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Energetic Hydrogen Atoms in High Frequency Plasmas

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Abstract. Generation of energetic hydrogen atoms, with energy in the range 4−8 eV, was detected throughout the volume of a surface wave generated (500 MHz) plasma column in H₂ at pressure \( p = 0.01 \) mbar. The H\( β \), H\( γ \), H\( δ \), and H\( ε \) line profiles were found to be bi-Gaussian towards the plasma column end. The kinetic temperatures corresponding to the Doppler broadening of the H\( β \), H\( γ \), H\( δ \), lines are higher than the rotational temperature of the hydrogen molecular Fulcher-α band and the wall temperature. At pressure \( p = 0.2 \) mbar, the kinetic temperature of excited H (\( n = 4−7 \)) atoms, as determined from the fitting of the spectral lines with a single-Gaussian profile, increases with upper level principal quantum number. The experimental results have been analyzed in the framework of a global self-consistent kinetic model describing this surface wave sustained plasma column.

1. Introduction

The analysis of Balmer line shapes has usually been applied to detect energetic hydrogen atoms in various types of gas discharges [1, 2]. The presence of such atoms results in extended “wings” in the line profiles. The Balmer lines spectra emitted by different types of DC glow and RF discharge plasmas have typical multimode behaviour, i.e., they exhibit widely broadened “wings” and a sharp top [3, 4]. Different processes and mechanisms can be at the origin of such phenomena. Usually two or three components of the line profiles may be clearly distinguished [4]. The central, narrow component originates from low-energy dissociative excitation and direct electron impact excitation processes. Collisions of highly energetic electrons with vibrationally excited H\( 2 \) molecules result in dissociative excitation, whose products may have high kinetic energies depending on the molecular state [1]. Dissociative broadening contributes to the overall processes, but it does not explain far-lying “wings” found in some DC and RF discharges, corresponding to fast atoms with kinetic energies of hundreds of electron volts. Since high DC electric fields are present in near-electrode sheaths, excessive broadening may result from acceleration of charges such as H\(^+\), H\(_3\)\(^+\) ions, with subsequent conversion into fast neutrals. Two sources of these fast atoms have been suggested, viz., charge exchange collisions between fast ions and the background H\(_2\) gas molecules producing energetic atoms that move towards the electrode and the formation of energetic H atoms at the electrode surface due to fast ion bombardment [4–7]. Microwave and HF discharges are, however, free of such strong DC electric fields and the radiated profiles usually exhibit single mode behaviour [8, 9]. Nevertheless, generation of fast H atoms, with energies in the range 2–4 eV, in microwave plasma has also been reported in [10]. In a series of works, selective hydrogen line broadening has been detected in microwave...
discharges and its afterglows when there is no significant broadening of noble gas lines or hydrogen molecular lines [8, 11, 12].

This study presents spectroscopic measurements of Balmer lines emitted by a surface wave sustained high frequency H\textsubscript{2} plasma source operating at $\omega/2\pi = 500$ MHz and low pressure conditions (0.01–0.3 mbar). Results on the line shape and the emission intensities of excited H($n = 4$–$7$) hydrogen atoms, and the emission intensities of the Q-branch of the Fulcher-α band [$d^3\Pi_u (v = 0) \rightarrow a^3\Sigma_g^+ (v = 0)$] are presented and discussed. Bi-Gaussian shape of the H\textsubscript{β}, H\textsubscript{γ}, H\textsubscript{δ}, H\textsubscript{ε} lines detected at a pressure $p = 0.01$ has been observed. Different average energies have been determined from the measured Balmer lines and the rotational distribution of hydrogen molecular lines. The results are analyzed in the framework of a previously developed self-consistent model describing the entire discharge structure [13]. This model couples in a self-consistent way wave electrodynamics, electron and heavy particles kinetics, and gas thermal balance (see [13] for details).

2. Experimental set-up and conditions

A classical surface wave sustained discharge has been used as a plasma source. The discharge is created using a surfatron-based set-up (figure 1) [14]. The microwave power is provided by a 500 MHz generator, whose output power was varied from 40 to 250 W. The discharge takes place inside a Pyrex tube with internal and external radii of 2.25 and 2.5 cm, respectively (figure 1).

![Figure 1. Experimental set-up](image)

The background gas is injected into the discharge tube at flow rates from 0.4 to 20 sccm under laminar gas flow conditions. The electromagnetic surface waves are coupled into a Pyrex tube via the launching gap of a surfatron and travel along the interface between the plasma and the tube. The discharge is sustained by the wave electric field. The wave 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 towards the plasma column end. Under the present conditions, this corresponds to a decrease
in electron density from about \((1−1.5) \times 10^{10} \text{ cm}^{-3}\) at the beginning of the plasma column to about \((2−3) \times N_{\text{cr}} \ (N_{\text{cr}} \approx 3.09 \times 10^{9} \text{ cm}^{-3})\). 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 ranges in the limits 0.1–0.2 W/cm³. Estimations indicate that the effective electric field intensity sustaining the discharge ranges from about 5 V/cm to 10 V/cm.

