $Ar^*(3p^5 4s)({}^3P_2)$ densities obtained for the case of 2 % of hydrogen in the initial gas flow. The procedure to correct for the non-linear relation between the measured absorption values and the argon population densities has been described in detail previously [6]. From Fig. 3 the same conclusion as for the hydrogen excited atoms can be derived: because of the decrease of n_e in the expansion, and the production by recombination, the radial profile of Ar* (4s) downstream becomes broader. The measured H*(n=2) densities are in the $10^{14} - 10^{16}$ m^{-3} range, and the Ar* (4s) densities are in the range of $10^{15} - 10^{18}$ m^{-3}.

4. PARTICLE KINETICS IN THE EXPANDING PLASMA

4.1 General kinetic scheme

The analysis of the rates of various processes for a specific condition in the expanding plasma shows, that as soon as a plasma contains very small amount of H_2 molecules, then the charge transfer leading to the formation of molecular positive ions (with subsequent dissociative recombination), becomes the dominant reactions for recombination and for the population of the H*(n=2) state in the plasmas:

$$Ar^+ + H_2 \xrightarrow{k_1} ArH^+ + H, \tag{1}$$

and

$$ArH^+ + e \xrightarrow{k_2} Ar + H^*(n=2). \tag{2}$$

$$Ar^+ + H_2 \xrightarrow{k_3} H_2^+ + Ar, \tag{3}$$

and

$$H_2^+ + e \xrightarrow{k_4} H + H^*(n=2). \tag{4}$$

The low energy behavior for the charge transfer reaction $Ar^+ + H_2$ is dominated by the proton transfer reaction leading to the formation of ArH+ (1) [8]. The recommended temperature dependence of the cross section σ_2 and rate coefficient k_2 based on a power law fit of the rate constant k_2 for temperatures T from 20 to 5000 K yields that $k_2 = 1.45 \cdot 10^{-15}(\hat{T})^{0.14}$ m^3 s^{-1} to within 10 % [9]. Here $\hat{T}$ is in eV. The cross section for the formation of H_2^+ by charge transfer according to Eq. (3) has been taken from the measurement for slow ion formation [10]. In the temperature range from 1000 to 10000 K the cross section for the reaction (3) is almost constant with $\sigma_3 \simeq 10^{-19}$ m^2. This yields rate coefficient $k_3 \simeq 10^{-15}$ m^3 s^{-1}.

The reactions of dissociative recombination of molecular ions (2) and (4) are usually very effective and often are the main reason for charged particles recombination in plasmas [11]. Reactions (2) and (4) lead to the population of mainly the H*(n=2) state, since compared to the others, only these reactions are exothermic: the positive excess of energy for the dissociative recombination reactions with the participation of vibrationally non-excited molecular ions ArH^+ and H_2^+ is approximately 0.7 eV.

4.2 Subsonic expansion (z $\geq$ 40 mm)

From a kinetic analysis one can easily show that using plasma parameters that have been measured in the subsonic expansion region, the elementary processes controlling the H*(n=2) population density are primarily the charge transfer reaction, leading to the formation of ArH^+ (1) with subsequent dissociative recombination Eq. (2), and radiative transition decay through the partly reabsorbed Lyman-α spectral line. Therefore, assuming that the charge transfer reaction is rate limiting, which is true for $n_e \geq 10^{-2} \cdot n_{H_2}$, the kinetic balance equation could be derived:

$$n_{H_2} n_e k_1 - n_{H^*(n=2)} A_{21} \Lambda_{21} = 0, \tag{5}$$

where Λ_{21} and A_{21} are the escape factor and radiative transition probability for resonance Lyman-α radiation.

The escape factor Λ_{21} now appears to be the determining factor on the H*(n=2) population density. It is related to the optical depth $\overline{kR}$ of the absorbing medium. The relation between escape factor and optical depth has been calculated for Voigt emission profiles in [12] for the case of cylindrically symmetric plasmas.

In the framework of the validity of the kinetic equation Eq. (5) one more important conclusion can be drawn: the density of hydrogen excited atoms $H^*(n=2)$ can serve as an indicator of the presence of argon ions and hydrogen molecules in the expanding plasma under investigation.

4.3 Supersonic expansion ($z \leq 40$ mm)

In the supersonic expansion one can use the same description of the kinetic phenomena as in the subsonic one, but only if the assumption is right, that hydrogen molecules (which are circulating in the vessel), can penetrate into the supersonic region of the expanding plasma. If so, then the characteristics of the various chemical reactions are valid for the position $z = 20$ mm in the supersonic expansion as well. A more likely explanation of the high density of $H^*(n=2)$ atoms in the supersonic expansion is the penetration of H_2 molecules to the expansion directly from the cascaded arc followed by the reactions Eqs. (1) - (4). Inspite of the high temperatures in the arc [3], a certain amount of hydrogen molecules has a chance to survive near the cold walls of the arc channel. Since the gas density near the cold walls of the channel must be high, some fraction of the hydrogen molecules can enter the supersonic expansion as well. Then, of course, a speculative question about the amount of H_2 in the supersonic expansion arises.

