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ON THE USE OF ATOMIC HYDROGEN LINE SHAPES FOR THE EXCITED HYDROGEN ATOMS TEMPERATURE DETERMINATION IN A GLOW DISCHARGE

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Abstract. Stark splitting coupled with Doppler spectroscopy of the hydrogen H_β and H_γ lines is applied for simultaneous determination of local electric field and temperature of excited H atoms in the cathode fall region and in the beginning of the negative glow of Grimm-type glow discharge in pure hydrogen and in an argon-hydrogen mixture. Temperature measurements showed that, in pure hydrogen discharge, at least two groups of excited atoms exist: "slow", with average energies in the range from 3.4 eV to 8.2 eV and "fast", ranging between 80 eV and 190 eV. In argon-hydrogen discharge, excited hydrogen neutrals with average energies between 32 eV and 43 eV are detected only. The origin of these energetic neutrals is related to the presence of H^+ and H_3^+ ions in pure hydrogen, and to the dominant role of H_3^+ ion in argon-hydrogen mixture. For both gases, in the negative glow region, the increase of the exited hydrogen atoms temperature is detected and explanation suggested.

1. INTRODUCTION

Several studies of atomic-hydrogen line shapes in the vicinity of the cathode, in various types of glow discharges (Benesch and Li, 1984; Cappelly *et al.*, 1985; Baravian *et al.*, 1987; Li Ayers and Benesch, 1988; Barbeau and Jolly, 1990; Kuraica and Konjević, 1992; Lavrov and Melnikov, 1993), has shown Balmer lines shapes with an extraordinary wings development. The extensive far wings indicate the presence of excited hydrogen atoms with very high velocities. As shown by both theory and experiment (Petrović *et al.*, 1992 and references [4,10] therein), those energetic hydrogen neutrals originate from incident H^+, H, H_2^+, H_2 and H_3^+, whose backscattered fragments from the cathode are almost entirely H atoms. On their way back through the discharge, they collide mainly with matrix gas and excite (Kuraica and Konjević, 1994).

In this work, temperatures of excited hydrogen atoms are spectroscopically measured in the cathode fall and at the beginning of the negative glow region of the plane cathode and cylindrical hollow anode abnormal glow discharge of the Grimm-type (Grimm, 1968), operating in pure hydrogen and in argon with a small (3%) admixture of hydrogen. Experimental setup is fully described elsewhere (Kuraica *et al.*, 1992; Videnović *et al.*, 1996), so only minimum theoretical details will be given here for clearness.

In the cathode fall region, the presence of external electric field predominantly determines the shape of hydrogen Balmer lines. Therefore, the theory of polarization dependent Stark splitting has to be employed (see detailed explanation in Videnović *et al.*, 1996). Placing the polarizer parallel or perpendicular to the discharge axis, we have selected components with $\Delta m = 0$ or $\Delta m = \pm 1$ i.e. π or σ polarization, respectively. All components (10 - for the both H_β π and σ profiles, 14 and 13 - for the H_γ π and σ profiles, respectively) form the appropriate π or σ overall profile. In the cathode fall region, we assumed Doppler broadening only, since the plasma broadening effects in this region are negligible. Therefore, to each Stark component we have assigned a Gauss function only, which takes into account Doppler and instrumental broadening. Considering overall profile as the superposition of all Gaussians, we have fitted it to the experimental recordings, by varying the electric field intensity E and the temperature T of hydrogen atoms. In the negative glow region, the difference between π and σ profiles disappears ($E \approx 0$), and the fitting procedure is reduced to the variation of T only. Here we shall discuss only the best-fit temperature results.

To facilitate the above short review of the theoretical basis of our measurements, typical examples of the H_β and H_γ spectra recordings emitted from the cathode fall region of pure hydrogen discharge and their best fits are given in Fig. 1. Here it should be pointed out that, in the pure hydrogen discharge, best fits of experimental profiles are obtained assuming that two groups of excited hydrogen atoms exist: one with temperatures around 5 eV (so called "slow" neutrals) and another group with temperatures around 100 eV ("fast" neutrals). It is important to mention also, that by fitting a single experimental profile, results of local electric field, temperatures of "slow" T_s and "fast" T_f excited hydrogen atoms and their relative concentrations are obtained simultaneously, see Fig. 1.

