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Spectroscopic measurement of atomic hydrogen level populations and hydrogen dissociation degree in expanding cascaded arc plasmas

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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 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 H₂ admixtures in Ar ranging from 0.7% to 10% with good accuracy. The measured H*(n = 2) densities are in the 10^{14}-10^{16} m⁻³ range, and Ar*(4s) densities are in the range of 10^{15}-10^{18} m⁻³. 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.

I. INTRODUCTION

Hydrogen plasmas have important applications in many areas of modern science and technology, in particular in surface modification techniques, such as deposition, etching, implantation, and the desorption of boundary layers of solids and liquids. In connection with these topics, a special interest arises in the development and characterization of high intensity sources of reactive hydrogen atoms. For example, it has been shown that hydrogen atom beams are of principal importance in the various schemes for deposition of diamond coatings. In the semiconductor technology, H atoms are effective in the removal of oxide layers on surfaces, and in the passivation of amorphous silicon and polysilicon films. Furthermore, the kinetics of hydrogen atoms in plasmas and on surfaces are of great importance in understanding the process of negative hydrogen ion formation in volume and surface production of negative ions. In fusion experiments, atomic hydrogen plays a significant role in plasma-wall interaction. The use of highly dissociated hydrogen plasmas has become a common procedure in the cleaning of the inner surfaces of fusion reactors.

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. On the other hand, experimental methods can be employed to determine the density of H atoms.

Optical emission spectroscopy is the main technique to measure the hydrogen excited states population density and hydrogen plasma dissociation degree (cf. for example Refs. 8-10). In all experiments detailed kinetic modeling, including information about the electron energy distribution function (EEDF) was required to interpret the measured data and to derive the total density of ground state hydrogen atoms in the plasma from the experimental data on the atomic hydrogen excited states population density.

In the past strong vacuum ultraviolet (VUV) continuum, radiated by a pulsed gas discharge, was used to apply the technique of resonance fluorescence and of the absorption of continuum radiation to determine the ground state hydrogen atom absolute densities in the plasma. Radiation of the Lyman-α line generated by a microwave discharge lamp has been used to measure linear absorption of this line in the positive column of a glow discharge. To determine the H atom density accurately one must have detailed information on the shape of the Lyman-α line both in emission and in absorption. In Ref. 13 the line shape has been measured with a very high resolution VUV spectrometer.

Eenshuistra et al. applied the method of resonance-enhanced multiphoton ionization (REMPI) to measure the hydrogen atom absolute density emanating from a hydrogen volume source of negative ions. The technique of four-wave sum-frequency mixing (FWSM), as a method of VUV radiation production has been successfully applied for the determination of the density and the temperature of ground state hydrogen atoms by measurement of the absorption of Lyman-β and Lyman-γ radiation. Pealat et al. used coherent anti-Stokes Raman scattering (CARS) for the estimation of the atomic hydrogen absolute density by checking the differences between the measured and predicted molecular hydrogen population densities.

With the advent of narrow-band tunable VUV laser-induced fluorescence (LIF) becomes possible to measure the hydrogen excited state population density and to estimate the total H atoms density and the hydrogen plasma dissociation degree (cf. for example Refs. 8-10). In all experiments detailed kinetic modeling, including information about the electron energy distribution function (EEDF) was required to interpret the measured data and to derive the total density of ground state hydrogen atoms in the plasma from the experimental data on the atomic hydrogen excited states population density.
characteristics of hydrogen atoms in the ground state by the direct absorption of VUV radiation. This method has been used to measure H atom temperatures and densities in glow discharges, and the H atom density in gas, produced by thermal dissociation. A multiphoton (2+1) absorption LIF technique is employed for the detection of ground state H atoms in a subatmospheric pressure Ar/H₂ arc discharge, and in the low-pressure post-discharge of a microwave induced H₂ plasma. The population density of hydrogen atoms in the first excited state H*(n = 2) was determined by visible LIF using Balmer-α absorption. Again this LIF signal is related to the ground state density by means of a theoretical model. Because of the complicated character of the electron energy distribution function (EEDF) near the excitation threshold of atomic excited states the accuracy of the determination of the ground state population is low in this case.

The review presented of the literature shows, mainly that 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≥2) in ionizing plasmas are usually not accurate enough. Other reliable data on the EEDF behavior near the excitation thresholds of the excited states is required.

The aim of this article 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 have been used to obtain the H(n = 1) density.

II. PLASMA SOURCE

In Fig. 1 the outline of the expanding cascaded arc with the optical setup for performing emission and absorption spectroscopy is shown. The mixture of hydrogen and argon is injected at flow rates adjustable over a range from 10 to 400 standard cm³ s⁻¹ (scm/s). The pressure in the channel is about 0.5 bar (0.5×10⁵ Pa). The total current can be adjusted from 30 to 90 A, with the voltage in the range of 50–150 V, so the power density in the arc is high, of the order of 10⁶ W/m³. 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 10²⁵ m⁻³, and an ionization degree of about 10%.

