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Citation for published version (APA):

Wijtvliet, R. G., Felizardo, E., Tatarova, E., Dias, F. M., Ferreira, C. M., Nijdam, S., Veldhuizen, E. V., & Kroesen, G. M. W. (2009). Spectroscopic investigation of wave driven microwave plasmas. *Journal of Applied Physics*, 106(10), 103301-1/7. [103301]. <https://doi.org/10.1063/1.3259429>

DOI:

[10.1063/1.3259429](https://doi.org/10.1063/1.3259429)

Document status and date:

Published: 01/01/2009

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Spectroscopic investigation of wave driven microwave plasmas

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(Received 29 July 2009; accepted 13 October 2009; published online 17 November 2009)

Large H atom line broadening was found throughout the volume of surface wave generated He–H₂ and H₂ microwave plasmas at low pressures. The measured Doppler temperatures corresponding to the H _{β} , H _{γ} , H _{δ} , H _{ϵ} , and H _{ζ} line profiles were found to be higher than the rotational temperature of the hydrogen molecular Fulcher- α band and the Doppler temperature of the 667.1 nm singlet He line. No excessive broadening has been found. The Lorentzian and Gaussian widths as determined by fitting the spectral lines with a Voigt profile increase with the principal quantum number of the upper level. In contrast, no such dependence for the Gaussian width has been observed in an Ar–H₂ discharge. No population inversion has been observed from measurements of the relative intensities of transitions within the Balmer series.

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I. INTRODUCTION

The study of the emission of “mixed gas” plasmas reveals many surprising results, especially when hydrogen is one of the gases. Anomalous, even extreme, hydrogen line broadening was found in a number of mixed discharge plasmas excited via direct current (dc) or radio frequency (rf) electric fields.^{1–5} The Balmer line spectra emitted by these discharges have typical multimode behavior, with widely broadened “wings” (“fast” hydrogen) and a sharp top (“slow” hydrogen). The results have usually been explained in terms of Doppler shift and broadening due to the acceleration of charges (such as H⁺, H₂⁺, and H₃⁺ ions) in the high dc electric fields present in the sheath regions of these discharges. The acceleration of hydrogen ions in these dc fields is followed by neutralization and generation of fast excited H atoms. This is the origin of the “wings” in the spectra. Strikingly excessive Balmer- α line broadening has been observed in He–H₂(10%) microwave discharge,⁶ but this has not yet been confirmed by other research groups. On the contrary, measurements of H α line profiles emitted by microwave discharges under similar conditions have not revealed excessive broadening.^{7–10}

Nevertheless, selective hydrogen line broadening has been detected in microwave discharges and their afterglows when there is no significant broadening of noble gas lines or hydrogen molecular lines.^{8,9,11} A possible explanation for such selective heating of H atoms may be connected with the main creation processes of excited H atoms, namely, ion conversion and electron impact dissociation. Furthermore, hyperthermal hydrogen atoms have surprisingly been detected at atmospheric pressure Ar–H₂ microplasma jets, where the H($n=3$) temperatures were found to range from 12,000 to 19,600 K.¹² It is now clear that hydrogen line broadening causes controversy so that more experimental observations are currently needed in order to try to elucidate the mecha-

nisms and processes behind this phenomenon in different types of discharges. The aim of this experimental work is to address some of these problems.

This article presents spectroscopic measurements in He–H₂ and Ar–H₂ low-pressure plasmas generated by a surface wave of frequency $\omega/2\pi=2.45$ GHz. Results on the line shape and the emission intensities of excited hydrogen and helium atoms, and the emission intensities of the Q-branch of the Fulcher- α band [$d^3\Pi_u(v=1) \rightarrow a^3\Sigma_g^+(v=1)$] are presented and discussed. Different temperatures are determined from the measured hydrogen and helium emission line shapes and the rotational distribution of hydrogen molecular lines. Furthermore, the population distribution of excited H atoms is determined from measurements of the relative intensities of transitions within the Balmer series.