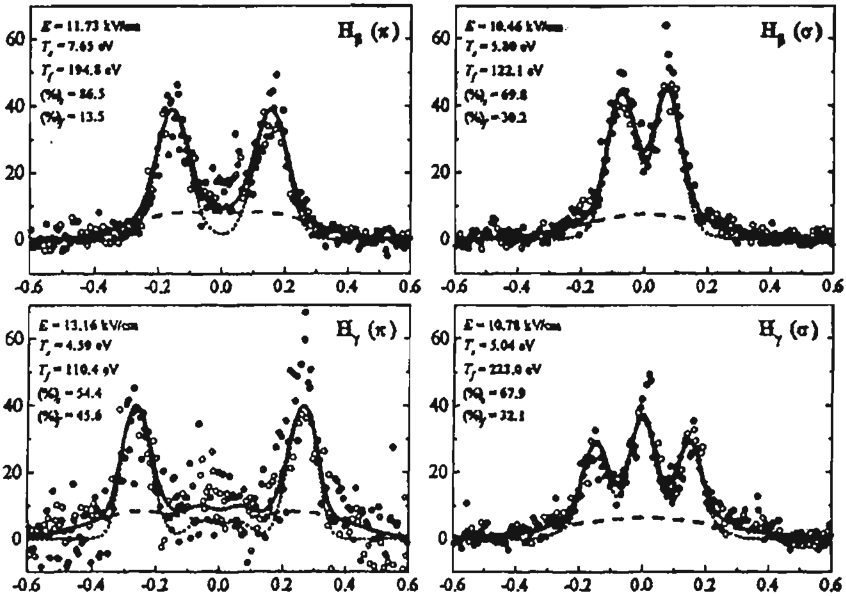

Fig. 1. Typical polarized H_β and H_γ profiles recorded at 0.025 cm from the cathode of the pure hydrogen discharge and their best fits (solid lines), obtained assuming that two groups of excited hydrogen atoms exist: "slow" (dotted lines) and "fast" (dashed lines). Intensities are given in a.u. On abscissa axis, relative wavelengths (in nm) are given. Discharge conditions: 228 Pa, 30 mA, 920 V.

2. RESULTS AND DISCUSSION

The measurements have been performed at pressures of 195, 228 and 250 Pa and discharge currents of 20, 30 and 40 mA in pure hydrogen, and 240, 320 and 425 Pa of argon-hydrogen mixture (97% Ar : 3% H_2), at currents of 20 and 30 mA.

The origin of two groups of excited hydrogen atoms in pure hydrogen discharge may be related to the presence of H^+, H_2^+ and H_3^+ ions which are accelerated in the cathode fall region. Striking the cathode, these ions are neutralized, fragmented into atoms and reflected back towards the negative glow region. After the reflection from the cathode, neutrals collide mainly with H_2 and excite, see e.g. Kuraica and Konjević (1994). It could be shown (Videnović *et al.*, 1996) that only two groups of hydrogen atoms, originated from H^+ and H_3^+ ions, have enough energy to exceed threshold for Balmer lines excitation. "Slow" H atoms, whose average temperatures in different experimental conditions vary in our case from 3.4 - 8.2 eV are, most likely, excited in collisions of hydrogen atoms from H_3^+ with H_2. On the other hand, the origin of "fast" excited H atoms, with average temperatures between 80 eV and 190 eV, may be related to energetic H^+ ions only, see Videnović *et al.*, 1996. The typical axial distributions of both "slow" and "fast" excited hydrogen atoms temperature are shown in Fig. 2. The temperature distributions show a decrease with the distance from the cathode, which corresponds well with decreasing energy of the reflected atoms. An unexpected rise of the temperature in the negative glow region, see Fig 2, could be related to the additional collision processes with electrons; whose concentration is rather large ($\approx 10^{14}$ cm^{-3}, see Kuraica *et al.*, 1992). Here, most likely, one has a superposition of profiles originating from two different excitation processes: one resulting from collisions with heavy particles, and another - collisions of fast neutrals with electrons. Assuming an exponential decrease of the number of reflected energetic atoms due to collisions with the matrix gas, a simple calculation using total cross section data (Phelps, 1990) for collisions of neutral hydrogen atoms at 133.4 eV with H_2 at $p = 228$ Pa, $T_g = 1000$ K and $L = 0.158$ cm shows that about 18% of the reflected "fast" H atoms arrive at the negative glow without a collision. In this region they collide with both electrons and matrix gas which results in two groups of excited atoms with different temperatures. Since electrons change the internal atom energy only, the group with larger temperature is the one from atom-electron collisions. Therefore, the resulting profile is broader than in the cathode fall region. Unfortunately, the spectral resolution (see Videnović *et al.*, 1996) does not allow us to separate these two profiles, and the results for average temperatures in the negative glow region in Fig. 2 represent some kind of an average value.