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. For the reactor settings summarized above, at a background pressure of 40 Pa, an arc current 45 A and a gas flow rate of 58 scc/s, the experiments and model calculations for pure argon plasmas show the following: in the supersonic region the particles are accelerated to velocities up to ≈4000 m/s. During this expansion the electron and heavy particle temperatures decrease down to ≈1500–2000 K, and the electron density decreases down to ≈10¹⁹ m⁻³. At a distance of about 30–50 mm from the nozzle of the arc (depending on the pressure in the vessel) a stationary shock occurs. The temperatures and the electron density rise again to about 3000–3500 K, and typically ≈4×10¹⁹ m⁻³. Beyond the shock the plasma expands subsonically and the plasma composition remains almost constant (frozen) in pure argon. The temperatures drop gradually to about 2000–2500 K and the density decreases slowly in the subsonic expansion.

In Refs. 22 and 28 an expanding argon cascaded arc plasma with different amounts of hydrogen added, was studied using the techniques of Thomson–Rayleigh scattering and optical emission spectroscopy. The electron density and temperature, neutral particle density and excited hydrogen atoms H*(n ≥ 3) absolute population densities have been determined as a function of the axial position in the expansion. The admixture of a small amount of hydrogen to the flow leads to a dramatic—up to three orders of magnitude de-
where \( k_{i j} \) is the spectral absorption coefficient, \( N_i \) and \( N_k \) are the population densities of the particles in lower and upper quantum levels of the radiative transition, \( g_i \) and \( g_k \) are the statistical weights, \( \lambda_0 \) is the wavelength, \( A_{ii} \) is the transition probability (Einstein coefficient).

In the case of the absorption of spectral lines on the background of a continuum spectrum, the value of total absorption \( A_g \) is defined as the ratio of the absorbed energy to the incident intensity. 

\[
A_g = \int_0^\infty \left[ 1 - \exp(-k_{i j}) \right] d\nu = \frac{I_0 - I_{\nu c}}{I_0},
\]

where \( \Delta \nu_c \) is the spectral width of the section of continuum spectrum, convoluted with the apparatus profile which is admitted through the spectrometer slit (\( \Delta \nu_c > \Delta \nu_{line} \)), \( l \) is the optical path length.

Hence, after the measurements of \( \Delta \nu_c \) and \( (I_0 / I_{\nu c}) / I_0 \), with known values of \( A_{ki} \), \( g_i \), \( g_k \), and \( l \), from (1) and (2) one can determine the absolute concentration of the absorbing particles \( N_i \) (of course, if \( N_i > N_k \), which almost always takes place in gases and plasmas).

A highly sensitive spectroscopic setup, using the principle of optical absorption, has been developed. The system uses a high resolution monochromator for wavelength selection and a stagnating high pressure cascaded arc as a bright external light source.

### III. OPTICAL ABSORPTION SPECTROSCOPY DIAGNOSTIC

#### A. Absorption theory

A major advantage of absorption spectroscopy is its ability to measure with good accuracy absolute concentrations of reactive species such as free radicals, because of the high absorption coefficients of these species. By this method one can simultaneously measure the absolute concentrations of a large number of components, if the external light source used is a broadband continuum radiator. The absorption spectroscopy experiment has been described in detail elsewhere.

Therefore, here, we present only the basics of the method.

Briefly, the principle of absorption spectroscopy consists in the experimental determination of an integral absorption coefficient \( \int_0^\infty k_{i j} d\nu \). For homogeneous media the following relation can be derived:

\[
\int_0^\infty k_{i j} d\nu = \frac{\lambda^2_0}{8\pi n} \frac{g_k}{g_i} A_{ki} N_i \left( 1 - \frac{g_i}{g_k} \frac{N_i}{N_k} \right),
\]

where \( k_{i j} \) is the spectral absorption coefficient, \( N_i \) and \( N_k \) are the population densities of the particles in lower and upper quantum levels of the radiative transition, \( g_i \) and \( g_k \) are the statistical weights, \( \lambda_0 \) is the wavelength, \( A_{ii} \) is the transition probability (Einstein coefficient).

#### B. Optical system

In Fig. 1 the optical setup for performing the measurements is shown. As a light source a cascaded arc specially designed for the purpose of emitting high intensity radiation is employed. The arc almost has the same construction as the cascaded arc used as the plasma source. The intensity of the continuum radiation is very high, only a factor ~10 lower, than according to Planck. Although some lines in the spectrum can be distinguished (due to the argon gas used in the light source), these lines are strongly Stark broadened and one can consider the arc as a continuum source even in these lines.

During the experiments with the lenses L1 and L2 a parallel light beam is created, and passed on by a beam splitter B. Rotating the chopper C makes it possible to image a selected signal on the detection system. By using the mirror M1 a reference measurement of a external light source signal
I, can be obtained. The mirrors M3, M4 with the lens L3 can be translated, which enables axial and lateral scanning. The beam is focused on the entrance slit of the monochromator by the optical system, consisting of the lenses L4 and L5. In the current experiments the diameter of detection volume on the axis of the vessel was ~1 cm.

The optical system was calibrated positioning a tungsten ribbon lamp in the vessel, and recording the spectrum at a known true temperature of the ribbon. The detection section consists of a 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.