II. EXPERIMENTAL SETUP AND DIAGNOSTIC METHODS

An experimental study of the spectral broadening of the Balmer lines of atomic hydrogen has been performed in He–H₂, Ar–H₂, and H₂ plasmas at low pressure conditions ($p=0.36$ mbar). A classical surface wave sustained discharge has been used as a plasma source.^{13,14} The discharge is created using a waveguide surfatron-based set-up (Fig. 1). The microwave power is provided by a 2.45 GHz generator (Sairem), whose output power was varied from 40 to 250 W. The generator is connected to a waveguide (WR-340) system, which includes an isolator, a three-stub tuner, and a waveguide surfatron as the field applicator. The system is terminated by a movable short-circuit, which allows the maximization of the electric field at the launcher position. The discharge takes place inside a quartz tube with internal and external radii of 7.5 and 9 mm, respectively, which is inserted perpendicularly to the waveguide wider wall (Fig. 1). The background gas is injected into the discharge tube at flow rates from 0.4 to 20 SCCM under laminar gas flow conditions.

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FIG. 1. (Color) (a) Experimental setup; (b) Calculated phase diagrams (ω/ω_{pl} vs βR , where ω_{pl} is the electron plasma frequency and β is the axial wave number) of the surface wave (Ref. 8). The phase diagrams for two values of ν_{en}/ω (ν_{en} is the electron-neutral momentum transfer collision frequency), typical for the conditions considered, are presented.

The electromagnetic waves are coupled into the quartz tube via the launching gap of the surfaguide and they can travel in both directions (positive and negative) along the interface between the plasma and the tube. The discharge considered (positive direction of propagation) is sustained by the electric field of a surface wave, which simultaneously propagates and creates its own propagation structure. The wave power is progressively dissipated by the plasma electrons along the wave path and the absorbed power per unit length, as well as the electron density, decrease gradually toward the plasma column end. During its propagation, the wave follows the dispersion law shown in Fig. 1(b). In accordance with the experimental observations, the wave starts propagating with normalized wave numbers of approximately $\beta R \approx 0.5$ – 0.6 , then βR increases until it reaches a “turning point” (due to collisional effects) and decreases to approximately the same value of βR as the initial one.^{13,15} Under the present conditions, this corresponds to a decrease in electron density from about $(8\text{--}5) \times 10^{12}$ cm⁻³ ($\omega/\omega_{pl} \approx 0.2$ – 0.25 , where ω_{pl} is the electron plasma frequency) at the beginning of the plasma column to about $(2\text{--}3) \times N_{cr}$ ($N_{cr} \approx 7.4 \times 10^{10}$ cm⁻³) at the column end. At a distance of 3 cm from the launcher the electron density is in the range 2×10^{12} – 5×10^{12} cm⁻³ for the different mixture compositions used.

As is well known, the mean energy needed to create an

electron-ion pair in microwave discharges varies significantly in different gases.¹⁶ Therefore, different power densities are necessary to sustain a plasma column of the same length (~ 7 cm) for all the conditions considered here. Taking into account the total power delivered to the launcher and subtracting the reflected power, one can estimate the average absorbed power per unit volume. It varies from about $0.5\text{--}3$ W/cm³, when the hydrogen percentage changes from 5 to 70% in Ar–H₂ mixtures, and from 2.8 to 5 W/cm³ when the H₂ percentage ranges from 5 to 85% in He–H₂ mixtures. For electron densities in the range $(3\text{--}5) \times 10^{12}$ cm⁻³ in Ar–H₂ and $(2\text{--}2.5) \times 10^{12}$ cm⁻³ in He–H₂ mixtures, the mean power needed to create an electron-ion pair can roughly be estimated: it is about $(6\text{--}8) \times 10^5$ eV/s and $(1\text{--}8) \times 10^7$ eV/s in Ar–H₂ and He–H₂, respectively. These are typical values for microwave discharges.¹⁶ By applying the local power balance equation, an estimation of the microwave electric field intensity sustaining the discharge can readily be made.¹⁷ It ranges nearly from 23 to 30 V/cm in Ar–H₂ and from 70 to about 100 V/cm in He–H₂.

