Eur. Phys. J. D **32**, 347–354 (2005)
DOI: 10.1140/epjd/e2004-00192-1

THE EUROPEAN PHYSICAL JOURNAL D

Excessive hydrogen and deuterium Balmer lines broadening in a hollow cathode glow discharges

N.M. Šišović[1], G.Lj. Majstorović[2], and N. Konjević[1,a]

[1] Faculty of Physics, University of Belgrade, 11001 Belgrade, P.O. Box 368, Serbia and Montenegro
[2] Military Academy, 11105 Belgrade, Pavla Jurišić - Šturma 33, Serbia and Montenegro

Received 13 August 2004 / Received in final form 1st November 2004
Published online 4 January 2005 –

Abstract. Results of a Doppler spectroscopy study of hydrogen and deuterium Balmer lines in the stainless steel and copper hollow cathode glow discharge, operated in pure hydrogen, deuterium and mixtures of inert gases with hydrogen, are reported. For all gases and gas mixtures plasma observations perpendicular to electric field revealed the excessively large Doppler broadening. By changing mode of glow discharge operation, the Doppler broadened line profiles in helium-hydrogen mixture are recorded parallel to the discharge electric field as well. The excessively broadened part of the H_α line profile is shifted towards blue or red wavelength by changing the direction of electric field vector. The presence of large excessive Balmer lines broadening in pure hydrogen and in its gas mixture with neon as well as shifting of the excessively broadened part of line profile by means of electric field is in contradiction with the resonance transfer model proposed by Mills et al. in several publications, see e.g. [IEEE Trans. Plasma Sci. **31**, 338 (2003)].

PACS. 32.30.Jc Visible and ultraviolet spectra – 32.70.-n Intensities and shapes of atomic spectral lines – 52.80.Hc Glow; corona – 52.70.Kz Optical (ultraviolet, visible, infrared) measurements – 52.20.Hv Atomic, molecular, ion, heavy-partical collisions – 52.40.Hf Plasma-material interaction; boundary layer effects

1 Introduction

The shape of Balmer lines in some gas discharges operated in hydrogen and hydrogen gas mixtures with inert gases exhibit unusual multicomponent behaviour, see e.g. Figures 2–7. The origin of narrowest part of the profile is related to the Doppler broadening of thermalized excited hydrogen atoms H^*, located primarily in the negative glow region of discharge. Broader middle part of the line profile is related to excited hydrogen atoms H^*, generated in electron collisions with molecular hydrogen. These processes cause either dissociative excitation or dissociative ionization of H_2, which produce H^*, see e.g. [1]. The Doppler temperature of H^* generated by these processes does not exceed 10 eV [1]. The pedestal of line profile is very broad indicating that energetic excited hydrogen atoms having energies larger than hundreds electron volts are present in discharge, for more information see e.g. [2] and references therein. As pointed out already, the origin of narrow- and medium-width part of line profile, see Figures 2–7, may be explained on the bases of well established processes. The explanation of the broadest part — pedestal of the line profile is nowadays a source of controversy.

Two models are used to explain this phenomenon which is frequently called in literature the excessive Doppler line broadening. One explanation is based on well established Collision Model (CM) [2,3] evolved from the model applied to low-current, low pressure DC hydrogen discharge [4] to explain excessive Doppler broadening of the H_α line. According to this model [2–4], the main sources of fast excited hydrogen atoms are H^+ and H_3^+ ions that are involved in an asymmetric charge-exchange reaction with H_2. Due to relatively small cross sections for collisions with H_2, these ions are efficiently accelerated towards cathode. Some of them, on their way to cathode, collide with H_2, and produce fast excited hydrogen neutrals, H^*, moving in the same direction. The rest of accelerated ions reach cathode, where they neutralize or neutralize and fragmentize and, as a result of all interactions with cathode, fast H atoms are directed back towards anode. These reflected atoms in the collisions with H_2 produce also fast excited atoms H^*. The collisions of fast H atoms with sputtered cathode material plays also an important role in CM [2,3].

To avoid further confusion in relation to earlier work by the same group of authors, it should be pointed out that CM model used in [2,3] supersedes earlier models, see references in [2].