IV. 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 sec/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 in the vacuum vessel. In the latter situation a pure argon plasma 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=3) have been determined. The measured atomic hydrogen excited states densities are in the range of (1–3)×10^13 m^{-3} for the H*(n=3), (0.7–2)×10^13 m^{-3} for the H*(n=4), and (0.5–1.5)×10^13 m^{-3} for the H*(n=5) (see also Ref. 22). These measurements were used in order to make a direct comparison possible with a similar experiment in which the plasma parameters n_e, T_e, and n_0 have been measured by Thomson–Rayleigh scattering, quoted in Refs. 22 and 25. 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 ~30%.

Absorption measurements have been performed simultaneously on several argon spectral lines, and on the hydrogen H_{α} line. For typical parameters of the expanding cascaded arc plasma at a distance z=20 mm from the exit of the cascaded arc (see Table I), the ratio between Lorentzian and Gaussian components for the Ar spectral line is less than 0.01. Therefore for the calculation of the absorption coefficient k_{p} we assume a pure Gaussian line profile

\[ k_{p} = k_{0} \cdot \exp \left[ - \frac{2 \sqrt{\ln 2} \cdot (\nu - \nu_{0})^2}{\Delta \nu_{d}} \right] , \]  

where k_{0} is the absorption coefficient in the center of the line, \Delta \nu_{d} is the width (FWHM) of the absorption line, which for pure Doppler spectral line broadening depends only on the heavy particle temperature and on the atomic/molecular weight of the absorbing particles.\textsuperscript{7}

The measured values of the total absorption A_{g} can directly be related to an integral absorption coefficient \int_{0}^{\infty} k_{p} dv in accordance with Eqs. (1) and (2). The absorption length l in our case is calculated by means of a tomographic Abel inversion procedure.\textsuperscript{31,36}

For the examination of the absorption method three spectral lines with the same lower level of radiative transitions of argon – 3p^2 4s(3P, 1), but with different (up to 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 compared with the earlier obtained values and it was shown that average values can be chosen for the final fit.\textsuperscript{31,34} 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. 34).

In all experimental cases the absorption of the hydrogen H_{α} line was weak k_{p} \ll 1, so the expression for the total absorption A_{g}, Eq. (2) can be simplified significantly

\[ A_{g} = \Delta v_{c} \frac{I_{g0} - I_{g1}}{I_{0}} = \int_{0}^{\infty} \left[ 1 - \exp(-k_{p}) \right] dv = \int_{0}^{\infty} k_{p} dv = \frac{\lambda_{g}^{2} \cdot g_{k}}{8 \pi g_{i}} A_{g} N_{i}, \]

where we used already the condition \frac{g_{i} N_{i} k_{p}}{g_{k}} \ll 1. From Eq. (4) it is clear that for the determination of a product N_{g}A_{g} it is sufficient to measure only the value of the relative absorption (I_{g0} - I_{g1})/I_{0}, and the selected spectral band width of the light source \Delta v_{c} determined by monochromator. In this case for the interpretation of the experimental data it is not necessary to know the H_{α} spectral line shape (i.e., the mechanisms of the line broadening) for the determination of the atomic hydrogen H*(n=2) population density. The absorption length l in this case follows from an extrapolation fit of the measured lateral profiles using Gaussian density profiles of the plasma beam.

In Fig. 2 the radial dependencies of the hydrogen H*(n=2) density obtained for the different axial positions in the expansion and the various percentages of the hydrogen in the initial gas mixture are shown. Figure 2 clearly illustrates the sensitivity of the method. With an effective length of only ~2–6 cm, the detected local atomic (n=2) hydrogen density is about 10^{14} m^{-3}, with an accuracy of 20%. The reached detection limit may be improved significantly by additional application of a multiple-reflection system.\textsuperscript{37} From this figure it appears that downstream the radial profile of H*(n=2) becomes broader, as a consequence of the decrease of n_e in the expanding plasma.

In Fig. 3 the dependencies of the hydrogen H*(n=2) axial density are given as a function of various hydrogen percentages in the gas flow. It appears that the density always drops monotonically between the points z=20 and 40 mm.
At the same time, between the points \( z = 40 \) and 70 mm the density either rises, or drops, depending on the specific percentage of hydrogen in the total gas flow.

Figure 4 illustrates the radial distribution of the argon \( 3\rho^5s \) \( (3\rho_0, 3\rho_1, 3\rho_2, \) and \( 1\rho_1) \) densities obtained for the different axial positions in the expansion for the case of 2\% hydrogen in the initial gas flow. The procedure to correct for the nonlinear relation between the measured absorption values and the argon population densities has been described in detail previously.\(^{34}\) From Fig. 4 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 \( \text{Ar}^*(4s) \) downstream becomes broader.

