

Diagnostics of the magnetized low-pressure hydrogen plasma jet : molecular regime

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Diagnosics of the magnetized low-pressure hydrogen plasma jet: Molecular regime

Zhou Qing, D. K. Otorbaev,^{a)} G. J. H. Brussaard, M. C. M. van de Sanden,^{b)} and D. C. Schram

Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Optical emission and absorption spectroscopy and double Langmuir probe diagnostics have been applied to measure the plasma parameters of an expanding magnetized hydrogen plasma jet. The rotational temperature of the excited state $H_2(d^2\Pi_u)$ has been determined by analyzing the intensity distribution of the spectral lines of the Fulcher- α system of H_2 . The gas temperature in the plasma, which is twice the value of the rotational temperature is equal to ≈ 520 K. Several clear indications of presence of the “hot” electrons have been observed in the plasma: (1) Langmuir probe measurements ($T_e \approx 1.4$ eV), (2) appearance of the Fulcher- α system of H_2 (excitation potential $\Delta E = 13.87$ eV), (3) low rotational temperature ($T_{rot}^* \approx 260$ K) of the excited $H_2(d^3\Pi_u)$ molecules, (4) local excitation in the plasma of Ar I ($\Delta E = 15.45$ eV), and Ar II ($\Delta E = 19.68$ eV) spectral lines, (5) local excitation in the plasma of He I ($\Delta E = 23.07$ eV and $\Delta E = 24.04$ eV) spectral lines. Optical actinometry has been applied to measure the absolute density of hydrogen atoms and hydrogen dissociation degree in the plasma. The measured absolute density of hydrogen atoms are in the $(1-1.4) \times 10^{20} \text{ m}^{-3}$ range, and the corresponding dissociation degree of the hydrogen plasma is in the range of 8%–13%. © 1996 American Institute of Physics. [S0021-8979(96)01914-7]

I. INTRODUCTION

Hydrogen plasma have been widely used in different research and application fields and have become a promising research subject. In microelectronics hydrogen containing plasmas have been utilized in the thin film deposition,^{1,2} surface cleaning and passivation techniques.^{3,4} It has been established that high quality diamond films are grown in a hydrogen diluted plasma, and that the atomic hydrogen present in these plasmas is essential for the quality of the films.⁵ Apart from this, atomic hydrogen sources have been utilized in surface treatment of iron archaeological artefacts to protect the artefacts after the excavation against post-corrosion without inducing any surface damage.^{3,6} The research of hydrogen plasmas has also a direct bearing to controlled thermonuclear fusion project. Heating of the fusion plasma by injection of neutral beams produced by neutralization of negative ions from a negative deuterium (hydrogen) ion source has been suggested as a key technology to reach the plasma conditions needed for energy production by thermonuclear fusion.⁷

Apart from the mentioned applications the study of hydrogen plasmas is also of fundamental interest. Since the hydrogen molecule is the simplest diatomic molecule, the experimental results of hydrogen plasmas are often used to test models of molecular plasmas in modern astrophysics and plasma physics. Furthermore, the experimental results can provide a clear kinetic scheme for the hydrogen plasma itself, i.e., knowledge on the mechanisms of ionization and recombination, excitation and de-excitation, formation and quenching processes.

Hydrogen plasmas can be created in different ways, e.g., in dc glow discharges, rf plasmas, microwave plasmas, in a hollow cathode arc etc.⁸⁻¹¹ To obtain a high enthalpy flow, it can be also created at higher pressures, e.g., by a so-called cascaded arc,¹² which is a kind of wall stabilized high electron density plasma, and which is the subject of this article. Previous research shows that the cascaded arc is an ideal design to create a stable arc plasma with high electron density as well as an expanding plasma for both plasma studies and applied research.^{13,14} It has been shown that the expanding cascaded arc plasmas have potential prospect in different application fields; e.g., using a cascaded arc as a light source for spectroscopy,¹⁵ as a particle source for surface modification,¹³ silicon thin film deposition,¹⁶ carbon thin film deposition¹⁷ and passivation protection technique for archaeological artefacts.⁶ Mostly noble gases are used to feed the arc plasma, but exceptionally molecular gases like H_2 and SF_6 are added.^{19,20}

The aim of this research is to develop a hydrogen radical source for the rising interest in hydrogen plasma applications. The plasma is first created in a cascaded arc. The treatment plasma is obtained by the expansion of the arc plasma into a low background pressure vessel. The work of de Graaf²¹ has been devoted to develop the hydrogen arc source to obtain an expanding hydrogen plasma beam. Special attention has been given to the dynamics and kinetics of non-magnetized expanding hydrogen plasmas at moderate pressures (≈ 100 Pa). It was demonstrated that in hydrogen at these “high” pressure in the expansion an anomalously high recombination occurs, which leads to a very effective destruction of charges.²¹ In this article the lower pressure range (≈ 5 Pa) is explored in order to avoid or reduce this recombination. At these lower pressures collisional confinement is not effective and magnetic confinement of electrons and ions

^{a)}Permanent address: Laboratory of Plasma Spectroscopy, Kyrgyz National Academy of Sciences, Chui prospect 265 A, Bishkek 720071, Kyrgyzstan.

^{b)}Corresponding author.

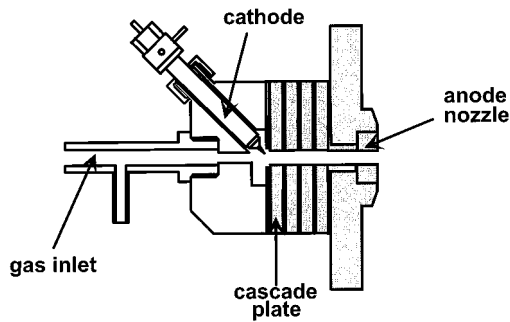


FIG. 1. Cascaded arc setup.

is needed to obtain a high electron density expanding plasma. Therefore this work focuses on magnetized expanding hydrogen plasmas at low pressure.

For the expanding plasma it has been shown¹⁸ that depending on operational conditions and magnetic field strength two specific regimes of the expanding hydrogen plasma can be obtained, which can be characterized by different emission characteristics. Based on the observed spectroscopic characteristics, we have named these two specific regimes the “atomic” regime and the “molecular” regime.

II. PLASMA SOURCE AND EXPANSION

A. Cascaded arc setup

The cascaded arc used in this work consists of three main parts, namely cathode section, cascade plates section and anode section as shown in Fig. 1. In this type of arc a plasma is generated in a cylindrical channel consisting of a number of plates. The arc discharge is stabilized by the water cooled channel walls. The power dissipation is relatively high, typically of the order of 5 kW, and the carrier gas (argon, nitrogen, hydrogen) is flowing at a rate typically between 5 and 100 standard $\text{cm}^3 \text{s}^{-1}$ (sccs).^{13,18} The plasma is initiated by the application of a high voltage pulse to the cathode ($V_{\text{pulse}} \approx 1 \text{ kV}$, $t_{\text{pulse}} \approx 1 \text{ s}$), and the arc plasma is sustained by drawing a high current (30–100 A) between the cathode tips and the anode at a lower voltage (80–150 V). The arc plasma is always started using pure argon since lower power is needed to generate an argon plasma. By this procedure the lifetime of the cascaded arc set up can be significantly extended. After the argon arc becomes stable, the hydrogen concentration in the flow is slowly increased from 0% until 100%, and a pure hydrogen arc plasma is obtained through a transition from an argon arc to a hydrogen arc. The power needed to generate and sustain an arc is determined by arc length, or the number of the cascade plates. The longer the arc, the more the input power is needed. In this experiment, a four plate arc is used.^{13,18}

B. Different regimes of an expanding plasma

The arc plasma is first generated in the cascaded arc (pressure at exit $\approx 50\text{--}100 \text{ mbar}$) and then expands into a low pressure vessel ($p \approx 5 \text{ Pa}$) (Fig. 2). As it was mentioned at moderate pressures in the vessel ($\approx 100 \text{ Pa}$) an expanding hydrogen plasma shows a strong recombination of hydrogen

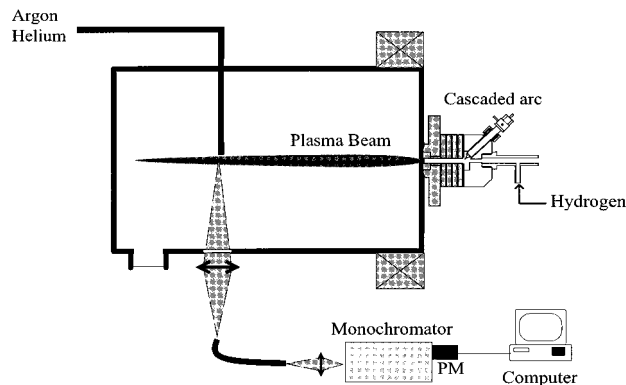


FIG. 2. Expanding cascaded arc plasma and the spectroscopy setup, with the geometry, used for the local excitation of the Ar and He spectral lines.

atomic ions.²¹ This strong recombination can not be explained by atomic processes. In pure argon plasmas, recombination has been shown to be a relatively weak process.¹⁴ The anomalous recombination of H_2 containing plasma is due to charge exchange of the atomic ion H^+ with H_2 molecules to form the molecular ion H_2^+ , which recombines fast by dissociative recombination. In order to avoid the recombination, the charge exchange between the primary H^+ ions and H_2 molecules has to be reduced which can be achieved by decreasing the hydrogen molecule density. However, then the mean free paths become larger and fast diffusion starts to reduce the charged particle density. Therefore a magnetic field is applied to confine the expanding plasma and by this to reduce outward diffusion and thus to increase the plasma density. To obtain a magnetized expanding plasma beam, a magnetic field coil is mounted in front of the cascaded arc.