The optical system used consisted of a 1.25 m focal length (visible light) Jobin-Yvon Spex 1250 spectrometer, with a holographic ruled diffraction grating \((2400 \text{ g/mm}^{-1})\) that provides a nearly flat response between 300 and 800 nm, equipped with a liquid-nitrogen cooled CCD camera. The slit was set at 10 μm in all cases. The light emitted by the plasma is collected perpendicularly to the discharge tube axis by a bundle optical fibre. The measurements correspond to some radially averaged value over the plasma cross-section. The spectral profiles of the \(H_\beta, H_\gamma, H_\delta, H_\epsilon\) lines, corresponding to the transitions \(H[(n = 4−7) \rightarrow (n = 2)]\) have been measured. The temperature of the gas molecules was determined from measurements the \(H_2\) rotational temperature using the Q-branch of the Fulcher-α band rotational spectrum \([\sigma^3 I_0 (v=0) \rightarrow \sigma^3 \Sigma_g^+ (v=0)]\) in the 600–617 nm wavelength range [8].

![Graphs showing Balmer lines fitted with Gaussian profiles](image)

**Figure 2.** Measured profiles of Balmer lines fitted with Gaussian profiles: (a) \(H_\gamma\) line; (b) \(H_\beta\) line.

### 3. Results and discussion

In general, the experimental profile is a convolution of the Doppler, instrumental, natural (lifetime), Stark, van der Waals, and resonance profiles and of fine structure [15]. The instrumental function width was determined to be \(\Delta \lambda_{\text{app}} = 0.04 \text{ Å} \). Taking into account the typical electron densities and microwave electric field intensities for the present conditions, Stark, van der Waals and resonance broadening may be ignored. So, we can assume that the experimental profiles are a convolution of the Doppler and instrumental profiles. In order to determine the “pure” Doppler broadening, the fine structure of the Balmer lines has also been taken into account [16]. The measured profiles of the \(H_\beta, H_\gamma, H_\delta, H_\epsilon\) lines (\(H_\beta\) is critical because of self-absorption) are well fitted by single- or two- Gaussian profiles (much better than by a Voigt profile) as shown in figures 2(a, b). GRAMS/32® and Mat Lab based software have both been used for this fitting. The bi-Gaussian profiles are observed at the lower pressures (figure 2(a)), but when pressure increases up to 0.2 mbar the broad base disappears and the bi-Gaussian profiles become single ones (figure 2(b)). At low pressures, the broad base is observed to develop downstream, as the distance from the launcher increases (figure 3). After such fittings, the average kinetic energies corresponding to Doppler broadening have been determined assuming Maxwellian energy distributions. A cascade approximation [17] has been applied to obtain the average kinetic energy corresponding to \(H_\gamma\) Doppler broadening.
The axial variation of the fractional population of energetic atoms in the level \( n = 5 \) is shown in figure 4, for a pressure of 0.01 mbar. Figure 5 shows the axial variation of the atomic kinetic temperature as inferred from the analysis of the H\(_{\gamma}\) line, at 0.2 mbar pressure. Also shown here for comparison is the theoretical prediction from the model of reference [13].

The axial variation of the rotational temperature corresponding to the rotational band of the transition \( \text{d}^3\text{T}_u (\nu = 0) \rightarrow \text{a}^3\Sigma_g^+ (\nu = 0) \) is shown in figure 6, for the same conditions as in figure 5. Also shown for comparison is the axial variation of gas temperature predicted by the theoretical model as well as that of the wall temperature, obtained from infrared sensitive measurements using an optical thermometer. As seen from figures 5 and 6, the measured rotational temperatures are much lower than the atomic ones, which brings evidence for selective heating of H(\( n = 5 \)) atoms.