From Figs. 2–4 it can be seen that for the expanding plasma in hydrogen-argon gas mixtures the absorption spectroscopy allows us to determine with good accuracy the absolute densities of the first excited levels of atomic hydrogen and argon. For the \( \text{H}_2 \) admixtures in \( \text{Ar} \) ranging from from 0.7\% to 10\% the radial profiles of both \( \text{H}^*(n=2) \) and \( \text{Ar}^*(4s) \) have been measured for axial positions from 20 to 70 mm from the exit of the cascaded arc. The measured \( \text{H}^*(n=2) \) densities are in the \( 10^{14} - 10^{16} \) m\(^{-3}\) range, and the \( \text{Ar}^*(4s) \) densities are in the range of \( 10^{15} - 10^{18} \) m\(^{-3}\).
FIG. 3. The axial dependencies of the hydrogen $H^+(n=2)$ absolute density on the axis of the plasma as function of various molecular hydrogen percentage in the gas flow: (1) 0.7% $H_2$, (2) 1.4% $H_2$, (3) 2% $H_2$, (4) 3% $H_2$, (5) 5% $H_2$, (6) 10% $H_2$.

V. PARTICLE KINETICS IN THE SUB- AND SUPERSONIC REGIONS OF THE EXPANDING PLASMA

A. General kinetic scheme

We will show that the dominant electron-ion-excited state processes in our expanding cascaded arc plasma with small admixtures of $H_2$ in Ar are the formation of $ArH^+$ and $H_2^+$ followed by dissociative recombination of electrons with $ArH^+$ and $H_2^+$ and resulting in the production of $Ar^+(4s)$ and $H^*(n=2)$. The loss of $Ar^+(4s)$ and $H^*(n=2)$ atoms is governed by the escape of the resonance radiation to the walls.

The measured population density of $H^*(n=2)$ state can be compared with a model calculation which takes into account the particle transport as well as the elementary collisional and radiative kinetic processes in the plasma. In the expansion the situation is quasistationary and one can use the time-independent mass balance equation

$$\nabla \cdot (nw) = \left( \frac{\partial n}{\partial t} \right)_s,$$

with $n$ and $w$ the density and velocity of the species concerned. The source term on the right-hand side is built up by several production and destruction processes, depending on the internal plasma parameters in the expansion. As an example in Table I the atomic, molecular, ionic, and electronic parameters are presented for the experimental condition of 1.4% of hydrogen in the total gas flow in the expanding cascaded arc plasmas.

The reactions of direct electronic excitation, dissociation, and ionization of the atoms and molecules have not been taken into account since in the first approximation the plasma under investigation can be considered as a recombinating system with electron and heavy particle translational temperatures in the range of $1500-4000$ K.22,25,26

FIG. 4. The radial dependencies of the argon $3p^44s$ ($3P_0$, $3P_1$, $3P_2$, and $1P_1$) absolute densities obtained for the different axial positions in the expansion of argon-hydrogen arc for the case of 2% of molecular hydrogen in the gas flow: (C) for axial position $z=20$ mm, (D) for $z=40$ mm, (E) for $z=70$ mm. 

The kinetic analysis of various processes in the expanding plasma shows, that the spatial gradients are small and the entire left-hand side of Eq. (5) can be neglected. In the subsonic part and the end of the supersonic part in the shock region this is true by a wide margin. At axial position \( z = 20 \) mm it still holds by an order of magnitude. A list of the main collisional and radiative processes determining the population density of the \( \text{H}^*(n = 2) \) state in the subsonic expansion is given in Table II. Using the data as an example for the case of an admixture of 1.4% of hydrogen in the total gas flow, the relevance of each process is illustrated. The present discussion is limited to such low \( \text{H}_2 \) concentrations that the charge transfer mechanism of recombination\(^{38} \) (where only the hydrogen positive ions play a role in the recombination kinetics) becomes unimportant.

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 \( \text{H}_2 \) 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 \( \text{H}^*(n = 2) \) state in the plasmas

\[
\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}, \tag{6}
\]

and

\[
\text{ArH}^+ + e \rightarrow \text{Ar} + \text{H}^*(n = 2), \tag{7}
\]

\[
\text{Ar}^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{Ar}, \tag{8}
\]

and

\[
\text{H}_2^+ + e \rightarrow \text{H} + \text{H}^*(n = 2). \tag{9}
\]

The low energy behavior for the charge transfer reaction \( \text{Ar}^+ + \text{H}_2 \) is dominated by the proton transfer reaction leading to the formation of \( \text{ArH}^+ \) (6).\(^{38-40} \) The recommended temperature dependence of the cross section \( \sigma_{e} \) and rate coefficient \( k_{3} \) based on a power law fit of the rate constant \( k_{2} \) for temperatures \( T \) from 20 to 5000 K yields that \( k_{2} = 1.45 \times 10^{-15} (T)^{0.14} \text{m}^3 \text{s}^{-1} \) to within 10%.

\[
\text{H}^* + e + e \rightarrow \text{H}^*(n = 2) + e, \tag{10}
\]

\[
\text{Ar}^+ + e + e \rightarrow \text{Ar}^* + e. \tag{11}
\]

In Ref. 47 the rate constant for three particle recombination Eq. (10) for hydrogenlike atoms has been derived using the shock front the electron temperature and heavy particle temperature, as has been shown in the recent publication of Meulenbroeck et al.,\(^{46} \) become equal due to the electron-heavy particle interaction.