As it was mentioned the two regimes can be distinguished depending on the applied magnetic field, which we define as the atomic regime and the molecular regime. The two regimes can also be reached by varying the pressure (in the range from 2 to 70 Pa while simultaneously varying the magnetic field from 40 to 7 mT) suggesting that confinement of the plasma plays an important role. The main feature of the regime at relatively large magnetic fields is that the plasma emits strong hydrogen Balmer lines. There is no observable molecular spectrum in the measured wavelength range. Therefore we name this regime the atomic regime.²² The main characteristic of the regime at relatively small magnetic field is that not only hydrogen Balmer lines, but also strong hydrogen molecular lines are observed. We name this regime the molecular regime. This regime is reached by decreasing the magnetic field (by lowering the coil current I_B from 250 A to 50 A) continuously from the atomic regime. In this article the results of diagnostics of the molecular regime of an expanding magnetized hydrogen plasma jet will be presented.

III. DIAGNOSTICS

A. Optical emission and absorption spectroscopy

Figure 2 shows the line intensity measuring system used in the experiment. The system consists of a computer con-

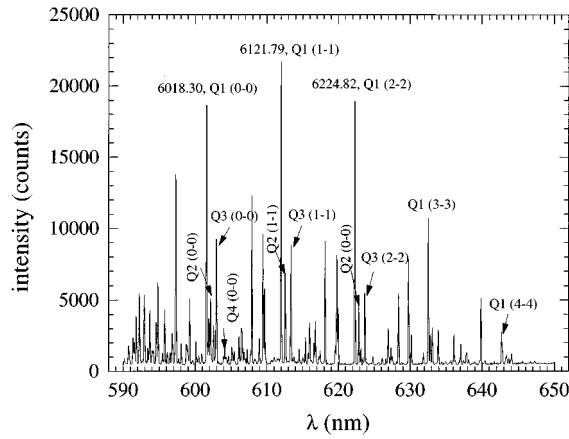


FIG. 3. Part of the Fulcher- α spectrum of molecular hydrogen in an expanding plasma. Experimental conditions $Q=8$ scc/s, $I_{\text{arc}}=50$ A, $I_B=50$ A, $P=5$ Pa, $z=18$ cm.

trolled two dimensional translation setup, a computer controlled monochromator, a photomultiplier, a quartz fiber, a signal discriminator, TTL converter and a digital counter. The signal is first focused on the detection surface of the quartz fiber by an optical system. Through the fiber, the light signal is transmitted to the monochromator. Behind the exit slit a photomultiplier is positioned. The resulting current pulses are converted into TTL pulses which are counted by the computer. 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. Figure 3 gives an example of a hydrogen spectrum which is typical for an expanding plasma in the molecular regime.

It can be shown that the plasma under study is optically transparent for the studied atomic and molecular spectral lines. It is known that the optical depth of a plasma kR is the value, which determines the transparency of the plasma. The optical depth can be expressed through the following formula:

$$\overline{kR} = \frac{\sqrt{\ln 2}}{4\pi\sqrt{\pi}} \cdot \frac{\lambda_{pq}^4}{c\Delta\lambda_{pq}} \cdot \frac{g_p}{g_q} \cdot A_{pq} n_q \cdot \mu R, \quad (1)$$

in which k is the absorption coefficient, n_q is the population density of the lower state of radiative transition, A_{pq} is the absolute radiative transition probability, λ_{pq} is the wavelength of the transition between state p and state q , R is the effective radius of the plasma beam, $\Delta\lambda_{pq}$ is the half width of the emission profile and μ a geometrical factor (for a cylindrical plasma beam, $\mu \approx 1.2$).²³

For the spectral lines under investigation, λ_{pq} is in the range of 360 nm to 660 nm, A_{pq} is in the range of 10^3 to 10^7 s⁻¹. In this experiment, the density of the state H($p=2$) is about 10^{16} m⁻³ as will be discussed later, the radius R is about 10^{-2} m and the linewidth $\Delta\lambda_{pq}$ is on the order of 10^{-11} m. The calculated optical depths for the hydrogen atomic and molecular lines for the present experimental conditions are in the range of $3 \cdot 10^{-3}$ to 10^{-6} , i.e., much less than 1. Therefore all discussed transitions between the hydrogen excited states can be considered as optically thin.

By employing the absorption spectroscopy technique one can measure the density of the lower state of the radiative transition. The method of optical absorption spectroscopy consists of the experimental determination of the integral absorption coefficient, which for a homogeneous medium is given by:²⁴

$$\int_0^\infty k_\nu d\nu = \frac{\lambda_0^2}{8\pi} \frac{g_p}{g_q} A_{pq} n_q \left(1 - \frac{g_q n_p}{g_p n_q} \right). \quad (2)$$

In this equation k_ν is the absorption coefficient, n_q and n_p are the densities of the relevant lower and upper excited states of the radiative transition, g_q and g_p are their statistical weights and λ_0 is the central line wavelength.

To determine the absorption coefficient k_ν for various radiative transitions the method of reabsorption with a mirror (which is identical to the method of two identical light sources²⁴) has been used. A concave mirror of reflectance r has been placed behind the plasma and the line intensity was measured with and without the mirror. The line absorption function A_L is defined as the ratio of the absorbed emission to the incident radiation:

$$A_L = \frac{\Delta I}{rI_1} = \frac{I_1 + rI_1 - I_2}{rI_1}, \quad (3)$$

where ΔI is the absorbed radiation and I_2 and I_1 are the radiation from the plasma with and without the mirror. In case of radiative transport of a single spectral line, the relation between A_L and the absorption coefficient k_ν is given by:²⁴

$$A_L = 2 - \frac{\int_0^\infty [1 - \exp(-2k_\nu l)] d\nu}{\int_0^\infty [1 - \exp(-k_\nu l)] d\nu}, \quad (4)$$

in which l is the observation length. When $A_L > 0$ absorption takes place and the density of the lower state of the transition can be derived from the determined A_L values. For low $k_\nu l$ values, i.e., $k_\nu l \ll 1$, A_L can be approximated by $k_\nu l / \sqrt{2}$.

To determine the line absorption function A_L from Eq. (3) the mirror reflection coefficient $r=r(\lambda)$ should be known. This coefficient $r(\lambda)$ can be measured using a spectral line for which the plasma is optically thin.²⁵ In that case $\Delta I=0$ in Eq. (3) and $r(\lambda)$ can be determined from the measured values of I_1 and I_2 . The measured $r(\lambda)$ is the effective reflection coefficient which includes the transmission losses of the vessel windows. The described method of self-absorption has been successfully checked for the first excited state of argon Ar($3p^5 4s$) by comparison of this indirect method with a direct absorption measurement.¹⁷ In the absorption spectroscopy experiment we assume l (or R) to be equal to the plasma beam diameter. Once l (or R in (1)) is known the absolute population densities can be determined using the experimental value for A_L and Eq. (1).