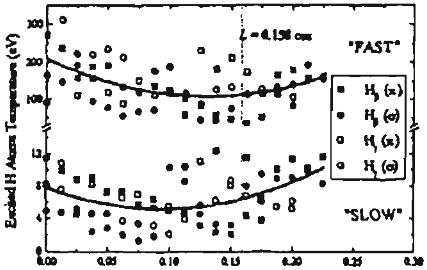

Fig. 2. Axial distribution of "slow" and "fast" excited hydrogen atoms temperature in the Grimm glow discharge operating in pure hydrogen at 228 Pa, 30 mA, 920 V.

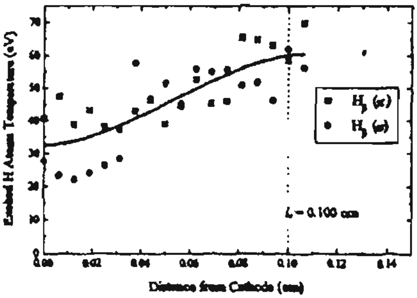

Fig. 3. Axial distribution of the excited hydrogen atoms temperature in the Grimm glow discharge, operating in the argon-hydrogen mixture at 320 Pa, 30 mA, 820 V.

The discharge in the argon-hydrogen mixture is, in comparison to pure hydrogen, located closer to the cathode, with smaller lengths of the cathode fall region. Due to the interference of the Ar I and Ar II lines with the hydrogen H_γ line in argon-hydrogen mixture, the measurements are performed using π and σ profiles of the H_β only. Contrary to pure hydrogen, here one cannot distinguish several groups of excited hydrogen atoms with different velocities in the procedure of H_β π and σ profiles fitting. Namely, only excited H atoms with energies in the range 32 - 43 eV exist. The overall profiles are smooth, without distinct characteristic peaks induced by "slow" excited atoms in pure hydrogen, see Fig. 1. It is very interesting to note that the temperatures of excited hydrogen atoms in the argon-hydrogen mixture are between those of "slow" and "fast" atoms in pure hydrogen. In the gas mixture, the role of argon is important for the very efficient production of H_3^+ after the following reactions: $Ar^+ + H_2 \rightarrow ArH^+ + H$ and $ArH^+ + H_2 \rightarrow H_3^+ + Ar$. Another two reactions contribute considerably to the increase of H_3^+ concentration in argon-hydrogen mixture: $Ar^+(3p^5\ {}^2P^0{}_{1/2}) + H_2 \rightarrow Ar + H_2^+$ and $H_2^+ + H_2 \rightarrow H_3^+ + H$, see Kuraica and Konjević (1994). Therefore, H_3^+ is now the dominating hydrogen ion and backscattered H atoms from the cathode originate mainly from this ion. In comparison with the pure hydrogen discharge, where "fast" H atoms originate from reflection of H^+, and "slow" from reflection of H_3^+ ions, here we have excited atoms formed in reflection of H_3^+ ions only. However H_3^+ ions gain more energy in the cathode fall region due to the higher transparency of argon (mass ratio 3:40) than the hydrogen matrix (3:2). Typical axial distribution of the excited hydrogen atoms temperature in the argon-hydrogen mixture discharge is shown in Fig. 3. From this figure one can see that the effect of the excited hydrogen atoms temperature increasing towards the negative glow region is even more pronounced in the argon-hydrogen mixture than in pure hydrogen, see Fig. 2. The similar explanation could be drawn: in addition to the excitation of back-reflected hydrogen atoms by collisions with matrix gas, they are excited in collisions with electrons. Once again, assuming an exponential decrease of the number of reflected energetic atoms due to collisions with matrix gas, a simple calculation using total cross section data (Phelps, 1992) for collisions of H atoms at 75 eV with argon at a pressure of 320 Pa and gas temperature (T_g) of 1000 K, shows that, for a cathode fall length of 0.1 cm, as many as 66% of the reflected neutrals reach the negative glow region without any collision. Their higher concentration in comparison with pure hydrogen, makes this effect more pronounced in the argon-hydrogen discharge.

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