The optical system used consists of a 1.25 m focal length (visible light) Jobin–Yvon Spex 1250 spectrometer, with a holographic ruled diffraction grating (2400 g mm⁻¹) that provides a nearly flat response between 300 and 800 nm, equipped with a liquid-nitrogen cooled charge coupled device camera. The slit was set at 10 μ m in all cases. The light emitted by the plasma is collected perpendicularly to the discharge tube axis by an imaging optical fiber. A collimator located in front of the optical fiber defines the discharge volume from where the plasma radiation is collected. The measurements correspond to some radially averaged value over the plasma cross-section. It should be noted, however, that the central part gives the main contribution to the integral intensity detected. The optical fiber was placed at a distance $\Delta z = 3$ cm from the front line of the launcher. The plasma emission in the 300–800 nm range has been investigated. The spectral profiles of the H α , H β , H γ , H δ , H ϵ , and H ζ lines, corresponding to the transitions H[($n=3\text{--}8$) $\rightarrow$ ($n=2$)] have been measured. In a series of independent measurements, the H₂ rotational temperature has been determined using the Q-branch of the Fulcher- α band rotational spectrum [$d^3\Pi_u(v=1) \rightarrow a^3\Sigma_g^+(v=1)$] in the 600–617 nm wavelength range. The temperature corresponding to the Doppler broadening of He singlet line at 667.8 nm was also determined.^{8,9} The latter temperatures can be taken as a measure of the background gas temperature. The line intensities have been corrected for the spectral response of the overall system.

The measured Balmer line profiles have been fitted by a Voigt function, which results from the convolution of a Gaussian profile (due to Doppler and instrumental broadening) with a Lorentzian profile (due to Stark and instrumental broadening). A GRAMS/32[®] software has been used to this end. Therefore, the Lorentzian ($\Delta\lambda_L$) and Gaussian full widths at half maximum ($\Delta\lambda_G$) have been separated. The quality of the fitting is demonstrated in Fig. 2 where a comparison between experimental and calculated Voigt spectra is shown for different conditions. The fittings so achieved are very good, as $R^2 > 0.99$ and RMS errors less than 5% are

FIG. 2. (Color) Measured profiles of Balmer lines fitted with a Voigt profile: (a) H_{ζ} line measured in Ar(50%)–H₂(50%) mixture; (b) H_{ϵ} line measured in He(85%)–H₂(15%) mixture; (c) H_{ζ} line measured in pure H₂ discharge. The Lorentzian and Gaussian widths extracted from the fitting are shown together with the corresponding errors (in brackets). The instrumental broadening is included. The Voigt width is calculated from Gauss and Lorentz widths according to (Ref. 18). The correlation R^2 and root mean square (RMS) error are indicated.

achieved. Since the Gaussian and Lorentzian widths so obtained include a contribution of the instrumental function, an accurate estimation of the latter has been made using a krypton spectral lamp (Frederiksen SR-Kr). The instrumental profile is very well fitted by a Voigt function (the Voigt full width at half maximum is 7.1 p.m.).¹⁸ The Gaussian and the Lorentzian widths of the instrumental Voigt function have been determined for a large number of Kr lines in the spectral range 400–800 nm and taken into consideration.

Typical values of the measured Lorentzian ($\Delta\lambda_L$) and Gaussian widths ($\Delta\lambda_G$) of the Balmer spectral lines when the instrumental broadening is subtracted are presented in Tables I and II for different conditions. As can be seen, $\Delta\lambda_L$ increases with the upper level principal quantum number, as expected when Stark broadening is in play (assuming Stark broadening results in a Lorentzian profile). The largest $\Delta\lambda_L$ value is obtained in Ar(95%)–H₂(5%) discharge, where the electron density reaches higher values (up to 5×10^{12} cm⁻³). The electron density corresponding to the obtained $\Delta\lambda_L$ of H_{γ} is about $(3\text{--}3.5) \times 10^{12}$ cm⁻³ (using the extrapolation of the theory given in Ref. 19), in close agreement with the predictions based on the wave dispersion law.