B. Langmuir probes

A Langmuir double probe setup was used to determine electron temperature (T_e) and density (n_e) (Fig. 4). A potential difference is applied between the two floating probes. The current passing through the probes is measured (cf. Ref. 26):

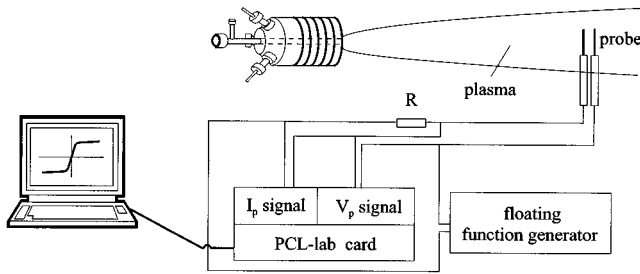


FIG. 4. Schematic overview of the Langmuir double probe setup.

$$\frac{I_p - I_i^-}{I_i^+ - I_p} = \frac{S_{p1}}{S_{p2}} \cdot \exp\left(\frac{eV_p}{kT_e}\right), \quad (5)$$

with I_p the current through the probes at applied potential difference V_p , I_i^{\pm} the saturation currents at large positive and negative potentials, and $S_{p1,p2}$ the surfaces of the probes. After plotting the left hand side of Eq. (5) on a semi-logarithmic scale, the slope at $V_p=0$ will yield the electron temperature. The electron (ion) density n_e can be determined from the saturation currents (cf. Ref. 27):

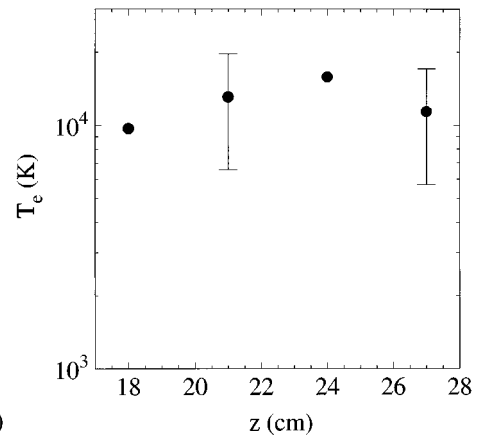
$$I_i = \kappa_i \cdot e \cdot n_e \cdot S_p \cdot \sqrt{\frac{kT_e}{m_i}}, \quad (6)$$

where κ_i (≈ 0.6) is a geometrical factor for the ion flow towards the probe,²⁸ and m_i the ion mass.

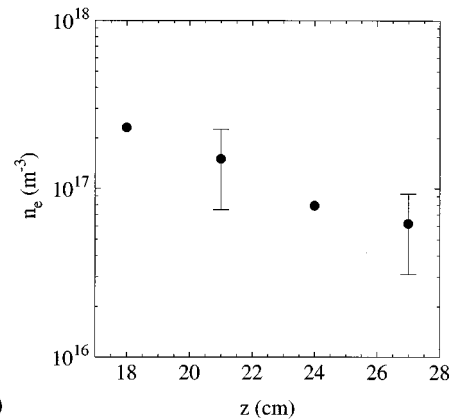
Although the electron current to the probe is significantly reduced by the presence of a magnetic field, it is still proportional to the Boltzmann factor $\exp(eV/kT_e)$.²⁹ Therefore Eq. (6) remains valid. In Fig. 5 the results of T_e and n_e in the molecular regime of an expanding hydrogen plasma, determined by the Langmuir double probe measurements are given. The assumption made in the calculations that H_2^+ is the dominant positive ion in the plasma. In principle it is necessary to verify some requirements of the use of the Langmuir probe theory in a magnetized plasma, since in the magnetic field the trajectories of the charged particles can be disturbed, so the collection efficiency of the charged particles by a probe will be influenced.²⁷ However, it can easily be shown, that for the particular experimental conditions the basic requirement of the probe theory is still valid, since the Larmor radii both for electrons and for ions are much larger than the Debye length.

IV. EMISSION OF FULCHER- α BAND OF H_2 AND GAS TEMPERATURE

Analysis of the relative intensity distribution of the rotational spectral lines of electronically-excited molecules are widely used as a method of determination of the gas temperature of low-temperature plasmas.⁸ The parameter to be measured is the rotational excitation temperature T_{rot}^* , which is associated with the molecular distribution over the rotational levels of the excited electronic-vibronic (vibronic) states. The rotational distributions of the electronically-excited molecules were usually similar to a Boltzmann distribution. Therefore it is often assumed that the rotational



(a)



(b)

FIG. 5. Axial dependencies of the electron temperature (T_e) and electron density (n_e) in the molecular regime of an expanding hydrogen plasma, measured by a Langmuir double probe.

temperature coincides with the translational gas temperature T_g .³⁰ However, since at low densities the radiative lifetimes of excited molecules are usually shorter than the characteristic time for rotational relaxation,^{31,32} the relation between rotational temperature and gas temperature requires special attention.

In order to determine the temperature of the neutral particles in an expanding hydrogen plasma (the gas temperature), we measured the rotational distribution of hydrogen molecules of the electronically-excited state $H_2(d^3\Pi_u)$. For this purpose we used the radiative transitions, which correspond to Fulcher- α system of H_2 . The Fulcher- α system is the result of radiative transition $H_2(d^3\Pi_u \rightarrow a^3\Sigma_g^+)$ (cf. Fig. 6), and has been chosen for two reasons. First, the lines of this system in the red part of the visible spectrum are fairly far apart from one another and dominate over the spectral lines associated with other transitions. Second, for the Fulcher- α system all necessary molecular constants have been studied most thoroughly.³³⁻³⁵ In this section we will discuss the properties of the radiative state $H_2(d^3\Pi_u)$, the excitation mechanism of this state in the conditions of an expanding plasma, and the method of gas temperature determination from analysis of the rotational spectrum of H_2 .

A. The Fulcher- α spectrum

For a hydrogen molecule, both the electronic ground state $H_2(X^1\Sigma_g^+)$, and the considered electronically excited

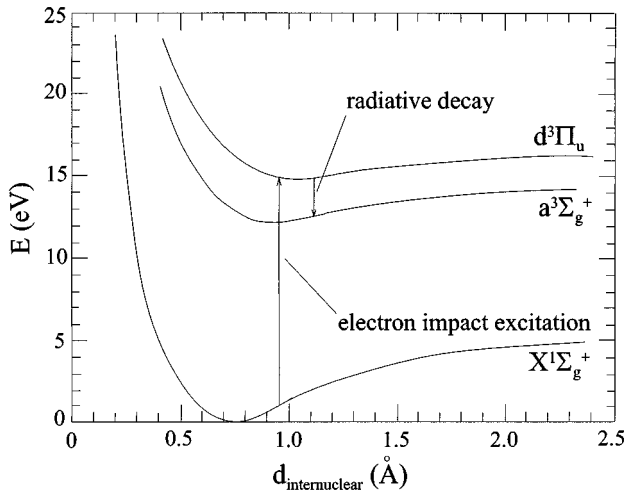


FIG. 6. Potential energy curves for hydrogen molecule.

states $H_2(d^3\Pi_u)$ and $H_2(a^3\Sigma_g^+)$ belong to Hund's case (b).³⁶ The triplet splitting in the $H_2(d^3\Pi_u)$ and $H_2(a^3\Sigma_g^+)$ states are negligible.³⁵ For the $H_2(d^3\Pi_u)$ state the rotational levels split into two components due to Λ -type doubling, where one is symmetric and applies to para-hydrogen, and the other is antisymmetric and applies to ortho-hydrogen. This results into two distinguishable series of rotational levels denoted as the Π^+ and Π^- components.

For the $H_2(d^3\Pi_u \rightarrow a^3\Sigma_g^+)$ transition the relevant selection rules are:

$$\Delta J = 0, \pm 1, \quad \Delta K = 0, \pm 1.$$

Since the triplet splitting of both states are negligible, only three branches appear in the spectrum; P , Q and R . It means that one can treat the $H_2(d^3\Pi_u \rightarrow a^3\Sigma_g^+)$ transition simply as a $^1\Pi_u \rightarrow ^1\Sigma_g^+$ transition.

It is known that only levels of identical symmetry combine,^{30,37} that is why the lines of the Q -branch always have the lower Λ component as upper state (i.e., Π^- component); this is the case of $H_2(d^3\Pi_u)$ state. As a result the lines of the Q -branch determine the populations of the rotational levels of the $H_2(d^3\Pi_u)$ state for para-hydrogen with even numbers of J' , and for ortho-hydrogen they determine the populations of the levels with odd numbers of J' . The $H_2(d^3\Pi_u^+)$ states are perturbed by the Σ states,^{34,37} which influence the intensity of P - and R -branches.³⁸ Therefore the line intensity of only Q -branch of the Fulcher- α system have been used to determine the relative population density of rotational levels of $H_2(d^3\Pi_u^-)$ state.