Another model, named the Resonance Transfer Model (RTM) is developed by Mills et al., see e.g. [5,6] and references therein, to explain the same phenomenon — excessive hydrogen Balmer lines broadening. According to this model, the plasma, formed by a resonance transfer

[a] e-mail: nikruz@ff.bg.ac.yu

mechanism, involves the species providing a net enthalpy of an integer multiple of 27.2 eV (2 × 13.6 eV — ionization energy of H) and atomic hydrogen. The gaseous constituents of RT plasma, apart from hydrogen, are certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV. For example, since the ionization energy Ar^+ to Ar^{2+} is 27.6 eV and therefore, singly ionized argon is a candidate for RT process. Another candidate is He^+ ion, which ionizes at 54.417 eV what is 2×27.2 eV. The ionization reaction of Sr to Sr^{5+}, has a net enthalpy of reaction of 188.2 eV, which is about 7×27.2 eV. Since Ar^+, He^+ and Sr each ionize at an integer multiple of the potential energy of atomic hydrogen, a discharge with one or more of these species present with hydrogen is anticipated to form RT plasma [5,6]. In accordance with RTM, one can find many more candidates for RT plasma formation in the presence of atomic hydrogen.

The RTM has several drawbacks. The most important one: the RTM does not explain process that converts internal energy of the ions formed by RT into fast excited hydrogen atoms used to detect excessive line broadening. Further, the authors [5] claim that in pure hydrogen conditions for RT plasma also exist and consequently the excessive broadening should be present. Since, the ionization energy of hydrogen is 13.6 eV, two hydrogen atoms can provide a net enthalpy equal to the necessary resonance energy of 27.2 eV for a third hydrogen atom. This statement implicitly implies three-body collision, $H^+ + H^+ +$ H. This process, however, has a very low probability in low-pressure discharges. On the basis of this mechanism, the authors [5] expect generation of unusually low energy H atoms for the phenomenon of excessive broadening with energies slightly above the electron temperature. The effect is expected to be more pronounced with greater hydrogen concentration such as that achieved near or on the cathode in RF and glow discharge. It is interesting that the authors [5,6] never detected experimentally the excessive broadening of Balmer lines in pure hydrogen, while in a number of publications, see e.g. [2–4,7–13], the excess broadening is reported with Doppler temperatures far exceeding electron temperature, see also results in Tables 1 and 2. Furthermore, the RTM can't explain the presence of excessive Balmer line broadening in gas mixtures of hydrogen with neon, which is detected in [11,12], see also Tables 1 and 2 and with krypton [11]. The authors [5,6] ignore all previous publications [4,7–13] reporting presence of large excessive Balmer lines broadening in H_2 and in Ne–H_2 and Kr–H_2 and, on the bases of their own experiments [5,6], claim without any comment of earlier works that no excessive broadening in these cases exists.

Finally, in order to test simultaneously the validity of RTM and CM the authors performed an experiment [5] with a low-pressure microwave induced discharge (MID). Namely, according to CM, the presence of relatively large electric field in discharge is essential for excessive line broadening while it is of no importance for RTM. Thus, the detection of excessively broad Balmer lines profiles in MID with an inherent low electric field would be a final proof in favor of RTM. The authors of RTM reported excessively broad Balmer line shapes in MID [5]. However, in two other experiments performed simultaneously in two different laboratories no excess broadening is detected in MIDs [14].

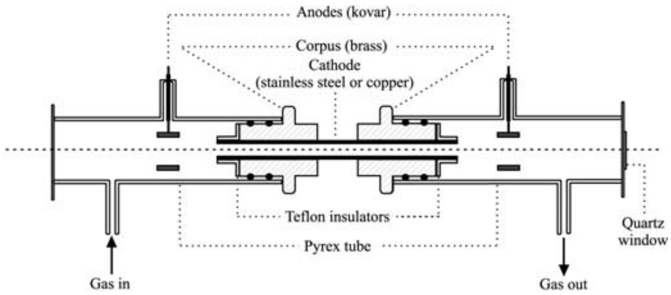

Fig. 1. The hollow cathode discharge tube.