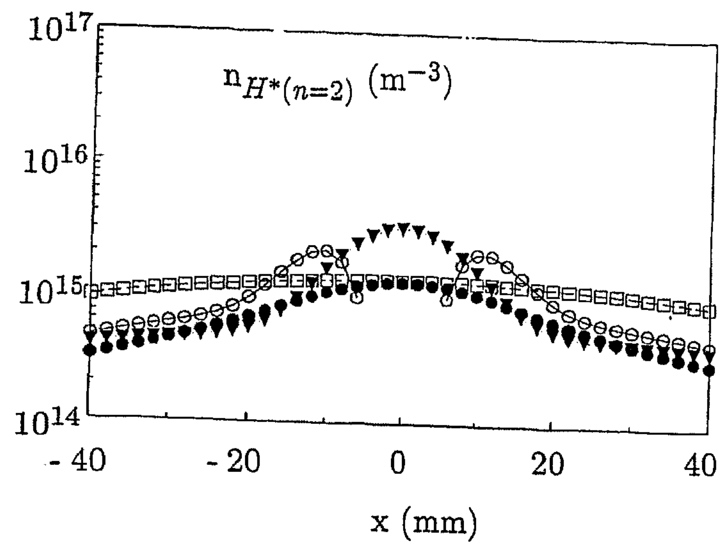

Figure 4. The radial dependences of the hydrogen $H^*(n=2)$ absolute density for the different axial positions in the expansion of pure argon arc and 2 % of H_2 in the vessel: o - z = 20 mm, • - z = 30 mm, □ - z = 40 mm, ▽ - z = 70 mm.

In an attempt to solve the problem, a special measurements of the $H^*(n=2)$ density has been made, in which all the experimental conditions remained the same, but the hydrogen was introduced not into the cascaded arc itself, but directly into the vessel. The results of the measurements for a pure argon arc and an admixture of 2 % (from the total gas flow) of hydrogen in the vessel are presented in Fig. 4. For the situation discussed it can be seen that the absence of hydrogen molecules in the beginning of the expansion (z = 20 mm) leads to a lower H*(n=2) density compared with the case in which H_2 is injected into the arc. This is most prominent near the axis, where the density is practically equal to zero. The maximum of the H*(n=2) atoms density occurs at the radial position of r$\simeq$ 10-12 mm, i.e. outside the fast supersonic flow, where H_2 molecules exists. Hence one can conclude that hydrogen molecules from the vessel cannot penetrate into the beginning of supersonic expansion. At the same time in the case when H_2 has been introduced directly to the cascaded arc, a quite significant amount of H*(n=2) atoms exist already in the very beginning of the expansion (see Fig. 1). These two facts clearly indicates, that inspite of a high temperature in the cascaded arc, some of the hydrogen molecules (most likely from the regions close to the walls of the arc channel or nozzle) can survive, and penetrate to the beginning of the expansion.

4.4 Dissociation degree in the plasmas

From kinetic equations Eq. (5), and from the expression for the effective optical depth [12] one can determine the population density of the ground state of atomic hydrogen H(n=1), and hence the hydrogen dissociation degree in the plasmas if the molecular density is known. Absolute population densities of atomic hydrogen as a function of plasma parameters in the subsonic expansion, which have been calculated using Eq. (5) are presented in Table 1. From the atomic and molecular hydrogen densities one can easily find the dissociation degree of the plasma, which is determined as follows: $\beta = n_H/(n_H + 2n_{H_2})$.

TABLE 1.
Absolute Density of Atomic Hydrogen and Hydrogen Dissociation Degree.

	0.7 % H_2		1.4 % H_2		2 % H_2		3 % H_2	
$z, (mm)$	40	70	40	70	40	70	40	70
$n_H, 10^{19}(m^{-3})$	0.90	-	0.55	0.31	0.20	0.03	0.15	0.02
$\beta, (\%)$	50	-	22	10	7	0.7	3	0.4

From Table 1 it can be concluded that the atomic hydrogen density and the hydrogen plasma dissociation degree drops with increasing total concentration of hydrogen in the gas flow and downstream. The most probable cause for the decrease of the dissociation degree may be the fast diffusion of atomic hydrogen to the walls of the vessel and the effective admixture of molecular hydrogen, which is recirculating freely in the vacuum vessel, into the expanding plasma flow.

5. CONCLUSION

Optical absorption spectroscopy has been applied to measure the absolute population densities of the first excited levels of atomic hydrogen H*(n=2) and argon Ar*(4s) in the expanding cascaded arc plasma. It is demonstrated that for the expanding hydrogen-argon plasma the method allows us to determine both for H*(n=2) and Ar*(4s) the absolute density radial profiles for H_2 admixtures in Ar ranging from 0.7 to 10 % with good accuracy.

It has been shown, that the density of hydrogen excited atoms $H^*(n=2)$ serves as an indicator of the presence of argon ions and hydrogen molecules in the expanding plasma. Absence of $H^*(n=2)$ atoms in the supersonic expansion in the case when H_2 has been injected into the vessel shows that hydrogen molecules from the vessel cannot penetrate into the beginning of the supersonic expansion. At the same time when H_2 has been introduced directly to the cascaded arc a quite significant amount of $H^*(n=2)$ atoms exists already in the very beginning of the expansion. This fact clearly indicates, that in spite of a high temperature in the cascaded arc some of the hydrogen molecules (most likely from the regions close to the walls of the arc channel) can survive, and which then penetrate from the arc to the beginning of the expansion.

A kinetic model is used to understand the evolution of $H^*(n=2)$ density in sub- and supersonic regions of the expanding plasma, and estimate the total atomic hydrogen population density and the dissociation degree in the subsonic expansion. The results in most of the cases indicate a moderately low H atoms ground state density ($\leq 6 \cdot 10^{18}$ m^{-3}), and dissociation degree in the plasma (≤ 22 %), which drops with the distance from the exit of the cascaded arc, and with increasing hydrogen concentration in the plasma. The reasons for the decrease of the dissociation degree may be fast diffusion of atomic hydrogen to the walls of the vessel and effective admixture of molecular hydrogen, freely recirculating in the vacuum vessel, into the expanding plasma.

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