TABLE I. Molecular constants of the ground state $H_2(X^1\Sigma_g^+)$, and electronically excited states $H_2(d^3\Pi_u)$ and $H_2(a^3\Sigma_g^+)$.

State	E_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α (cm ⁻¹)
$d^3\Pi_u$	112702	2371.58	66.27	30.364	1.545
$a^3\Sigma_g^+$	107777	2664.83	71.65	34.261	1.671
$X^1\Sigma_g^+$	0	4395.2	117.99	60.809	2.993

Since vibrational and rotational interaction is insignificant in the $H_2(d^3\Pi_u)$ state, the line strengths can be calculated with the Hönl-London formula:^{30,37}

$$S_{J,J+1} = \frac{1}{2} 12 J(2t+1) \quad (P\text{-branch}),$$

$$S_{J,J} = \frac{1}{2} (2J+1)(2t+1) \quad (Q\text{-branch}), \quad (7)$$

$$S_{J,J-1} = \frac{1}{2} (J+1)(2t+1) \quad (R\text{-branch})$$

with $t=0$ for even J' values, and $t=1$ for odd J' values.

Figure 3 shows an example of a part of the hydrogen Fulcher- α spectrum measured in an expanding hydrogen cascaded arc plasma in the molecular regime.

The molecular constants for the ground state $H_2(X^1\Sigma_g^+)$, and for the electronically excited states $H_2(d^3\Pi_u)$ and $H_2(a^3\Sigma_g^+)$ are listed in Table I.³⁹ The spectral positions of the rotational lines, which belong to the Q -branch of the vibrational-rotational transitions of the Fulcher- α system are presented in Table II.³³⁻³⁵

B. Determination of rotational temperature

In general the intensity of the radiation between the rotational levels of the electronic-vibrational excited states can be expressed:

$$I_{\nu',\nu''} = n_{p',v',J'} \cdot A_{\nu',\nu''} h \nu_{\nu',\nu''} \frac{\Delta\Omega}{4\pi}, \quad (8)$$

in which $n_{p',v',J'}$ is the population of an electronically excited state p' , with vibrational quantum number v' , and rotational quantum number J' , $\nu_{\nu',\nu''}$ and $A_{\nu',\nu''}$ are the wavenumber and the transition probability for the given spectral line, $\Delta\Omega$ is the solid angle of observation and h is Planck's constant. In the adiabatic approximation, the corresponding transition probability $A_{\nu',\nu''}$ is a product of electronic, vibrational and rotational fractions and can be expressed as:^{30,37}

$$A_{\nu',\nu''} = \frac{64\pi\nu_{\nu',\nu''}^3}{3h} \cdot A_{p',p''} \cdot q_{v',v''} \cdot S_{J',J''}, \quad (9)$$

where $q_{v',v''}$ is the so called Franck-Condon factor, which determines the distribution over the vibrational transitions.^{30,37}

In the case that the rotational distribution of the upper state of a molecular radiative transition is a Boltzmann distribution, the intensities of the rotational lines $I_{\nu',\nu''}$ are directly linked to the rotational temperature through:

$$\ln\left(\frac{I_{\nu',\nu''}}{\nu_{\nu',\nu''}^4 \cdot S_{J',J''}}\right) = -\frac{hc}{kT_{\text{rot}}^*} \cdot F(J') + \text{const}, \quad (10)$$

TABLE II. Spectral positions of the rotational spectral lines (in nanometers), which belong to the Q -branch of the (0-0), (1-1), and (2-2) bands of the Fulcher- α system of H_2 .

Transition	$Q1$	$Q2$	$Q3$	$Q4$	$Q5$	$Q6$
(0-0)	601.83	602.38	603.19	604.27	605.61	607.20
(1-1)	612.18	612.72	613.54	614.62	615.96	
(2-2)	622.48	623.03	623.84	624.92	626.25	

in which $F(J')$ is the energy of the upper level in cm^{-1} , k is Boltzmann's constant and c the velocity of light. The plot of the $\ln(I_{i \rightarrow n} / \nu_{i \rightarrow n}^4 \cdot S_{J', J''})$ versus the rotational term values $F(J')$ gives a so-called Boltzmann plot. The rotational temperature can be obtained from the slope of this plot.

C. Determination of gas temperature

In a low pressure plasma, the radiative lifetimes of the molecules in the electronically excited states τ_{rad} are often much shorter than the characteristic time of rotational relaxation τ_{rel} . The only exceptions are the ground state and the metastable states of the molecules. Therefore, the mechanism of excitation of rotational levels in the electronically excited states is important in plasma diagnostics since the determination of the gas temperature is based on the analysis of the relative intensities of the rotational lines in the electronic-vibrational (vibronic) bands of the molecular spectra.

The previous investigation³² shows that in a broad range of plasma conditions a Boltzmann rotational distribution in the ground electronic state of the molecules images to a Boltzmann rotational distribution in the excited electronic states despite the substantial change of angular momentum of a molecule during a direct electron impact. However, due to the fact, that the rotational constants of the ground state B^0 and excited state B' are different, and the difference is especially large for the hydrogen molecule (cf. Table I), the rotational temperature of the ground state T_{rot}^0 and the rotational temperature of the excited state T_{rot}^* will in general be different. From Eq. (10) and the expression for the rotational term it is easy to obtain a relation between the two temperatures with good accuracy:

$$\frac{T_{\text{rot}}^0}{T_{\text{rot}}^*} = \frac{B^0}{B'}. \quad (11)$$

Therefore to determine the gas temperature of a hydrogen plasma from a rotational spectral line intensity distribution, it is necessary to assume that the hydrogen molecular excited state $H_2(d^3\Pi_u)$ is excited from the hydrogen molecular ground state $H_2(X^1\Sigma_g^+)$ by direct electron impact and decay to $H_2(a^3\Sigma_g^+)$ occurs spontaneously. These two assumptions will be discussed in more detail in the next section.

D. Excitation mechanism and gas temperature in an expanding hydrogen plasma

To determine the rotational temperature of an expanding hydrogen plasma in the molecular regime, the first five lines belonging to the Q -branch of the first three diagonal vibrational states of (0-0), (1-1) and (2-2) transitions in the Fulcher- α spectrum have been measured. The measurements

were carried out by a lateral scanning of these Q -branch lines at axial positions from 18 to 30 cm downstream of the arc nozzle.

Figure 7 shows an example of a lateral profile measurement. The procedure of Abel inversion was applied to derive local values of the emission coefficients, and the relative densities of rotational levels of $H_2(d^3\Pi_u)$ state. As can be seen from the measurements, the expanding plasma is strongly confined to a narrow beam with a width approximately equal to 1.5 cm.

The Boltzmann plot for $Q(0-0)$, (1-1) and (2-2) series measured at the center of the beam for $z = 18$ cm are given in Fig. 8. As can be seen the Boltzmann plots give straight lines. This fact indicates that the rotational levels of the excited hydrogen molecules $H_2(d^3\Pi_u)$ follow a Boltzmann distribution. Therefore the rotational temperature T_{rot}^* can be derived from the slope of the Boltzmann plot. The three Q bands are measured independently and T_{rot}^* can be obtained from each of the measured bands. The relatively small difference in the T_{rot}^* values determined from different Boltzmann plots show that the T_{rot}^* value determined in the experiment is accurate (the error is estimated to be smaller than 20%).

To draw conclusions for the ground state molecules from the measurements of electronically excited molecules, it is important to know the excitation and de-excitation mechanisms of the radiative excited states. In principle a more detailed analysis of excitation of $H_2(d^3\Pi_u)$ state in an expanding hydrogen plasma is required since both heavy particles and electrons can be involved in the collisional processes. Generally speaking it is a complicated kinetic

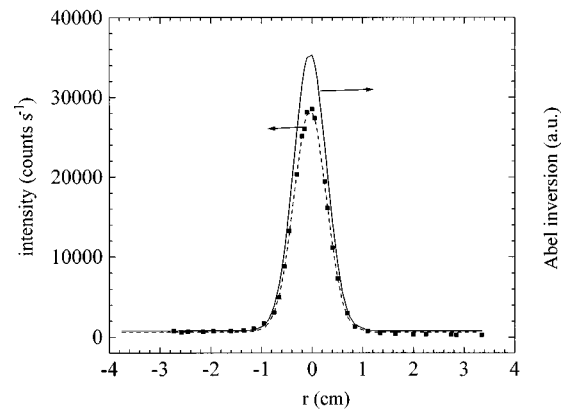


FIG. 7. Example of the experimental and radial profiles of the $Q1$ spectral line of the Fulcher- α transition in an expanding plasma. Experimental conditions $Q=8$ scc/s, $I_{\text{arc}}=50$ A, $I_B=50$ A, $P=5$ Pa, $z=18$ cm. (■) the experimental data, (---) Gaussian profile (—) after Abel inversion.