Moreover, a subtractive procedure has been applied in order to determine the “pure” Doppler broadening in the Gaussian part, taking into account the fine structure of the Balmer lines.²⁰ The fine structure splitting consists of seven closely related components corresponding to transitions between sublevels s , p , and d . Each line is Doppler broadened so that the actual spectrum is the sum of seven Gaussians. As is known, when the kinetic temperature decreases the fine structure splitting starts to influence the Balmer lines shape. Figure 3 presents calculated H_{γ} line spectra corresponding to the transition $H(n=5) \rightarrow H(n=2)$ for eight different kinetic temperatures. As seen, for temperatures lower than about 1000 K the fine structure splitting must be taken into account. The corresponding temperatures have been determined from Doppler broadening assuming a Maxwellian distribution of the atoms according to the well known formula

$$\Delta\lambda_D = 7.16 \times 10^{-7} \lambda \sqrt{\frac{T}{M}}, \quad (1)$$

where M is the atomic mass and λ is the central wavelength.

The temperature of the gas molecules was determined from measurements of the rotational distribution of excited molecular bands of H₂. The rotational temperature provides a measure of the gas temperature if the rotational relaxation time by collisions is much smaller than the radiative lifetime. In this case, the rotational distribution is close to a Boltzmann distribution with a temperature equal to the translational temperature of the mixing particles. In the present work, the rotational temperature measurements were performed using the Q branch of the Fulcher- α rotational spectrum [$a^3\Sigma_g^+(v'=1) \rightarrow d^3\Pi_u(v=1)$] in the range near 615 nm. For example, Fig. 4 shows the hydrogen molecule emission in the wavelength range of 611–617 nm. For the $d^3\Pi_u$ state, the small value of the spin-orbit interaction constant implies that the triplet splitting is negligible, which corresponds to a nearly pure Hund’s case b coupling. The $a^3\Sigma_g^+$ state is well described by a pure Hund’s case b coupling and the rota-

TABLE I. Lorentz and Doppler widths (in pm) derived from Voigt fitting of Balmer emission lines in He-H₂ mixtures and pure hydrogen. The instrumental broadening is subtracted. The errors are shown in brackets.

% H ₂	$\Delta\lambda$ [pm]	H _{γ}	H _{δ}	H _{ϵ}	H _{ζ}
5%	$\Delta\lambda_L$	...	~1.5	~2.2	...
	$\Delta\lambda_G$	14.5(24%)	14.2(25%)	13.9(25%)	...
30%	$\Delta\lambda_L$	...	~1	~1.2	...
	$\Delta\lambda_G$	15.5(23%)	15.5(17%)	16.7(16%)	...
100%	$\Delta\lambda_L$	...	~1	~1	2.2(48%)
	$\Delta\lambda_G$	15.7(16%)	16(16%)	17.1(16%)	18.2(10%)

tional fine structure can be neglected. When the rotational distribution follows Boltzmann's law, the line intensity can be written as¹¹

$$I_{\text{em}} \propto (2N+1)(2\Gamma+1)\exp\left(-\frac{B_v N(N+1)hc}{kT_{\text{rot}}}\right).$$

It is generally accepted that the rotational constant of the ground state B_v can be considered instead of that of the excited state. Here, Γ is the total nuclear spin; $\Gamma=0$ for the parastate H₂ and $\Gamma=1$ for the orthostate H₂. The rotational lines alternate in intensity due to the statistical weight $2\Gamma+1$ ($\Gamma=0$ and $\Gamma=1$ for N even and odd, respectively). The rotational temperature is experimentally determined by plotting $\ln I_{\text{em}}/(2N+1)(2\Gamma+1)$ as a function of $N(N+1)$. The rotational distribution of the line intensities of the Fulcher α band nearly follows Boltzmann's law as seen in Fig. 4. The rotational temperature is calculated taking into account the Hönl-London factors.¹¹