The cross section for the formation of \( \text{H}_2^+ \) by charge transfer according to Eq. (8) has been taken from the measurement for slow ion formation.\(^{42-44} \) In the temperature range from 1000 to 10 000 K the cross section for the reaction (8) is almost constant with \( \sigma_{e} = 10^{-19} \text{m}^2 \) (see also Ref. 45). This yields rate coefficient \( k_4 = 10^{-15} \text{m}^3 \text{s}^{-1} \).

The reactions of dissociative recombination of molecular ions (7) and (9) are usually very effective and often are the main reason for charged particles recombination in plasmas.\(^{46} \) The rate constants for the reactions of dissociative recombination of vibrationally nonexcited molecular ions of the halogens (including hydrogen) (7) and (9) are typically \( k_{3,5,n} = 10^{-14} - 10^{-15} \text{m}^3 \text{s}^{-1} \) in the temperature range from 300 to 5000 K. For vibrationally excited molecular ions the rate constants may be approximately an order of magnitude larger.\(^{46} \) Reactions (7) and (9) lead to the population of mainly the \( \text{H}^*(n = 2) \) 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 nonexcited molecular ions \( \text{ArH}^+ \) and \( \text{H}_2^+ \) is approximately \( -0.7 \text{ eV} \). The dissociative recombination reactions of ground state molecular ions, created by charge exchange reactions, leading to the population of higher lying hydrogen excited states \( \text{H}^*(n \geq 3) \) are all endothermic: the deficit of energy in those cases is approximately \( \approx 1.2 \text{ eV} \) for \( \text{H}^*(n = 3) \), \( \approx 1.9 \text{ eV} \) for \( \text{H}^*(n = 4) \), etc. Therefore, for the effective population of atomic excited states \( \text{H}^*(n \geq 3) \) by the reactions of dissociative recombination, the molecular ions \( \text{ArH}^+ \) and \( \text{H}_2^+ \) must be vibrationally excited (vibrational quantum \( \hbar \omega \), for the hydrogen molecular ion is approximately \( 0.54 \text{ eV} \)).

Among the atomic processes first of all the reactions of electron-ion three particle recombination must be considered

\[
\text{H}^* + e + e \rightarrow \text{H}^*(n = 2) + e, \tag{10}
\]

\[
\text{Ar}^+ + e + e \rightarrow \text{Ar}^* + e. \tag{11}
\]
a diffusion approximation for the excited states. In Ref. 48 the recombination coefficient has been determined experimentally for a helium plasma. Both results give for electron temperatures below 3000 K the value \( k_2 = 1.1 \times 10^{-20} \left( T_e \right)^{-9/2} \text{ m}^6 \text{s}^{-1} \). Recent measurements of the three particle recombination rate constant Eq. (11) in argon\(^{26}\) were in agreement with the behavior commonly found \( k_1 \) in the literature, showing the \( T_e^{-9/2} \) dependence, but the absolute value for the rate constant was approximately three times lower \( - k_1 \approx 3.3 \times 10^{-21} \left( T_e \right)^{-9/2} \text{ m}^6 \text{s}^{-1} \). According to Ref. 47 the recombination coefficients for different elements are all approximately equal for low electron temperatures \( (T_e \approx 2000 \text{ K}) \). The reason is that the recombination for low temperatures is mainly to highly excited atomic states, for which the energy spectrum for all elements is hydrogenlike. For the calculation of the rates of the three particle recombination reactions Eqs. (10) and (11) we use the data from Ref. 26. Unfortunately no information on the rate constants for the particular excitation of \( \text{H}^*(n = 2) \) state in the three-body electron-ion recombination is available in the literature. For calculation of the excitation rates of \( \text{H}^*(n = 2) \) via the reaction Eq. (10) we use the total three-body recombination rate constant. This approximation can be considered as an upper limit estimation for the rate constant \( k_1 \) too.

For the kinetic of atomic hydrogen quantum state \( \text{H}^*(n = 2) \) the radiative processes must be considered as well: cascade radiative transitions between the excited states

\[
\lambda_1 \quad \text{H}^*(n = 3) \rightarrow \text{H}^*(n = 2) + h \nu_{\text{Balmer}},
\]

and radiative transition to the ground state

\[
\lambda_2 \quad \text{H}^*(n = 2) \rightarrow \text{H}(n = 1) + h \nu_{\text{Lyman-\alpha}}.
\]

Numerical data on the radiative transition probabilities for the processes Eqs. (12) and (13) can be found in the well-known tables of Wiese et al.\(^{49}\)