In the recent paper [6] the authors of RTM reported study of the excessive H_α broadening in various discharges including hollow cathode discharge. The results in Table 1 [6] and discussion firmly state that excessive broadening is detected only in Ar and He mixtures with hydrogen while in H_2, and in mixtures Ne–H_2 and Xe–H_2 no effect is found. This result is expected on bases of their RTM. Since our earlier experiments dealing with excessive Balmer lines broadening were carried out primarily with a plane cathode abnormal glow discharge, see [2,3], in this paper results of the study of Doppler broadening in a hollow cathode glow discharge are reported. The discharge is operated either with stainless steel or copper hollow cathode in hydrogen or deuterium or in gas mixtures of helium, neon and argon with hydrogen. In addition, spectroscopic observations of the H_α broadening are carried out in the He–H_2 mixture discharge operated in a low-pressure high voltage regime with an electric field along the axis of hollow cathode. The results of excess Doppler broadening will be discussed from the point of view of CM and RTM.

2 Experimental

Newly developed hollow cathode glow discharge with stainless steel or with copper cathode is used, see Figure 1. The construction details follow basic concept of Pyrex-kovar design reported in [11]. Both cathodes were 100 mm long with 6 mm internal diameter. Kovar anodes, 5 mm long with 15 mm dia, are located at the both ends of cathode at a distance of 15 mm. The advantage of this glow discharge construction: the hollow cathode can be easily replaced while/or cleaning of the whole discharge tube from the sputtered material is simplified.

During the discharge operation cathodes were air cooled with a fan (110 mm dia; AC 220V/13W), placed 150 mm from discharge tube. The temperature of the outer wall of hollow discharge tube, ranging from 40 °C to 70 °C, was constantly monitored by K-type thermocouple.

The continuous flow of the working gas (hydrogen, deuterium or mixtures of inert gases with hydrogen) is sustained in the pressure range from 0.5 mbar to 2 mbar by means of needle valve and two-stage mechanical vacuum pump. To prevent oil vapour back-streaming from the vacuum pump, the zeolite trap is placed between discharge chamber and the pump. The gas pressure measurements are performed on the both sides of discharge tube with standard U-shaped oil manometers. During discharge operation difference of gas pressure between gas inlet and gas outlet from the discharge tube was about 30%. Within the experimental uncertainty spectroscopic line shape recordings do not show any difference between two sets of measurements from the gas inlet or gas outlet side. Results of gas pressure measurements represent an average value between gas inlet and gas outlet value.

To operate discharge in DC mode, a current stabilised power supply (0–2 kV, 0–100 mA) is used. The ballast resistor of 5 kΩ is placed in series with the discharge and power supply. For all measurements, the cathode was grounded.

The light along the axis of hollow cathode glow discharge is focused by a lens (focal length 150 mm) onto the entrance slit of scanning monochromator-photomultiplier system (0.3 m focal length with 600 g/mm reflection grating, blazed at 1.6 μm, and a reciprocal dispersion of 1.77 nm/mm in the third diffraction order). Spectral measurements are performed with Gaussian instrumental profile having 0.040 nm full half-width. Signals from photomultiplier are A/D converted, collected and processed by PC.

3 Results and discussion

Before one starts discussion and comparison of results obtained with different hollow cathode discharges of this study and data from [2,3,6] it is necessary to comment details of the spectra recording procedure in each experiment.

The hollow cathode glow discharge of the present experiment has diameter $R = 0.6$ cm and it is operated at 2 mbar, with discharge current from 50 to 90 mA and voltage varying from 250 V to 490 V. The authors in [6] used 7.2 cm long, 6.1 cm internal diameter hollow cathode made of perforated stainless steel operated at a pressure of 2 torr, discharge current of 0.2 A and voltage of 275 V. The value of pR in pure hydrogen is 0.9 torr cm in this experiment and 6.1 torr cm in [6]. Thus, both discharges in hydrogen were operating in a high pressure low-voltage regime ($pR > 0.5$ torr cm) [11,15,16]. In this regime, the electric field vector is directed perpendicular to the cathode surface. All spectroscopic observations in [6] are performed along electric field vector, while the line shape measurements in this work are carried out normal to electric field vector. In both cases, the excessive broadening can be detected. Our earlier experimental data on excessive Doppler broadening [2,3] are taken along an electric field in a plane cathode glow discharge (PCGD) and the shape of Balmer lines is found to be asymmetric with the larger blue wing, while in perpendicular case line shape is symmetric, see Figures 2–7.