III. RESULTS AND DISCUSSION

Figure 5 shows the measured rotational temperatures and the kinetic temperature derived from the broadening of the 667.8 nm singlet He line ($3^1D \rightarrow 2^1P$ transition) for He-H₂ plasmas with different fractional compositions. The measurements are made at a fixed axial position $\Delta z=3$ cm. The He line profile is well fitted by a Voigt function and the temperature has been determined as usual from the measured full width at half maximum of the line intensity. The instrumental full width at half maximum has also been deconvoluted. The values of T_{rot} corresponding to the transition [$d^3\Pi_u(v=1) \rightarrow a^3\Sigma_g^+(v=1)$] vary between 900 and 1100 K. It should be emphasized that the Doppler temperature corresponding to the helium 667.8 nm singlet line ranges between 900 and 1100 K for the same conditions as seen in the figure. Upon inspection of the figure, it is clear that the Doppler tempera-

tures are close to the rotational ones. Thus, these temperatures can be assumed as indicative of the gas temperature in the He/H₂ mixture.

A significant amount of data was collected in order to reliably detect trends in the Balmer line broadening in H₂, He-H₂, and Ar-H₂ microwave plasmas. Data on line broadening were systematically collected for the Balmer ($\alpha, \beta, \gamma, \delta, \epsilon, \zeta$) lines corresponding to the transitions $H[(n=3-8)] \rightarrow H[(n=2)]$ at fixed axial position $\Delta z=3$ cm from the launcher (see Fig. 1). The length of the generated plasma column is about 7 cm.

The variation of the kinetic temperatures for the He(70%)-H₂(30%) mixture and pure H₂ are shown in Figs. 6 and 7. A striking result is observed from these figures: hydrogen atoms excited in higher levels are hotter than those in the lower ones. For example, the kinetic temperature of $H(n=8)$ is higher than that of $H(n=4)$. As seen, the increase in kinetic temperature with the upper level principal quantum number is a systematic trend. What can be the reason for such a behavior? Keeping in mind the microwave electric field intensity values, the measured Gaussian width may be influenced by Stark splitting due to the microwave electric field. The linear Stark splitting caused by a microwave field with an average intensity $\langle E \rangle = E_0/\sqrt{2}$ (assuming that the microwave field at 2.45 GHz acts as a dc field) induces a broadening ΔE of the Balmer lines [$n \rightarrow 2$] given by²¹

$$\Delta E_n \text{ (eV)} \approx 7.9 \times 10^{-9}(n^2 - 4) \times \langle E \rangle \text{ (V/cm)}.$$

This extra broadening induces an error in determining the "pure" Doppler temperature. The results shown with triangles in Figs. 6 and 7 are the calculated kinetic temperatures when Stark splitting is taken into consideration and subtracted, assuming the highest value of the electric field intensity, i.e., 100 V/cm. As seen, the temperature increase with the upper level principal quantum number still remains.

TABLE II. Lorentz and Doppler widths (in pm) derived from Voigt fitting of Balmer emission lines in Ar-H₂ mixtures. The instrumental broadening is subtracted. The errors are shown in brackets.

% H ₂	$\Delta\lambda$ [pm]	H _{γ}	H _{δ}	H _{ϵ}	H _{ζ}
5%	$\Delta\lambda_L$	~1.8	~1.7	12(35%)	...
	$\Delta\lambda_G$	13.6(32%)	13.9(25%)	7.9(50%)	...
14%	$\Delta\lambda_L$	~1.6	~1.6	7.7(41%)	...
	$\Delta\lambda_G$	13.7(25%)	13.8(19%)	10(32%)	...
70%	$\Delta\lambda_L$	...	~1.3	~2.2	4.2(64%)
	$\Delta\lambda_G$	14.2(25%)	14.1(25%)	13.8(25%)	13(20%)

FIG. 3. (Color) Fine structure influence on the H_γ line shape.