The quantum state \( \text{H}^*(n = 2) \) consist of two sublevels—\( 2s \) and \( 2p \). Unperturbed hydrogen atoms in the \( 2s \) state are metastable and have a radiative lifetime to the ground state \( 1 \text{ s} \) of about 0.1 s. The \( 2p \) state, which is nearly degenerate with the \( 2s \) state (within 0.5 cm\(^{-1} \)), however, are connected to the ground state by ordinary dipole selection rules and have a radiative lifetime of \( \approx 2 \times 10^{-9} \text{ s} \). Therefore, unlike most of other atomic and molecular metastable species, hydrogen \( 2s \) metastable atoms are very sensitive to external perturbations which induce \( 2s \rightarrow 2p \) transitions quite efficiently. In the present experimental conditions metastable hydrogen atoms \( \text{H}^*(2s) \) are converted to the \( \text{H}^*(2p) \) atoms by collisions with electrons, argon, and hydrogen. The mean-free-path for collisional quenching of \( \text{H}^*(2s) \) estimated from the measured quenching cross sections by molecular hydrogen\(^{26}\) and argon\(^{51}\) will be less than 1 mm. Hence, we can assume that all the hydrogen atoms formed in the \( 2s \) metastable state are locally, rapidly equilibrated with the \( 2p \) resonance state. Note, that the same conclusion about a strong collisional coupling between the two metastable and two resonance sublevels of argon \( \text{Ar}^*(3p^44s) \) state have been derived from a direct measurement of the densities of all four sublevels of \( \text{Ar}^*(3p^44s) \) state in the expanding pure argon plasmas, which proved to be thermally populated.\(^{34}\)

B. Subsonic expansion (\( z > 40 \text{ mm} \))

From Table II one can see that using plasma parameters that have been measured in the subsonic expansion region, the elementary processes controlling the \( \text{H}^*(n = 2) \) population density can be shown to be primarily the charge transfer reaction, leading to the formation of \( \text{ArH}^+ \) (6) with subsequent dissociative recombination Eq. (7) (production), and radiative transition decay through the partly reabsorbed Lyman-\( \alpha \) spectral line (loss process). Therefore, assuming that the charge transfer reaction is rate limiting, which is true for \( n_e > 10^{-2} \cdot n_{\text{H}_2} \), Eq. (5) now becomes

\[
n_{\text{H}_2} n_e k_2 - n_{\text{H}_2} n_{\text{H}^*(n = 2)} \lambda_2 \Lambda = 0,
\]

where \( \Lambda \) is the escape factor for resonance Lyman-\( \alpha \) radiation.

The escape factor \( \Lambda \) now appears to be the determining factor on the \( \text{H}^*(n = 2) \) population density. It is related to the optical depth \( kR \) of the absorbing medium. The relation between escape factor and optical depth has been calculated for Voigt emission profiles in Refs. 52 and 53 for the case of cylindrically symmetric plasmas. In this treatment it was assumed that absorption and emission profiles of the spectral line can be described by the same Voigt profile and that the radial dependencies of the densities of the lower and upper levels of the transition are weak. The result, taken from Refs. 52 and 53, is presented in Fig. 5, where the escape factor \( \Lambda \) is given as a function of the effective optical depth \( kR \), for different values of the parameter \( a = \sqrt{\ln 2 (\Delta \lambda_L / \Delta \lambda_D)} \) where \( \Delta \lambda_L \) and \( \Delta \lambda_D \) are the Lorentzian and Gaussian parts (FWHM) of the Voigt line profile, respectively.

The effective optical depth is defined as:

\[
kR = \frac{\ln 2}{4 \pi \sqrt{\pi}} \frac{\lambda_{21}^4}{c \Delta \lambda_{21}} \frac{g_2}{g_1} A_{21} n_{\text{H}^*(n = 1)} \mu R,
\]

where \( \lambda_{21} \) is the wavelength of the radiative transition, \( \Delta \lambda_{21} \) is the half width (FWHM) of the emission profile, \( c \) is the...
velocity of light, $g_i$ are the statistical weights of corresponding levels, $A_{21}$ is the radiative transition probability, $n_i^{(n=1)}$ is the population density of the lower state of the transition, $\mu$ is a geometrical factor, and $R$ is the radius of the plasma beam. The constant $\mu$ varies between $1 \leq \mu \leq 1.4$. For the cylindrical geometry of the plasma beam $\mu=1.2^{52,53}$.

From Fig. 5 it is clear that to find a correlation between the escape factor and the effective optical depth one has to know the spectral line shapes, i.e., the mechanism of the spectral line broadening. For the highly ionized, low pressure plasma under investigation only two mechanisms for the spectral lines broadening may be important: Doppler and Stark effects. For charged particles densities of the order of $10^{19}$ m$^{-3}$ (which is typical for our experimental situation) an extrapolation both of the experimental data$^{54-57}$ and theoretical calculations$^{54,58}$ shows, that the Stark width (FWHM) of the Lyman-$\alpha$ line must be in order of $\approx 10^{-4}$ nm, which is at least 40 times smaller than the Doppler width (FWHM) of the same line at typical temperatures in the plasma of 2000–4000 K.$^{25}$ Hence for small optical depths, $kR \ll 3$, for the resonance Lyman-$\alpha$ transition of atomic hydrogen one can use a purely Gaussian approximation ($a=0$) to determine the relation between $\Lambda$ and $kR$.

In the framework of validity of the kinetic equation Eq. (14) 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.