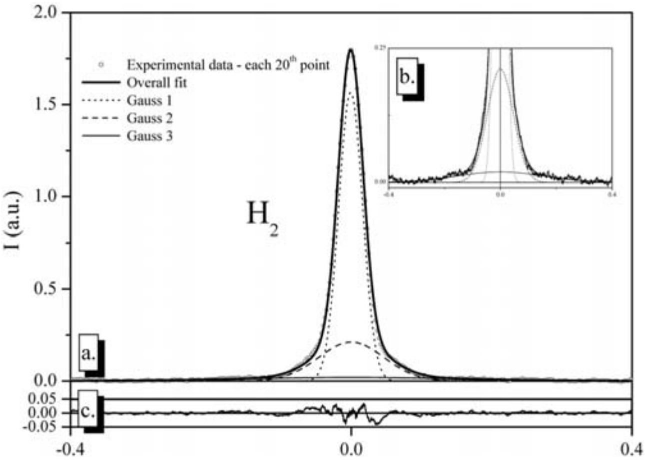

Fig. 2. (a) Typical H_α line shape recorded end-on in pure hydrogen with stainless steel cathode fitted with three Gaussians. Discharge conditions: front anode, $p = 2$ mbar, $U = 355$ V, $I = 90$ mA; (b) the enlarged part of H_α line shape indicating excessive broadening; and (c) residual plot.

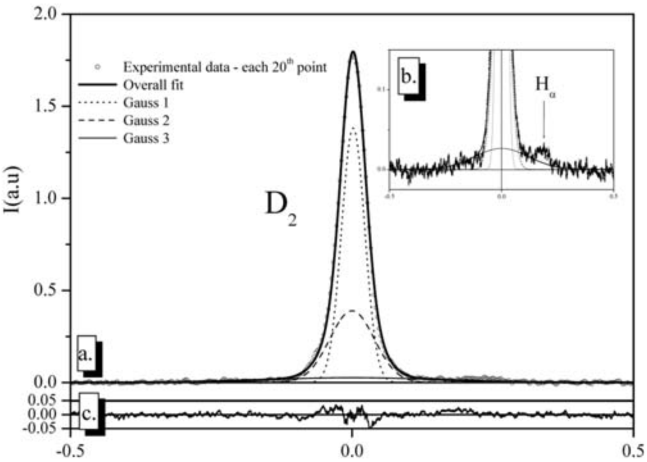

Fig. 3. (a) Typical D_α line shape recorded end-on in pure deuterium with stainless steel cathode fitted with three Gaussians. Discharge conditions: front anode, $p = 2$ mbar, $U = 374$ V, $I = 90$ mA; (b) the enlarged part of D_α line shape indicating excessive broadening; and (c) residual plot.

Besides high pressure low-voltage hollow cathode glow discharge regime, in our discharge source, another mode of operation at lower pressures and higher voltage is possible. In such a case, the electric field vector is coaxial with the hollow cathode axis and end-on spectroscopic observations could be performed along electric field [11], whose direction one can change by using one or another anode, see Figure 1. In our study, both modes of hollow cathode glow discharge operation can be easily achieved in the He–H_2 mixture and this possibility is utilized here to study influence of electric field direction to the shape of excessively broadened H_α line.