The observations may also be tentatively explained if one assumes that two group of excited H atoms with different temperatures, i.e., a “hot” and a “cold” group, are generated. As seen from Table I, increasing the H_2 percentage in He– H_2 mixtures leads to increasing values of the Doppler width ($\Delta\lambda_G$). The increase in the Gaussian width ($\Delta\lambda_G$) with the H_2 percentage can be strongly correlated with the generation of hot (H_h) hydrogen atoms due to electron impact dissociation of H_2 molecules and dissociative recombination processes $e+H_3^+\rightarrow H_2+H_h$. Note that simple estimations show that H_3^+ are the dominant ions in He– H_2 and H_2 plasmas under the present conditions.¹⁷ Due to the high electron temperature (3–5 eV) achieved in this type of discharge, dissociative recombination of electrons and H_3^+ can produce “hot” atoms excited at levels with principal quantum numbers as high as $n=7,8$. “Hot” excited H atoms can also be generated due to dissociation processes involving electrons and vibrationally excited H_2 molecules, such as

Here, H_2^* are hydrogen molecules excited in weakly bound electronic states with energy $\varepsilon = 17-19 \text{ eV} > \varepsilon_n + D_{H_2} + \Delta\varepsilon_k$, where ε_n are the excitation energies of the states $H(n=4-8)$, $D_{H_2}=4.48 \text{ eV}$ is the dissociation energy of hydrogen molecules and $\Delta\varepsilon_k=0.1-1.4 \text{ eV}$ is the kinetic energy shared by the two H atoms produced.

As is well known, the generated hot H atoms do not thermalize with the background gas under the present low pressure conditions.^{8,9,11} The group of “cold,” excited H atoms is generated by direct electron impact excitation from the ground state. At the end, the presence of these “hot” and “cold” atom fluxes may result in the observed increase of atomic temperature with the upper level principal quantum number. However, further investigations, both experimental and theoretical, are needed to elucidate this phenomenon.

Similar measurements have been performed in the Ar– H_2 mixture. The results obtained at the same axial position ($\Delta z=3 \text{ cm}$) and for different mixture compositions are

FIG. 4. (Color) Emission spectrum of the Fulcher- α band and corresponding Boltzmann plot of rotational line relative intensities measured in a pure H_2 plasma. The Boltzmann plot corresponds to the $d^3\Pi_u(v=1)\rightarrow a^3\Sigma_g^+(v=1)$ vibrational transition. FIG. 5. (Color) Atomic and rotational temperatures as a function of He– H_2 mixture composition measured at constant pressure ($p=0.36 \text{ Torr}$) and axial distance ($\Delta z=3 \text{ cm}$). The temperatures T_{1-1} correspond to the rotational line distribution within the $d^3\Pi_u(v=1)\rightarrow a^3\Sigma_g^+(v=1)$ vibrational transition. The stars correspond to the kinetic temperatures determined from Doppler broadening of the HeI 667 nm line. The plasma column length is approximately 7 cm for all the conditions considered. FIG. 6. (Color) Kinetic temperatures as a function of the upper level quantum number measured in He(70%)– H_2 (30%) plasma at pressure $p=0.36 \text{ mbar}$ and constant axial distance ($\Delta z=3 \text{ cm}$). Δ —taking into account Stark splitting.

FIG. 7. (Color) Kinetic temperatures as a function of the upper level quantum number measured in H_2 plasma at pressure $p=0.36$ mbar and constant axial distance ($\Delta z=3$ cm). Δ -taking into account Stark splitting.

presented in Fig. 8. As seen, no dependence of the hydrogen atom kinetic temperature on the upper level principal quantum number in Ar-H_2 mixture is observed, in contrast to the situation in pure hydrogen under the same operating conditions (i.e., pressure and microwave power supplied to the discharge). The same numerical procedure as used before was applied to determine the Gaussian part of the lines and the corresponding temperatures. The measured translational temperatures have nearly the same value (of about 1400 K) for all atoms H ($n=4-8$). The measured rotational temperatures corresponding to the vibrational transitions [$d^3\Pi_u(v=1) \rightarrow a^3\Sigma_g^+(v=1)$], which are shown in Fig. 9, are slightly below the kinetic temperatures of hydrogen atoms. In this case, hydrogen atoms are nearly thermalized with the background gas, contrary to the situation found in H_2 and He-H_2 mixtures.