C. 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$^{29}$), can penetrate into the supersonic region of the expanding plasma. If so, then the characteristics of the various chemical reactions presented in Table II are valid for the position $z=20$ mm in the supersonic expansion as well. Since such a suggestion is not obvious, let us consider the opposite case, when only the particles from the cascaded arc itself are present in the supersonic expansion.

In that case, the supersonically expanding plasma must contain only electrons, argon atoms and ions, hydrogen atoms and protons. As is shown in Ref. 29 it must be a fully dissociated plasma flow, since the temperature in the arc is high $\sim 1$ eV$^{29}$ and the probability for the recombination of atomic hydrogen in the expansion is very small. The only important channel for production of excited hydrogen atoms $H^*(n=2)$ in that case is the process of three-body recombination of the protons and electrons [Eq. (10)]. Thus for the case under consideration without molecular components in the supersonically expanding plasma the most important elementary processes for the kinetic of the $H^*(n=2)$ state are three-body electron-ion recombination (10), and partly reabsorbed radiative decay of the Lyman-$\alpha$ line (13)

$$n_{H^*} + n_e^2 \kappa_1 - n_{H^*(n=2)} A_2 \Lambda = 0.$$  

In order to balance the production and destruction rates for the hydrogen excited atoms $H^*(n=2)$ one has to suppose that for the supersonic expansion the plasma parameters are different from the ones in the subsonic expansion. For balancing the kinetic equation for the production and destruction of $H^*(n=2)$ two possibilities might be considered in principle, viz.: (a) production term Eq. (10), i.e., the rate constant of three-body recombination, is larger, and/or (b) destruction term Eq. (13), i.e., the escape factor for Lyman-$\alpha$ radiation, is smaller. To equalize the kinetic equation by increasing the production term one has to suggest that the electron temperature on the axis of the supersonic expansion is only $\approx 700$ K. Whereas to decrease the destruction term through the lowering of the escape factor one has to assume an extremely small translational temperature of the hydrogen excited atoms—only some degrees Kelvin.

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. (6)-(9). Inspite of the high temperatures in the arc$^{23}$ 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, then some fraction of the hydrogen molecules from there has a chance to enter to the supersonic expansion as well. Then, of course, a speculative question about the amount of $H_2$ in the supersonic expansion arises.

In an attempt to solve the problem, a special measurement 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% of molecular hydrogen in the vessel are presented in Fig. 6 for various axial positions in the expansion: $z=20$, 30, 40, and 70 mm. 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 previous case, more 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 $r=10-12$ mm, i.e., outside the fast supersonic flow, where $H_2$ molecules exist. 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 already exist in the very beginning of the expansion (see Fig. 2). These two facts clearly indicate, that despite 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.

At the same time, the results of Fig. 6 indicate that further downstream, but still in the supersonic expansion (position $z=30$ mm), some of hydrogen molecules already penetrate into the plasma beam, since the density of excited hydrogen atoms $H^+(n=2)$ significantly rises near the axis of the expansion, and even has maximum at position $r=0$.

One of the possible explanations of this phenomenon consists in the following. Hydrogen molecules in the vessel at kinetic temperatures of about 2000 K$^{30,31}$ have a thermal velocity of $\sim 4000$ m/s. If we assume that $H_2$ could penetrate to the supersonic expansion only if their velocity exceeds the velocity of the supersonically expanding argon plasma, then the conclusion arises, that: (1) in the beginning of expansion the velocity of the argon plasma must be about 4000 m/s, and (2) at the point $z=20$ mm the plasma velocity must be higher than 4000 m/s, and at the point $z=30$ mm—lower than 4000 m/s. This result is in good quantitative agreement with the experimental data for the axial profiles of the argon plasma velocities measured in the supersonic expansion by the Doppler shift of the argon spectral lines,$^{24}$ and also in good qualitative agreement with the calculated velocities of the argon atoms in supersonic part of the plasma.$^{24,27,59}$

It has been shown (see Sec. V B) that for the subsonic expansion the density of hydrogen excited atoms $H^+(n=2)$ might serve as an indicator of the presence of argon ions and hydrogen molecules at certain positions in expanding plasmas. Therefore, after comparison of the results presented in Figs. 3 and 6 for the axial positions $z=40$ and 70 mm, one can conclude, that near the axis the densities of $Ar^+$ and $H_2$ remains approximately the same in both situations. However, in the case when hydrogen is introduced into the vessel, the density of $H^+(n=2)$ atoms is slightly larger at the periphery of the expansion (this effect is more clear for the case of $z=70$ mm). This means, that at the periphery of the expansion the $H_2$ or/and $Ar^+$ densities must be larger in case of a pure argon expanding arc with hydrogen introduced into the vessel.

In principle, in a plasma with a high density of hydrogen atoms the resonance dissociative excitation transfer reaction might be effective

$$H^+(n=2) + H_2(X^1\Sigma_g^+, v=0) \rightarrow H(n=1) + H_2(b^3\Sigma_u^-)$$

$$\rightarrow H + H + H.$$  \(17\)

We might serve as an indicator of the presence of argon ions and hydrogen molecules in the arc.