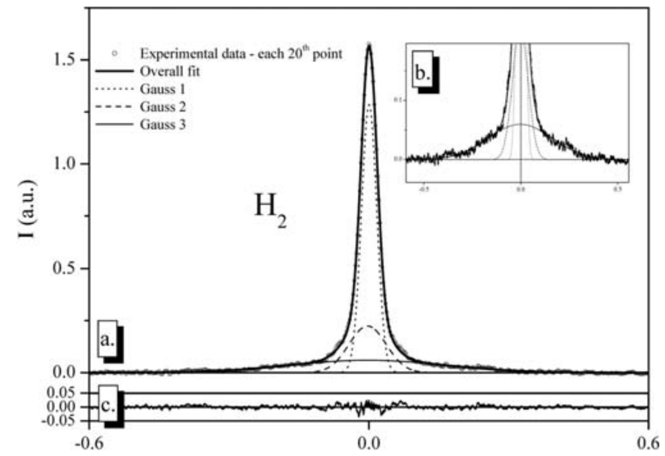

Fig. 4. (a) Typical H_α line shape recorded end-on in pure hydrogen with copper cathode fitted with three Gaussians. Discharge conditions: front anode, $p = 2$ mbar, $U = 440$ V, $I = 90$ mA; (b) the enlarged part of H_α line shape indicating excessive broadening; and (c) the residual plot.

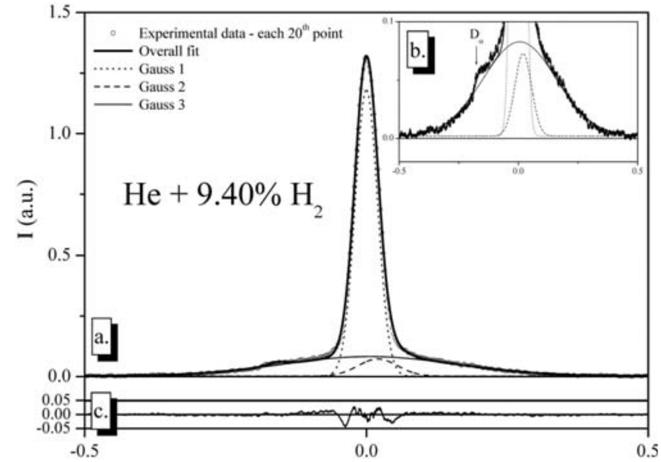

Fig. 6. (a) Typical H_α line shape recorded end-on in He–H_2 mixture (90.6%:9.4%) with copper cathode fitted with three Gaussians. Discharge conditions: front anode, p = 2 mbar, U = 323 V, I = 90 mA; (b) the enlarged part of H_α line shape indicating excessive broadening; and (c) the residual plot.

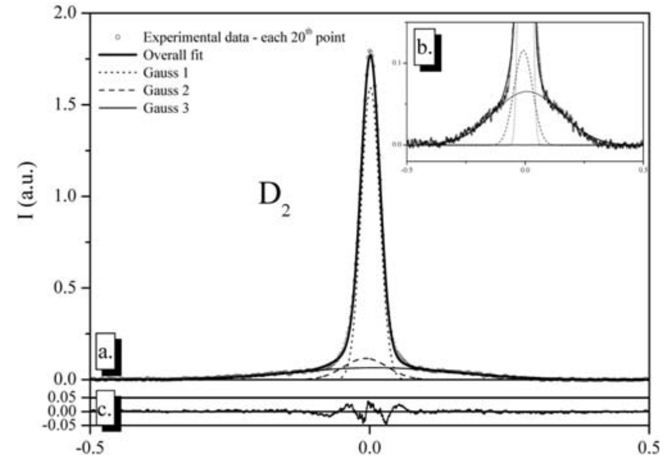

Fig. 5. (a) Typical D_α line shape recorded end-on in pure deuterium with copper cathode fitted with three Gaussians. Discharge conditions: front anode, $p = 2$ mbar, $U = 490$ V, $I = 90$ mA; (b) the enlarged part of D_α line shape indicating excessive broadening; and (c) the residual plot.