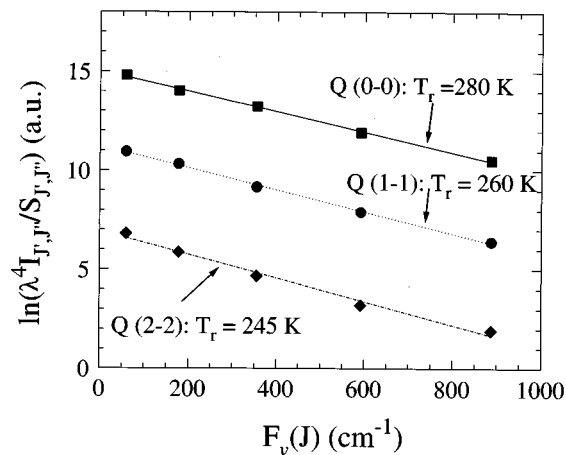


FIG. 8. Boltzmann plot of the first five lines of Q -branch in the (0-0) (■), (1-1) (●) and (2-2) (◆) rotational bands of the Fulcher- α system of H_2 . Plasma parameters are the same as in Fig. 7.

problem especially for a non-equilibrium molecular plasma. However, in this experiment, the measured rotational excitation temperature of the $H_2(d^3\Pi_u)$ state is very low, $T_{rot}^* \approx 260$ K (cf. Fig. 8). We can conclude that the collisions between the heavy particles are not responsible for the excitation of the hydrogen molecules. The only possible mechanism of the excitation of the hydrogen molecules in this regime is the direct electron impact from the ground state. Such statement can be made because in a low-temperature plasma all effective inelastic collisional processes between heavy particles are exothermic (see, for example, Refs. 8, 41). With that the excess of energy should be distributed among the various degrees of freedom (internal and translational) of the products after the reaction. As a result it should inevitably lead to the nonthermal molecular rotational population.^{8,42,43} Thus the rotational temperature of excited molecular states should be higher (and often much higher), than the gas temperature. Numerous examples of appearances of “hot” rotational distribution of diatomic molecules, produced by heavy particle interactions in low-temperature plasma have been given in literature.^{8,42,43} However, for direct electron excitation of the molecules from the ground state, the resulting rotational excitation temperature of the excited molecules should be low (comparable to the gas temperature). Electrons are rather ineffective in rotational (de)excitation because of their small mass.^{8,31,32}

In the conditions of an expanding plasma the characteristic time between the heavy particle collisions τ_{col} is in the order of 10^{-6} s [the total cross section for the collisions $H_2-H_2(d^3\Pi_u)$ is equal to $\sigma_{col} = 2.3 \times 10^{-18}$ m² (Ref. 40)]. This characteristic time is much longer than the radiative lifetime of hydrogen molecules in the $H_2(d^3\Pi_u)$ state, which is only about $\tau_{rad} = 31$ ns.⁴⁰ Therefore to determine the gas temperature we can use the method mentioned earlier, which is based on the fact that a Boltzmann rotational distribution in the ground electronic state of the molecules images to a Boltzmann rotational distribution in the excited electronic state. According to Eq. (11), the ratio of the rotational temperatures of the ground state molecules and the rotational

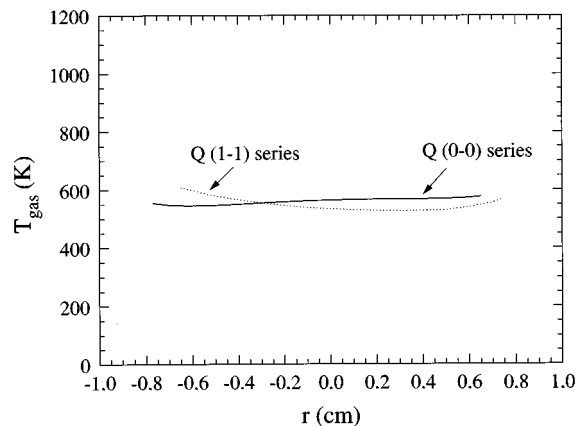


FIG. 9. Radial profile of the gas temperature in an expanding plasma, derived from emission of the Q -branches, belong to (0-0) (—), and (1-1) (---) rotational bands of the Fulcher- α system of H_2 . Plasma parameters are the same as in Fig. 7.

temperature of the excited molecules equals the ratio of the rotational constants of the two states. As the ground state $H_2(X^1\Sigma_g^+)$ rotational constant is twice as large as that of the $H_2(d^3\Pi_u)$ state,³⁹ the gas temperature $T_{gas} = T_{rot}^0$ is approximately twice the rotational temperature T_{rot}^* of the $H_2(d^3\Pi_u)$ state. Therefore the gas temperature in the molecular regime for the conditions in Fig. 8 is found to be approximately 520 K.

Figure 9 shows the experimentally determined gas temperature of an expanding hydrogen plasma in molecular regime. As can be seen inside the plasma beam the temperature profile is rather flat. The relative error in T_{gas} determined from the different vibrational bands is smaller than 20%.

V. LOCAL EXCITATION OF THE Ar AND He SPECTRAL LINES

We concluded in the previous section from the low gas temperature that hot electrons should be present. Possible methods to directly see these hot electrons is by injecting small amounts of an inert gas downstream. Since in this case the excitation can occur only by direct electron impact from the ground state, this experiment provides insight in the presence of high energy electrons. We used both argon and helium which were locally injected. The transportation of Ar and He to a particular local point in the plasma has been done through a thin cylindrical ceramic tube (Fig. 2). In the molecular regime of an expanding plasma we observed the appearance of the spectral line of neutral argon $Ar\ I(7d \rightarrow 4p)\lambda = 4876.26$ Å and $\lambda = 4887.95$ Å, and of ion argon $Ar\ II(4p^2D \rightarrow 4s^2D)\lambda = 4879.86$ Å. The excitation potential of these lines $\Delta E_2 = 15.45$ eV, and $\Delta E_3 = 19.68$ 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 $He\ I(3d \rightarrow 2p)\lambda = 5875.70$ Å ($\Delta E_4 = 23.07$ eV), and $He\ I(5d \rightarrow 2p)\lambda = 4026.20$ Å ($\Delta E_5 = 24.04$ eV). These experimental facts together with the Langmuir probe measurements, observation of the Fulcher- α system of H_2 (excitation potential $\Delta E = 13.87$ eV), with a low rotational temperature ($T_{rot}^* \approx 260$ K)

of the excited $H_2(d^3\Pi_u)$ molecules, provide a strong evidence of presence of the hot electrons in an expanding plasma. This observation will be used in the next section to determine the dissociation degree.

VI. DISSOCIATION DEGREE

We have found that in the molecular regime of an expanding hydrogen plasma the electronic quantum state $H_2(d^3\Pi_u)$ is excited by direct electron impact from the ground state $H_2(X^1\Sigma_g^+)$. Apparently in this plasma we have hot electrons, which can effectively excite the atomic and molecular radiative states from their respective ground electronic states. Thus it opens in principle a possibility to determine the dissociation degree of the hydrogen plasma by using optical actinometry.

A. Optical actinometry of plasma

One of the disadvantages of classical emission spectroscopy is that only the particle densities in the excited states can be measured. However, in many cases it is important to know the particle density in the ground electronic state. The ground state density determination from emission spectra requires detailed quantitative information on the mechanisms of excitation and de-excitation of excited species. For example, for the excitation of the radiative states by direct electron impact, it is necessary to know the electron energy distribution function near the excitation thresholds of the corresponding radiative states, which usually presents significant experimental difficulties.⁸

The method of optical actinometry has been found to be an effective diagnostic technique to measure the densities of the various species of the ground states.^{8,44-46} Actinometry provides an experimental method to determine the various radical densities by simply comparing their optical emission with the emission of an actinometer gas which is added to the plasma in a small and known amount. If for both the studied radical and actinometer, the radiative states are excited by direct electron impact from their respective ground states and the excitation energies are close to each other, the same group of electrons in the energy distribution will take part in the excitation of radiative states. Assuming that the analyzed radiative states are depopulated by radiative transfers (which is often the case of a low electron density and low pressure plasma) the spectral line intensities of both the actinometer and the studied radical are determined by the balance equations of their respective excited states:

$$\frac{dn_p^I}{dt} = k^I \cdot n_g^I \cdot n_e - n_p^I A_{p \rightarrow p'} = 0, \quad (12)$$

$$\frac{dn_q^{II}}{dt} = k^{II} \cdot n_g^{II} \cdot n_e - n_q^{II} A_{q \rightarrow q'} = 0. \quad (13)$$

In Eqs. (12) and (13) the superscript I denotes the studied plasma component, II denotes the actinometer, n_g is the ground state density, n_p and n_q the excited state densities of the plasma component and actinometer, respectively. The ratio of the excited state densities is then:

$$\frac{n_p^I}{n_q^{II}} = \frac{n_p^I A_{p \rightarrow p'}}{n_q^{II} A_{q \rightarrow q'}} \cdot \frac{k^{II}}{k^I}. \quad (14)$$

In the case that the rate coefficients for electron excitation are known the ground state of the radical can be determined simply from a comparison of the relative intensities of the species in emission.