Population inversion of excited atomic hydrogen has previously been observed in low-pressure water-vapor microwave plasmas from the relative intensities of the transitions within the Lyman and the Balmer series.²² A search for such a population inversion was also conducted here for H_2 , He-H_2 , and Ar-H_2 plasmas. To this end, the Balmer lines

FIG. 8. (Color) Kinetic temperatures as a function of the upper level quantum number measured in Ar-H_2 plasmas for different mixture compositions, constant pressure $p=0.36$ mbar and constant axial distance ($\Delta z=3$ cm). The plasma column length is nearly 7 cm at all the conditions considered.

FIG. 9. (Color) Rotational temperatures as a function of Ar-H_2 mixture composition measured at constant pressure ($p=0.36$ Torr) and axial distance ($\Delta z=3$ cm). The temperatures T_{1-1} correspond to the rotational line distribution within the $d^3\Pi_u(v=1) \rightarrow a^3\Sigma_g^+(v=1)$ vibrational transition. The plasma column length is approximately 7 cm for all the conditions considered.

have been analyzed. The resulting Boltzmann plots for He-H_2 and Ar-H_2 mixtures are shown in Figs. 10 and 11. The data are collected at a distance of 3 cm from the launcher for different mixture compositions. Results for pure hydrogen are also plotted as a reference. These plots show the relative line intensity divided by the corresponding transition probability and level degeneracy versus the excitation energy of the level n . As seen from these figures, no inversion of population is observed, but the deviations of the upper levels from a straight line plot indicate that the population density distribution is out of equilibrium. The distribution temperatures for the lower levels are approximately 1,500 (0.13 eV) and 1,400 K (0.12 eV) for He-H_2 and Ar-H_2 plasmas, respectively.

IV. CONCLUSIONS

Emission spectroscopy was used for the diagnostic of a surface wave sustained microwave plasma operating in helium-hydrogen and argon-hydrogen mixtures, and in pure hydrogen at low-pressure. The Doppler temperatures corresponding to the helium singlet line at 667.8 nm ($3^1D \rightarrow 2^1P$ transition) are the same as the rotational temperatures determined from the Q-branch of the Fulcher- α band

FIG. 10. (Color) Population distribution of hydrogen atoms in He-H_2 plasmas ($p=0.36$ mbar, $\Delta z=3$ cm) measured for different percentages of H_2 in He-H_2 mixture. The percentage of H_2 increases from 5% to 85% in the mixture (marked with an arrow). Data obtained in pure hydrogen plasma (100%) are also given as a reference.

FIG. 11. (Color) Population distribution of hydrogen atoms in Ar-H₂ plasmas ($p=0.36$ mbar, $\Delta z=3$ cm) measured for different percentages of H₂ in Ar-H₂ mixture. The percentage of H₂ increases from 5% to 85% in the mixture (marked with an arrow). The data obtained in pure hydrogen plasma (100%) are also given as a reference.

$[d\ ^3\Pi_u(v=1) \rightarrow a\ ^3\Sigma_g^+(v=1)]$ under the same conditions. The present results demonstrate that the kinetic temperature of emitting H atoms is higher than the background gas temperature in He-H₂ and H₂ plasmas. H atoms excited at higher electronic levels appear to be hotter than those in lower levels, i.e., an increase of kinetic temperature with upper level principal quantum number is observed in He-H₂ and H₂ plasmas. Note that, in contrast, no such dependence has been observed in the Ar-H₂ discharge. Work is in progress to investigate this effect under conditions of negligible Stark effect and to model the phenomena observed here. Finally, note that no population inversion was found in the present work from measurements of the relative intensities of transitions within the Balmer series, for all the conditions considered.