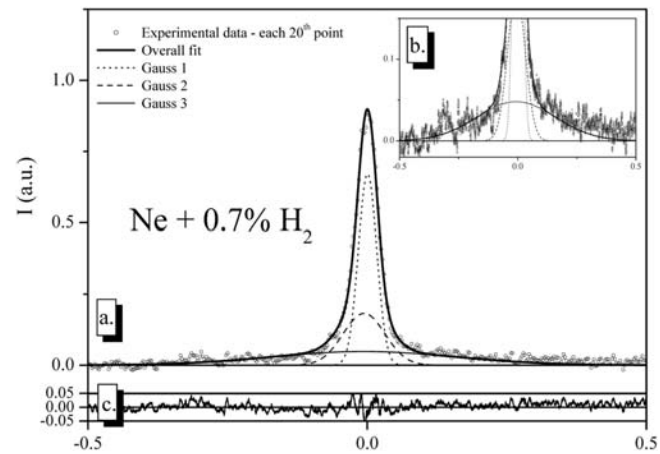

Fig. 7. (a) Typical H_α line shape recorded end-on in Ne–H_2 mixture (99.3%:0.7%) with copper cathode fitted with three Gaussians. Discharge conditions: front anode, p = 2 mbar, U = 250 V, I = 90 mA; (b) the enlarged part of H_α line shape indicating excessive broadening; and (c) the residual plot.

Typical examples of the H_α line shape recordings from the central region of stainless steel and copper hollow cathode high pressure low-voltage glow discharges are given in Figures 2–7. Since these figures do not allow comparison of the excited hydrogen and deuterium concentrations in gases and in gas mixtures, the profiles of H_α and D_α lines recorded from the copper hollow cathode discharge with the same sensitivity of the spectrometer-detection system are shown in Figure 8. Here, it should be noted that no attempt is made to correct central part of line profile for possible presence of self absorption, which may not be negligible in particular in He–H_2 mixture.

Three components can be distinguished in the overall fit of the symmetric H_α and D_α line shapes in pure gases and gas mixtures, see Figures 2–7: central narrow peak, broader middle part (extended plateau) and far drawn-out pedestal. The overall fit involving convolution of three Gaussians in Figures 2 to 7 may be justified in two ways: (i) three groups of excited hydrogen atoms are expected in the negative glow region: thermalized H^* typical for negative glow (Gauss 1); a group of H^* atoms produced by dissociation of H_2 molecules in collisions with high energy electrons (Gauss 2); and a group of H_f^* atoms generated in collisions of H_f reflected from the cathode with H_2 (Gauss 3) and (ii) a good quality of three Gaussian fit, see the residue plot in Figures 2c to 7c.

Table 1. Experimental conditions, relative contributions G_i/G_{total} (i = 1, 2, 3) and energies E_i (i = 2, 3) of hydrogen and deuterium neutrals obtained by applying three Gaussian fit to the H_α and $D_{\alpha g}$ profiles — glow discharge operating with stainless steel hollow cathode at $p = 2$ mbar.

gas	voltage (V)	current (mA)	G_1/G_{total} (%)	G_2/G_{total} (%)	G_3/G_{total} (%)	hydrogen/deuterium atom energy E_2 (eV)	E_3 (eV)
	324	50	65.9	26.7	7.4		
H_2	342	70	66.6	26.0	7.4	3 ± 10%	44 ± 5%
	355	90	67.4	25.1	7.5		
	345	50	58.3	32.2	9.5		
D_2	356	70	61.4	29.3	9.3	5 ± 10%	65 ± 5%
	374	90	64.2	26.3	9.5		
	249	50	67.8	23.5	8.7		
He+10.7%H_2	254	70	69.0	22.2	8.8	3 ± 10%	34 ± 5%
	258	90	70.5	20.7	8.8		
	225	50	60.4	26.8	12.8		
Ne+0.7%H_2	226	70	59.7	27.8	12.5	3 ± 10%	38 ± 10%
	226	90	58.9	28.6	12.5		
	283	50	9.0	2.5	88.5		
Ar+0.8%H_2	283	70	7.9	4.8	87.3	3 ± 10%	36 ± 10%
	283	90	6.3	6.0	87.7		
	280	50	9.2	2.8	88.0		
Ar+3%H_2	284	70	8.1	4.3	87.6	3 ± 10%	36 ± 10%
	284	90	6.2	6.3	87.5		