![Figure 3. Axial evolution of H\(_{\gamma}\) line (\( p = 0.01 \) mbar; \( L = 45 \) cm)](image)

![Figure 4. Axial variation of the fractional density of energetic excited atoms (\( n = 5 \))]
Data on the Balmer ($\beta, \gamma, \delta, \varepsilon$) line broadening have been recorded at fixed axial position $\Delta z = 15$ cm from the launcher at pressure $p = 0.2$ mbar. The length of the plasma column is 16 cm under such conditions. The kinetic temperatures determined from these lines are shown in figure 7. A striking result is observed: hydrogen atoms excited in higher levels appear to be hotter than those excited in lower ones. For example, the kinetic temperature of $H(n = 7)$ is higher than that of $H(n = 4)$. Let us try to find out the reason for such behaviour. Linear Stark splitting caused by a high frequency field with
an average intensity $\langle E \rangle = E_0 / \sqrt{2}$ (assuming that the microwave field at 500 MHz acts as a dc field) induces the following broadening $\Delta E$ of the Balmer lines $[n \to 2] [17]$

$$\Delta E_n (eV) \approx 7.9 \times 10^{-9} (n^2 - 4) \times \langle E \rangle [V/cm] \tag{1}$$

This broadening will add some additional “splitting temperature” to the Doppler temperature, i.e., some error in determining the “pure” Doppler temperature may occur. However, estimations show that this additional “splitting” temperature varies in only the range 5–50 K for the different levels, for a field $\langle E \rangle = 5–10$ V/cm. For example, for the level $n = 7$, for which the Stark effect is maximum, the error is less than 50 K, i.e., less than 5 %. For the lower levels the error is still much smaller. Hence, Stark splitting has negligible influence under the present conditions.

![Figure 7. Doppler temperatures of H($n = 4–7$) as a function of the upper level quantum number at pressure $p = 0.20$ mbar and axial distance $\Delta z = 15$ cm [$T_{gas} = 347$ K; $T_{vib} = 4840$ K; $kT_e = 3.48$ eV, $N_e = 1 \times 10^{10}$ cm$^{-3}$; [H]/[H$_2$] = 7.86 %; $E_{eff} = 5.02$ V/cm].](image)

The observed result can be tentatively explained if one assumes that three groups of excited H atoms are generated, viz., and “energetic”, a “warm” and a “cold” group, originating from different electron induced processes. “Cold” excited hydrogen atoms, with a temperature nearly equal to that of the background gas, are generated by direct electron impact excitation of ground state atoms:

$$H(1) + e \to H(n \geq 2) + e. \quad (R1)$$

“Warm” excited H atoms can be generated by dissociation processes involving electrons and vibrationally excited H$_2$ molecules, viz.,

$$H_2(X, v = 1–4) + e \to H_2^* (\epsilon = 17–19 \text{ eV}) + e \to H_{hot}(n = 1) + H_{hot} (n = 4–8) + e. \quad (R2)$$

Here, H$_2^*$ are hydrogen molecules excited in weakly bound electronic states, with energy $\epsilon = 17–19$ eV $> E_a + D_{112} + \Delta \epsilon_k$, where $E_a$ are the energies of the excited H($n = 4–8$) atoms, $D_{112} = 4.48$ eV is the dissociation energy of hydrogen molecules and $\Delta \epsilon_k = 0.1–1.8$ eV is the range of kinetic energies of the two H atoms resulting from dissociation. The total kinetic energy is therefore $\langle \Delta \epsilon_{kin} \rangle \approx \Delta \epsilon_{kin} / 2 \approx 0.9$
eV, on the average. These processes can be effective for the high electron temperature (up to 6 eV) and vibrational temperature of H₂(X) molecules, which are typical under the present conditions. Thus, there is a high population in the vibrational levels v = 1–4, for which the transitions (R2) have relatively large Frank-Condon coefficients.

Finally, the group of energetic H (n = 4–7) atoms is likely to be generated from wall electron-ion recombination. Close to the wall, the H⁺ ions are accelerated in a space charge sheath and, thus, may acquire high kinetic energy as they fall on the wall. These ions recombine with electrons at the wall and may return back to the gas as fast excited atoms, with kinetic energy \( e = E_{ion} + I - E_{e} \) (here, I is the ionization energy). At low pressures, the ion mean-free path \( \lambda \) is larger than the radius (for H⁺ with energy \( E_{ion} \geq 0.5 \text{ eV} \), \( \lambda \approx 3 \text{ cm at 0.01 mbar} \)), therefore H⁺ ions acquire a kinetic energy equal to the radial potential energy drop, which is of the order of the electron temperature (4–6 eV). As pressure increases this ceases to be the case and energetic atoms disappear as we have observed.