As was mentioned a typical actinometry technique consist of admitting into the gas under investigation the actinometers, usually Ar, He, and N_2 , which should not influence the plasma kinetics. This means usually that only a small concentration of actinometer is used. The assumption of optical actinometry have been validated first for fluorine and other halogen atoms with the noble gas or nitrogen as the actinometer (see Ref. 8). Later the technique was used for monitoring hydrogen atoms with argon as an actinometer.⁴⁷⁻⁴⁹ This requires a mixture of additional components to a minimum concentration to be able to detect the emission of the correspondent spectral lines. This inevitably will lead to a certain perturbation of the plasma properties. Those changes can be small, but unpredictable. That is, of course, a disadvantage of optical actinometry.

However, to determine the hydrogen plasma dissociation degree by actinometry technique, we can avoid the procedure of using another gas as an actinometer since the molecular hydrogen in the plasma can act as the actinometer. For example, to determine the mass dissociation degree of hydrogen plasma β the following relation can be used:

$$\beta = \frac{n_H}{n_H + 2n_{H_2}} = \frac{\gamma}{\gamma + 2}, \quad (15)$$

the only parameter that has to be measured is the ratio of atomic and molecular hydrogen densities in the plasma, $\gamma = n_H/n_{H_2}$.

B. Kinetic of hydrogen excited states

As has been mentioned the application of optical actinometry is based on two main assumptions: direct electron excitation from the ground states and radiative decay of the excited states. In general there are many elementary collisional and radiative processes occurring in the plasma at the same time. Among them stepwise excitation, excitation from upper levels by a radiative cascades, dissociative excitation, quenching of radiative states, and so on. They all may be important in the creation of the excited states and could therefore influence the actinometric determination of the dissociation degree.

The analysis of the rates of various processes for a specific condition in the expanding hydrogen plasma shows that the following elementary processes of excitation and de-excitation of radiative A^* and metastable A_m states of H and H_2 might be important (the symbol A stands for the ground state of H and H_2):

(a) Direct electron excitation:



(b) Stepwise electron excitation via the metastable states A_m :



(c) Quenching of metastable states A_m by heavy particles:



(d) Quenching of excited states A^* by heavy particles:



(e) Radiative decay:



Besides the reaction of dissociative electron excitation should be in principle also taken into account:



We will discuss these processes one by one.

(1) The excitation of hydrogen atoms by electron impact (reaction 16) is of special interest because it is the simplest electron-atom inelastic scattering problem. It is therefore considered as an important test for the different approximations, and has been the subject of many theoretical investigations (see, for example, Refs. 50–55). The models are based on a particular modification of the Bethe-Born formula,^{50,51} on the semi-empirical approaches, which have been built with the use of the data from accurate numerical computations,⁵² multiple-state close-coupling calculations,^{53,54} which predict resonances, etc.

On the experimental side, the amount of data is rather limited. The main difficulty consists on generation of the intense beam of atomic hydrogen. Most of the measurements were performed in respect to the excitation of the first excited states of $H^*(p=2)$ (see, for example, Ref. 55). The only known experimental results for the excitation of $H^*(p=3)$ are those of Walker and St. John,⁵⁶ of Mahan *et al.*,⁵⁷ and Williams.⁵⁸ However, it is rather important to mention, that Williams presented a near-threshold studies of excitation of both summed $H^*(p=2)$ and $H^*(p=3)$ states, and the separate $2P$, $3S$, $3P$, and $3D$ states by a direct electron impact. The typical excitation cross section of $H^*(p=3)$ state by direct electron impact has a maximum value of around $(0.9-1.2) \times 10^{-21} \text{ m}^2$,⁵⁸ which is also in good agreement with the results of theoretical calculations.^{51,54} We did not find in the literature reliable experimental data of the cross section of direct electron excitation from the ground $H(p=1)$ to the higher excited states of atomic hydrogen $H^*(p \geq 4)$. The only known experimental data are from Walker and St. John,⁵⁶ but the energy resolution of their study was insufficient to be used in practice. That is why we used calculated data from⁵¹ and⁵² as excitation cross sections

of $H^*(p \geq 4)$ states and normalized them to the experimental excitation cross section for the states $H^*(p=2,3)$.⁵⁸

The cross sections for reaction (16) with the excitation of molecular hydrogen from the ground $H_2(X^1\Sigma_g^+)$ to radiative state $H_2(d^3\Pi_u)$ are also known both from the theoretical calculations,⁵⁹ and from the direct experiments.^{60,61} In the interpretation of this experiment we used the most reliable, from our point of view, experimental excitation cross section of Möhlmann and de Heer,⁶¹ with a maximum value about $4.2 \times 10^{-22} \text{ m}^2$ at electron energy of 15.6 eV, which is close to the threshold of excitation.

(2) As it was mentioned already both theoretical and experimental data on the excitation cross section of the first excited (metastable) state of H (reaction (17)) is available from the literature (see also Refs. 62,63). The recommended excitation cross section is $(1-1.2) \times 10^{-21} \text{ m}^2$ at the maximum. The same value is valid for the excitation of lowest attractive electronic state of molecular hydrogen $H_2(a^3\Sigma_g^+)$ (which is in fact not a real metastable state^{64,65}). The typical excitation cross section of this state has a maximum value of $(0.8-1.4) \times 10^{-21} \text{ m}^2$.^{66,67}

(3) The excitation cross section of $H^*(p=3)$ state from the first excited state $H^*(p=2)$ is also known from the literature.^{51,54,55} The recommended cross section is $(0.8-1.0) \times 10^{-19} \text{ m}^2$. However, there is a lack of experimental data on the stepwise electron excitation cross sections (processes (17) and (18)) for $H^*(p \geq 3)$, as well as for $H_2(d^3\Pi_u)$ state. Therefore the semi-empirical atomic formulas from Drawin and Emard⁵¹ and Vainstein *et al.*⁵² have been used to estimate their values. This procedure is inaccurate especially in the case of molecular excitation. However, later we will show that the uncertainties in the excitation cross section for the reactions (18) do not influence the accuracy of the actinometry method.

(4) The collisional quenching coefficients for atomic hydrogen excited states are known from literature.^{68,69} Simple estimations, based on the data of^{68,69} show that in the pressure range of our experiments all collisional quenching processes are rather slow in comparison with the spontaneous decay (21) of the radiative states [reactions (20)] (see also Ref. 70). Influence of the collisional quenching processes can be considerable only for the metastable $2s$ sublevel of the $H^*(p=2)$ quantum state, because of high collision cross section of this level with H_2 .^{68,71} However, this process will lead only to de-population of the $H^*(p=2)$ state, and as a consequence has a small role on the stepwise excitation.

Numerical data on the atomic radiative transition probabilities can be found in the well-known tables of Wiese *et al.*⁷²

(5) Concerning molecular hydrogen, the radiative lifetime of hydrogen molecules in the excited state $H_2(d^3\Pi_u)$ $\tau_{\text{rad}}^d = 31 \text{ ns}$,⁴⁰ which is much smaller than the characteristic time between the heavy particle collisions τ_{col} (see previous section). The same conclusion is valid for the quantum state $H_2(a^3\Sigma_g^+)$, which has even smaller radiative lifetime of $\tau_{\text{rad}}^a = 10 \text{ ns}$.^{64,65}

(6) The reaction of dissociative excitation (22) of different states of atomic hydrogen has been studied for a fairly long time (see, for example, Refs. 73, 74). It was shown, that

the lower the principal quantum number of H^* and the higher the electron temperature, the higher the contribution of the dissociative excitation. This reaction becomes especially important for fast electron-molecule collisions (electron energy >10 eV). However, Lavro⁷³ shows, that for mean electron energies of 1–2 eV direct excitation is more effective than dissociative excitation even if the hydrogen dissociation degree is only about 1%. Since the dissociation degree of an expanding hydrogen plasma is larger (see later), we can conclude here, that the reaction of dissociative excitation is not important for the excitation of atomic hydrogen states.