ACKNOWLEDGMENTS

This study was funded by FCT/FEDER through the project “Ecological Plasma Laboratory” POCI/FIS/61679/

2004. Useful discussions with Professor Boris Gordiets and Dr. Mário Lino da Silva are greatly acknowledged.

- ¹S. Djurovic and J. R. Roberts, *J. Appl. Phys.* **74**, 6558 (1993).
- ²M. R. G. Adamov, B. M. Obradovic, M. M. Kuraica, and N. Konjevic, *IEEE Trans. Plasma Sci.* **31**, 444 (2003).
- ³N. Cvetanovic, M. M. Kuraica, and N. Konjevic, *J. Appl. Phys.* **97**, 033302 (2005).
- ⁴J. Phillips and C. Ku Chen, *Int. J. Hydrogen Energy* **33**, 7185 (2008).
- ⁵G. Baravian, Y. Chouan, A. Ricard, and G. Sultan, *J. Appl. Phys.* **61**, 5249 (1987).
- ⁶R. Mills and P. Ray, *J. Phys. D* **36**, 1535 (2003).
- ⁷S. Jovicevic, M. Ivkovic, N. Konjević, S. Popovic, and L. Vuskovic, *J. Appl. Phys.* **95**, 24 (2004).
- ⁸E. Tatarova, F. M. Dias, C. M. Ferreira, and N. Puac, *J. Appl. Phys.* **101**, 063306 (2007).
- ⁹E. Tatarova, F. M. Dias, N. Puac, and C. M. Ferreira, *Plasma Sources Sci. Technol.* **16**, S52-S56 (2007).
- ¹⁰S. Jovicevic, N. Sakan, M. Ivkovic, and N. Konjević, *J. Appl. Phys.* **105**, 013306 (2009).
- ¹¹L. Tomasini, A. Rousseau, G. Gousset, and P. Leprince, *J. Phys. D* **29**, 1006 (1996).
- ¹²C. Oliveira, J. A. Souza Correa, M. P. Gomes, B. N. Sismanoglu, and J. Amorim, *Appl. Phys. Lett.* **93**, 041503 (2008).
- ¹³F. M. Dias, E. Tatarova, and C. M. Ferreira, *J. Appl. Phys.* **83**, 4602 (1998).
- ¹⁴M. Moisan, M. Chaker, Z. Zakrzewski, and J. Paszczak, *J. Phys. E* **20**, 1356 (1987).
- ¹⁵E. Tatarova, F. M. Dias, C. M. Ferreira, and A. Ricard, *J. Appl. Phys.* **85**, 49 (1999).
- ¹⁶C. M. Ferreira, L. L. Alves, M. Pinheiro, and A. B. Sá, *IEEE Trans. Plasma Sci.* **19**, 229 (1991).
- ¹⁷B. Gordiets, M. Pinheiro, E. Tatarova, F. M. Dias, C. M. Ferreira, and A. Ricard, *Plasma Sources Sci. Technol.* **9**, 295 (2000).
- ¹⁸M. Lino da Silva, *J. Quant. Spectrosc. Radiat. Transf.* **108**, 106 (2007).
- ¹⁹P. Kepple and H. R. Griem, *Phys. Rev.* **173**, 317 (1968).
- ²⁰B. P. Lavrov, M. Kaning, V. L. Ovtchinnikov, and J. Ropcke, Proceedings of Frontiers in Low Temperature Plasma Diagnostics II, Bad Honnef, Germany, 17–21 February 1997 (unpublished), pp. 169–172.
- ²¹H. R. Griem, *Spectral Line Broadening by Plasmas* (Academic, New York, 1974).
- ²²R. Mills, P. Ray, and R. Mayo, *Appl. Phys. Lett.* **82**, 1679 (2003).