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This reaction becomes increasingly important for $H$ atom production$^{60}$ namely in the plasma with high density of hydrogen atoms, since then the optical depth for the Lyman-$\alpha$ radiation becomes larger [Eq. (15)], and hence more excited hydrogen atoms $H^+(n=2)$ have a chance to survive on the level.

D. Dissociation degree in the plasmas

From kinetic equations [Eqs. (14) and (16)] and from the expression for the effective optical depth [Eq. (15)] 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.

For example, in the subsonic expansion region the escape factor $\Lambda$ for the emission of Lyman-$\alpha$ radiation can be derived from the values of the neutral particles density $n_H$, the electron density $n_e$, and the measured population density of the atomic hydrogen first excited level $H^+(n=2)$. For the supersonic expansion without molecular components in the flow one has to know the proton and electron densities $n_{H^+}$ and $n_e$, and the density of $H^+(n=2)$ state. The rate constants $k_1$, $k_2$, and the transition probability $A_2$, which are needed for the determination of $\Lambda$ from Eqs. (14) and (16) are known from the literature.$^{35-41,47-49}$ Finally, from known $\Lambda$ one can determine the effective optical depths of the Lyman-$\alpha$ radiation in the plasmas by using the curve $a=0$ in Fig. 5.

Finally, to calculate the absolute population density of the state $H(n=1)$ from (15) one has to know the radius of the plasma beam $R$. As an effective radius of the plasma one could choose either the width of the radial distribution of $H^+(n=2)$ [known from the absorption spectroscopy measurements (see Fig. 2)], or the width of the radial distribution of the electron density $n_e$ (known from the Thomson scattering measurements$^{77,78}$) since the corresponding widths are approximately equal to each other (see also Ref. 24). That is important, since the atomic population density is inversely proportional [see Eq. (15)] to the effective radius $R$, which is monotonically rising downstream.$^{24,25}$ Experimentally determined values of the radius of the plasma beam for various conditions are presented in Table I.

Absolute population densities of atomic hydrogen as a function of plasma parameters in the subsonic expansion, which have been calculated using Eqs. (14), (15), and Fig. 5 are presented in Table III.

From the atomic and molecular hydrogen densities one can easily find the dissociation degree of the plasma-$\beta$, which is determined as follows:

$$\beta = \frac{n_{H^+}}{n_{H^+} + n_e}.$$  \(18\)

| TABLE III. Absolute density of atomic hydrogen $n_{H^+}$ and hydrogen dissociation degree $\beta$ in the subsonic expansion at different axial positions in the expansion as a function of the relative concentration of a hydrogen injected in the arc. |
|---|---|---|---|---|---|---|
| $x$ (mm) | 0.7% H$_2$ | 1.4% H$_2$ | 2% H$_2$ | 3% H$_2$ |
| 40 | 0.90 | 0.55 | 0.31 | 0.20 | 0.15 | 0.02 |
| 70 | 0.50 | 0.22 | 0.10 | 0.07 | 0.03 | 0.02 |

The dissociation degree is defined as

$$\beta = \frac{n_{H^+}}{n_{H^+} + n_e}.$$  \(18\)
\[ \beta = \frac{n_{31}}{n_{H^+} + 2 \cdot n_{H_2}}. \]  

Some uncertainty exists, of course, concerning the absolute density of molecular hydrogen in the expansion, because of the recirculation of the gaseous components in the vessel and the different acoustic velocities of argon and hydrogen. To calculate the dissociation degree from Eq. (18) we use as the absolute density of hydrogen molecules their density in the initial mixture of the gases.

From Table III 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 freely recirculating in the vacuum vessel, into the expanding plasma flow.

An accuracy of the discussed procedure as it can be seen from Eqs. (14) and (15), is limited by the accuracy in the determination of the escape factor: \( \Lambda = \frac{n_{H^+} n_{k_2}}{n_{H^+} n_{A_2}} \), and of the radius of plasma beam \( R \). Therefore both accurate experimental data on \( n_{H^+}, n_z, \) and \( R \), and detailed information on the constants \( k_2 \) and \( A_2 \), are required. Taking into account the experimental errors and the uncertainties in the kinetic coefficients, we estimate the relative error in the atomic hydrogen ground state density determination from Eqs. (14) and (15) within a factor of 2.

VI. 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 has been shown that the combination of a second cascaded arc as an extremely bright broadband light source with the high resolution spectrometer provide good accuracy. For an effective absorption length of \( \sim 2-6 \) cm, the detected local hydrogen population density was about \( 10^{14} \) m\(^{-3} \), within an accuracy of 20%.

It is demonstrated that for the expanding hydrogen-argon plasma 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. The measured \( H^*(n = 2) \) densities are in the range \( 10^{14} - 10^{16} \) m\(^{-3} \), and \( Ar^*(4s) \) densities are in the range \( 10^{15} - 10^{18} \) m\(^{-3} \).

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 \( \Pi^*(n = 2) \) 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 already exists 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 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 \( (\sim 6 \times 10^{18} \) m\(^{-3} \)), and dissociation degree in the plasma \( (\sim 22\%) \), 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 the 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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