(7) Concerning an expanding hydrogen plasma, we should also discuss the reaction of dissociative recombination which can populate the excited states of atomic hydrogen:^{21,70}



The rate constants for dissociative recombination of vibrationally non-excited molecular ions of the halogens (including hydrogen (23)) are typically $k_8 = 10^{-14} - 10^{-16} \text{ m}^3 \text{ s}^{-1}$ in the temperature range from 300 to 10000 K.⁷⁵ For vibrationally excited molecular ions the rate constants may be approximately an order of magnitude larger.⁷⁵ Reaction (23) leads to the population of only the $H^*(p=2)$ state since only those reactions are exothermic: the positive excess of energy for the dissociative recombination reactions of electrons with vibrationally non-excited molecular ions H_2^+ is approximately 0.7 eV. Dissociative recombination reactions of electrons with ground state molecular ions, created by charge exchange reactions leading to higher hydrogen excited states $H^*(p \geq 3)$ are all endothermic: the energy deficit in those cases is approximately 1.2 eV for $H^*(p=3)$, and 1.9 eV for $H^*(p=4)$, etc. Therefore, for the effective population of atomic excited states $H^*(p \geq 3)$ by the reactions of dissociative recombination, the molecular ions H_2^+ must be vibrationally excited (vibrational quantum $\hbar\omega_e$ for the hydrogen molecular ion is approximately ≈ 0.54 eV).

(8) The reaction of mutual neutralization:



also produces excited hydrogen atoms.⁴¹ Simple estimations, based on the rate constants of the direct electron excitation,^{51,58} and the mutual neutralization reactions,⁴¹ as well as on the densities of atoms and positive and negative ions show, that only in the case when the negative ions density is significantly higher than the electron density, mutual neutralization could be important. However, we believe this is not the case in the molecular regime of an expanding plasma. Additional confirmation of this statement can be found from analysis of the hydrogen atomic state population densities. The densities of the quantum states $H(p \leq 6)$ in the molecular regime (cf. Fig. 10) are several orders of magnitude lower than those in the atomic regime, where the mutual neutralization reaction, probably plays a dominant role for excitation of excited states H.

The kinetic analysis presented above shows that in the molecular regime of an expanding hydrogen low-pressure

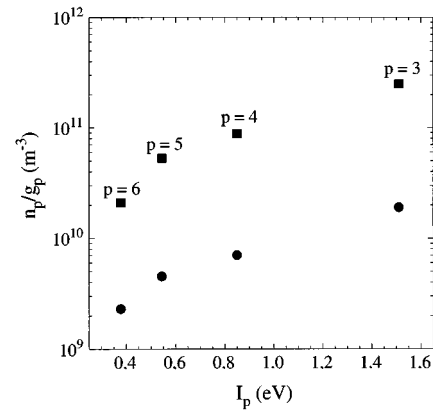


FIG. 10. The atomic hydrogen absolute population density n_p/g_p versus the ionization potential in the molecular regime of an expanding hydrogen plasma. (■) $z = 18$ cm, (●) $z = 27$ cm.

plasma the atomic radiative states $H^*(p \geq 3)$ and the molecular radiative state $H_2(d^3\Pi_u)$ are populated by a direct electron excitation from the ground states and depopulated by spontaneous radiative decay. Thus the conditions for using optical actinometry technique are satisfied. Note that we have derived the same conclusion independently for the radiative state $H_2(d^3\Pi_u)$ in the discussion of the gas temperature measurements from the rotational spectra of H_2 .

C. Expression for the dissociation degree of hydrogen plasma

In the case when the density of a particular radiative state is governed by the balance between the direct electron excitation from the ground state and spontaneous decay from this state, the ground state density is given by (cf. Eqs. (8) and (12)):

$$\begin{aligned} n_g &= s(\lambda) \frac{I_{p \rightarrow p'}}{n_e \langle \sigma(\epsilon) v_e \rangle \tau_{p'v'J'} A_{p \rightarrow p'} \nu_{p \rightarrow p'}} \\ &= s(\lambda) \frac{I_{p \rightarrow p'} \cdot \sum_{p'v'J'} A_{p \rightarrow p'}}{n_e \langle \sigma(\epsilon) v_e \rangle \cdot A_{p \rightarrow p'} \nu_{p \rightarrow p'}}. \end{aligned} \quad (25)$$

Here we used the definition of the radiative lifetime $\tau_{p'v'J'} = (\sum_{p'v'J'} A_{p \rightarrow p'})^{-1}$, and of the rate constant $\langle \sigma(\epsilon) v_e \rangle$ of the reaction of direct electron excitation ($\sigma(\epsilon)$ is the excitation cross section). Additionally the value of a spectral selectivity of the optical system $s(\lambda)$ has been introduced.

Finally, the following expression for the ratio of the atomic and molecular hydrogen densities in the plasma can be derived:

$$\begin{aligned} \gamma = \frac{n_H}{n_{H_2}} &= \frac{I_{q \rightarrow q'}^H}{I_{p \rightarrow p'}^{H_2}} \cdot \frac{\langle \sigma(\epsilon) v_e \rangle^{H_2}}{\langle \sigma(\epsilon) v_e \rangle^H} \cdot \frac{A_{p \rightarrow p'}^{H_2}}{A_{q \rightarrow q'}^H} \cdot \frac{\sum_{q'} A_{q \rightarrow q'}^H}{\sum_{p'v'J'} A_{p \rightarrow p'}^{H_2}} \\ &\quad \cdot \frac{\nu_{p \rightarrow p'}^{H_2}}{\nu_{q \rightarrow q'}^H} \cdot \frac{s(\lambda)^H}{s(\lambda)^{H_2}}. \end{aligned} \quad (26)$$

Using Eq. (26) the mass dissociation degree of hydrogen plasma can be obtained [see Eq. (15)].

D. Atomic hydrogen density and hydrogen dissociation degree

In order to determine the dissociation degree in an expanding hydrogen plasma and to validate the assumptions of direct electron excitation from the ground states and radiative decay of the excited states, the intensities of the three different atomic hydrogen Balmer spectral lines H_α , H_β and H_γ , as well as the intensities of the Fulcher- α molecular lines of the hydrogen molecule have been measured. Here we employed the fact that hydrogen excited states $H^*(p=3,4,5)$ will have different population densities depending on different collisional processes, as direct electron excitation, stepwise excitation, dissociative excitation or dissociative recombination.

In the discussed kinetic scheme the stepwise excitation processes (17) and (18) could in principle be important^{76,77}. Therefore, we made an attempt to measure also the population densities of the first excited states of the atomic and molecular hydrogen $H^*(p=2)$ and $H_2(a^3\Sigma_g^+)$, respectively. For this purpose the method of reabsorption with a concave mirror has been used.²⁵ The line absorption coefficients, corresponding to the radiative transitions $H^*(p=3 \rightarrow p=2)$ and $H_2(d^3\Pi_u \rightarrow a^3\Sigma_g^+)$ have been measured. For these transitions we did not observe any notable absorption within the accuracy of the reabsorption method. Therefore an upper side approximation of the population densities of $H^*(p=2)$ and $H_2^*(a^3\Sigma_g^+)$, can be given. For both states the densities should be lower than 10^{16} m^{-3} . As a consequence the stepwise excitation processes (17) and (18) can be neglected in the kinetic scheme (16)–(24).

Analysis of the experimental and theoretical data on electron impact excitation of atomic and molecular radiative states $H^*(p=3,4,5)$ and $H_2(d^3\Pi_u)^{51-61}$ show that the cross sections have similar shapes: a sharp rise near the thresholds, and a slow decrease for higher electron energies. Therefore, the ratio between the corresponding excitation cross sections can be used for the ratio between the rate constants of the direct electron excitation of H^* and H_2^* as a first approximation. Additionally in order to account for the difference in the thresholds of the atomic and molecular excitation processes a correction factor has been introduced to the calculation scheme.