At the higher pressure \( p = 0.2 \text{ mbar} \), there are therefore two groups of radiating H(n ≥ 2) atoms, a "warm" and a "cold" group, with kinetic temperatures \( T_{\text{warm}} \approx (2/3) \langle \Delta E_{\text{kin}} \rangle / 2 \) (R2) and \( T_{\text{cold}} \approx T_{g} \) (R1), respectively. The population distributions, \( N_{n}^{\text{warm}} \) and \( N_{n}^{\text{cold}} \), for both groups have been calculated in the framework of the above mentioned model [13]. The main radiative and collisional processes leading to population and depopulation of the energy levels for "warm" and "cold" atoms have been accounted for using a "single-quantum" approximation [17]. The following rate coefficient \( R_{n}^{\text{warm}} \) for generation of "warm" excited H atoms has been used:

\[
R_{n}^{\text{warm}} \approx k_{0} \times \exp \left( - \frac{E_{\text{ vib}}}{kT_{\text{ vib}}} \right) \times \exp \left( - \frac{17 - E_{\text{ vib}} + R_{Y}(1/16 - 1/n^{2})}{kT_{e}} \right) \times N_{e} \times [H_{2}] \tag{2}
\]

Here \( k_{0} \) is a constant; \( E_{\text{ vib}} = 0.54 \text{ eV} \) is the energy of the first vibrational level of H₂(X); \( T_{\text{ vib}} \) is the vibrational temperature of H₂(X) molecules; \( R_{Y} = 13.6 \text{ eV} \) is the Rydberg constant, \( N_{e} \) is the electron density and \([H_{2}]\) is the number density of hydrogen molecules. We assume that every "warm" atom has the average kinetic energy \( \langle \Delta E_{\text{kin}} \rangle / 2 \approx 0.45 \text{ eV} \), that is, the kinetic temperature of the ensemble of such atoms is \( T_{\text{warm}} \approx 3600 \text{ K} \). As to the rate coefficients for electron impact excitation of the levels \( n \geq 2 \) from the ground state \( n = 1 \), we assume that they scale approximately as \( n^{-3} \) [17].

It can now be shown that the interplay of the relative contributions of (R1) and (R2) can produce an increase in the temperature of the ensemble of both populations when \( n \) increases. The sum \( I_{n}(\lambda - \lambda_{n}) \) of two Gaussian profiles \( I_{n}^{\text{warm}}(\lambda - \lambda_{n}) \) and \( I_{n}^{\text{cold}}(\lambda - \lambda_{n}) \) with not strong (no more than a factor of \( \approx 5 \)) difference in temperatures \( T_{\text{warm}} \) and \( T_{\text{cold}} \) and with different relative intensities \( I_{n}^{\text{warm}} = N_{n}^{\text{warm}}/(N_{n}^{\text{warm}} + N_{n}^{\text{cold}}) \) and \( I_{n}^{\text{cold}} = N_{n}^{\text{cold}}/(N_{n}^{\text{warm}} + N_{n}^{\text{cold}}) \) \((I_{n}^{\text{warm}} + I_{n}^{\text{cold}} = 1 \text{ at } \lambda - \lambda_{n} = 0)\) can be approximated by a single Gaussian profile \( I_{\text{fit}}(\lambda - \lambda_{n}) \) with an ensemble temperature \( T_{n} \), that is,

\[
I_{n} = \frac{I_{n}^{\text{warm}}}{\sqrt{\pi aT_{\text{warm}}}} \exp \left[ - \frac{(\lambda - \lambda_{n})^{2}}{aT_{\text{warm}}} \right] + \frac{I_{n}^{\text{cold}}}{\sqrt{\pi aT_{\text{cold}}}} \exp \left[ - \frac{(\lambda - \lambda_{n})^{2}}{aT_{\text{cold}}} \right] \approx \frac{1}{\sqrt{\pi aT_{n}}} \exp \left[ - \frac{(\lambda - \lambda_{n})^{2}}{aT_{n}} \right] = I_{\text{fit}} \tag{3}
\]

Here, \( a = 1.85 \times 10^{-1} \lambda_{n}^{2} / \mu \), \( \mu \) is the mass of the radiating atoms (in atomic units), and the temperatures are expressed in K. The ensemble temperature \( T_{n} \) is given by:

\[
T_{n} = \left[ \left( \frac{I_{n}^{\text{warm}}}{T_{\text{warm}}} \right)^{2} + \left( \frac{I_{n}^{\text{cold}}}{T_{\text{cold}}} \right)^{2} + 2 \frac{I_{n}^{\text{warm}} I_{n}^{\text{cold}}}{\sqrt{T_{\text{warm}} T_{\text{cold}}}} \right]^{-1} \tag{4}
\]
As it can be readily seen, the increase of $T_n^{warm}$ from 0 to 1 leads to the change of $T_n$ from $T_n^{cold}$ to $T_n^{warm}$. It should be stressed that for $T_n^{warm} / T_n^{cold} \leq 5$ and $0.1 \leq I_{cold} \leq 0.9$ the mean square deviation between $I_{\lambda} (\lambda - \lambda_n)$ and $I_{FIT} (\lambda - \lambda_n)$ is much less than 5%. The calculated variations of kinetic temperature according to equation (4) are shown by the dashed line in figure 7. Good agreement between calculated and measured temperatures is obtained.

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