Calculation of radiative lifetime of atomic and molecular species in the plasma is a rather difficult procedure, mainly because of complicated problems of transport of the resonance radiation, i.e., the radiation from the excited to the ground electronic state.^{23,70} Usually resonance radiation has the largest transition probability,^{39,72} and in the case the plasma is optically thin for the resonance radiation, the radiative lifetime of the excited species is almost fully determined by the radiative transitions to the ground state. However, the plasma can also be optically thick for the resonance radiation. This occurs often for a low-temperature plasma since in such a plasma the ground electronic state density is normally much larger than that of any excited state. In this case the radiative lifetime of the excited states will be determined by radiative transitions between the excited states. In a hydrogen plasma the radiative properties of atoms and molecules should also be carefully analyzed in this respect.^{23,70}

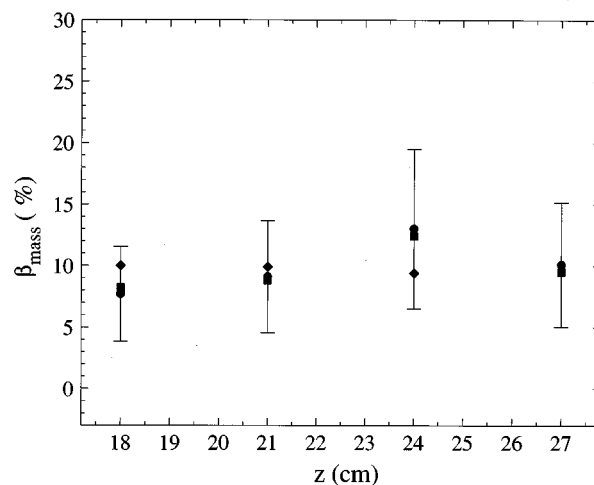


FIG. 11. Axial dependence of the dissociation degree of an expanding hydrogen plasma; (■) H_α measurements, (●) H_β measurements (◆) H_γ measurements. Experimental conditions $Q=8 \text{ scc/s}$, $I_{\text{arc}}=50 \text{ A}$, $I_B=50 \text{ A}$, $P=5 \text{ Pa}$, $z=18 \text{ cm}$.

For molecular hydrogen the only possible radiative transition from the radiative state $H_2(d^3\Pi_u)$ leads to $H_2(a^3\Sigma_g^+)$ state (Fulcher- α system of H_2).⁴⁰ The optical transition to the ground state is forbidden.^{30,39} Therefore the radiative transition probability for $H_2(d^3\Pi_u \rightarrow a^3\Sigma_g^+)$ is the inverse of the radiative lifetime of the $H_2(d^3\Pi_u)$ state. For atomic hydrogen the situation is more complicated, since all excited states have optically allowed transition to the ground state. A first estimate of the dissociation degree of an expanding hydrogen plasma in the molecular regime shows that it should be about 10%, i.e., the atomic hydrogen ground state density in this regime should be around 10^{20} m^{-3} . For this density the plasma's effective optical depth for the resonance L_α radiation will be $\approx 30-40$ and the escape factor for the resonance radiation will be $\approx 10^{-2}$.^{23,70} This means, that we can treat an expanding hydrogen plasma in the molecular regime as an optically thick media for resonance atomic radiation. Experimental results of the atomic excited states population densities were lower than 10^{15} m^{-3} , i.e., for this reason an expanding plasma will be optically transparent for the radiative transitions between the excited states. As a result, one can calculate with a good accuracy the radiative lifetimes of the atomic hydrogen excited states by using data on the radiative transition probabilities from Wiese *et al.*⁷²

The dissociative degree of an expanding hydrogen plasma determined with the above discussed procedure as a function of axial position using Eqs. (15), (26) is shown in Fig. 11. It can be seen that the results do not depend on which one of the atomic spectral lines H_α , H_β or H_γ have been chosen. Therefore, the experimental results provide a strong support for the assumptions that direct excitation by electrons from the ground states and radiative decay of the excited states dominate the kinetics. Furthermore, it supports the method of actinometry used to determine the dissociation degree.

The accuracy of the discussed procedure, as it can be seen from the relations (15) and (26), is determined by both the experimental accuracy (error in the spectral line intensi-

ties and calibration of the optical system) and by the uncertainty in the kinetic coefficients (electron excitation cross sections, radiative transition probabilities). Taking these errors into account, we estimate the error in the plasma dissociation degree to be within a factor of 2.

The absolute population density of the excited levels can also be used to obtain an effective electron temperature, i.e., the temperature needed to explain the observed excitation for a Maxwellian distribution. To this end we use the dissociation degree (Fig. 11) to determine the atomic hydrogen density ($1.1 \times 10^{20} \text{ m}^{-3}$), the Langmuir probe results on n_e ($1.0 \times 10^{17} \text{ m}^{-3}$), the population density of the $\text{H}(p=3)$ state ($3.6 \times 10^{12} \text{ m}^{-3}$), and the transition probability for H_α line in a corona model (all at $z=24 \text{ cm}$):

$$n_e \cdot n_1 \cdot k_{13}(T_{\text{eff}}) = n_3 A_{32}. \quad (27)$$

The resulting excitation rate is calculated to be $6.5 \times 10^{-18} \text{ m}^{-3} \text{ s}^{-1}$, which is equivalent to an effective temperature of 1.7 eV.⁵¹ Nonthermal distortions of the electron energy distribution function may exist in the low ionization degree of the molecular plasma. Therefore a somewhat higher effective temperature T_{eff} , than the bulk temperature as measured by the probe $T_e \approx 1.5 \text{ eV}$ (cf. Fig. 5) would be expected. We conclude that the obtained value is in agreement with experiment.

VII. CONCLUSION

The rotational temperature of hydrogen molecular excited state $\text{H}_2(d^3\Pi_u)$ has been determined by analyzing the relative intensity distribution of the rotational spectral lines of the Fulcher- α system of H_2 . A strong hydrogen molecular spectrum, and an estimated low rotational temperature of $\text{H}_2(d^3\Pi_u)$ molecules (260 K) indicate that in the molecular regime of an expanding hydrogen plasma the electronic quantum state $\text{H}_2(d^3\Pi_u)$ (excitation potential $\Delta E = 13.87 \text{ eV}$) is excited by a direct electron impact from the ground electronic state $\text{H}_2(X^1\Sigma_g^+)$. The gas temperature in the plasma is twice the value of the rotational temperature, i.e., approximately 520 K.

Several clear indications of presence of the hot electrons have been observed at the axial position of $\approx 24 \text{ cm}$ from the nozzle of the arc. Among them: (1) Langmuir probe measurements ($T_e \approx 1.4 \text{ eV}$), (2) appearance of the Fulcher- α system of H_2 (excitation potential $\Delta E = 13.87 \text{ eV}$), (3) low rotational temperature ($T_{\text{rot}}^* \approx 260 \text{ K}$) of the excited $\text{H}_2(d^3\Pi_u)$ molecules, (4) local excitation in the plasma of Ar I ($\Delta E = 15.45 \text{ eV}$) and Ar II ($\Delta E = 19.68 \text{ eV}$) spectral lines, (5) local excitation in the plasma of He I ($\Delta E = 23.07 \text{ eV}$ and $\Delta E = 24.04 \text{ eV}$) spectral lines.

Optical actinometry has been applied to measure the absolute density of hydrogen atoms and hydrogen dissociation degree in an expanding magnetized plasma. It has been shown, that for the molecular regime of an expanding plasma the atomic $\text{H}^*(n=3,4,5)$, and molecular $\text{H}_2(d^3\Pi_u)$ radiative quantum states are excited 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.

It has been shown that the effective optical depth, and the escape factor for the resonance atomic L_α radiation are

$\approx 30-40$, and $< 10^{-2}$, respectively. Therefore an expanding plasma can be treated as an optically thick medium for the resonance atomic radiation. The 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 H_2 . The densities were lower than 10^{15} m^{-3} , and for this reason an expanding plasma will be optically transparent for the radiative transitions between the excited states.

It is demonstrated that the results does not strongly depend on the atomic spectral lines H_α , H_β or H_γ that have been used for these diagnostics. That is additional strong support that these spectral lines are generated by direct electron impact from the ground state and to the optical actinometry method to determine the dissociation degree as a whole.

The measured absolute density of hydrogen atoms is in the $(1-1.4) \times 10^{20} \text{ m}^{-3}$ range, and the dissociation degree of the hydrogen plasma is in the range of 8%–13%. Within experimental accuracy both values are independent of the axial position. That is an indication that for the given experimental conditions the recirculation gas flowing in the vessel are rather important. At the same time both processes of H_2 dissociation, and of H recombination are slow, and do not influence the kinetics of hydrogen atoms in the plasma.

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