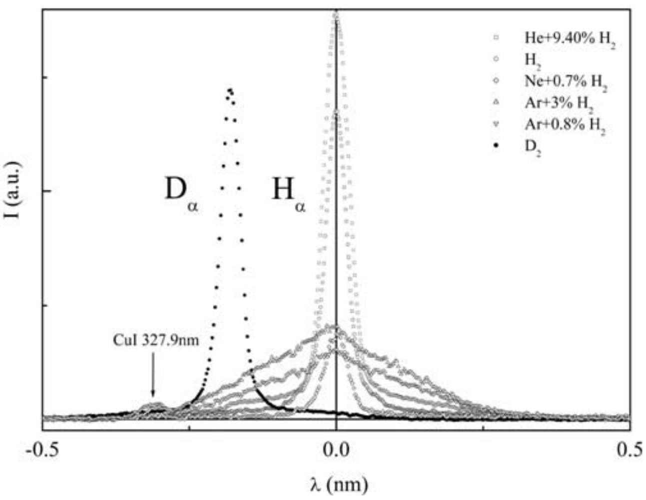

Fig. 8. The comparison of relative intensities of the H_α and D_α lines in all gases and gas mixtures for the copper hollow cathode discharge. Discharge conditions: front anode, $p = 2$ mbar, $I = 90$ mA, U — see Table 2.

The discharge conditions, relative contributions of Gauss 1, 2 and 3 to the total line fit and full half-widths of Gauss 2 and 3 in energy unit scale for the stainless steel and copper hollow cathode discharge operated in a high pressure low-voltage regime are given in Tables 1 and 2, respectively. The results derived from the H_β and H_γ line recordings for copper cathode discharge match well within experimental uncertainty with the H_α data in Table 2. Since the results for H_α line are determined with highest accuracy only these results are given in Table 2.

The width of Gauss 1 is well within instrumental profile what in energy unit scale corresponds to $E_1 \approx 0.7$ eV, except in He–H_2 mixtures where, most likely, due to self-absorption Gauss 1 is observed with larger half-width of 0.017 nm and 0.023 nm from stainless steel and copper hollow cathode discharge, respectively. It is interesting to note also that relatively small shift towards longer wavelengths (≈+0.020 nm) of fitted Gauss 2 in respect to Gauss 1 is detected only in this gas mixture with both hollow cathodes. The position of applied anode, front or rear, see Figure 1, did not change the direction of shift.

The temperatures derived from the width of Gauss 2 are always 3 eV, with an exception of deuterium discharge where $E_2 = 5$ eV is detected.

The results for energies of fast excited hydrogen and deuterium atoms derived from the width of Gauss 3, see Tables 1 and 2, see also examples in Figures 2–7, show that the excessive H_α or D_α line broadening is present in both hollow cathodes discharges under all studied experimental conditions. Furthermore, there is nothing exceptional about discharge operating in He–H_2 and Ar–H_2 mixtures where, according to RTM, resonance transfer catalysts He^+ and Ar^+ are present: the profiles, recorded from our discharges operating in He–H_2 mixtures, have a typical multipart component structure in contrast to a single excessive broadened profile recorded in the same gas

Table 2. Experimental conditions, relative contributions G_i/G_{total} ($i = 1, 2, 3$) and energies E_i ($i = 2, 3$) of hydrogen and deuterium neutrals obtained by applying three Gaussian fit to the H_α and D_α profiles — glow discharge operating with copper hollow cathode at $p = 2$ mbar.

gas	voltage (V)	current (mA)	G_1/G_{total} (%)	G_2/G_{total} (%)	G_3/G_{total} (%)	hydrogen/deuterium atom energy E_2 (eV)	E_3 (eV)
H_2	415	50	53.2	22.5	24.3	$3 \pm 10\%$	$56 \pm 5\%$
	430	70	53.0	22.4	24.6		
	440	90	52.5	22.9	24.6		
D_2	465	50	66.6	10.8	22.6	$5 \pm 10\%$	$89 \pm 5\%$
	470	70	66.7	11.0	22.3		
	490	90	65.2	11.3	23.5		
He+9.40%H_2	310	50	61.5	5.2	33.3	$3 \pm 10\%$	$49 \pm 5\%$
	318	70	60.7	5.8	33.5		
	323	90	60.2	6.4	33.4		
Ne+0.7%H_2	235	50	45.5	22.4	30.5	$3 \pm 10\%$	$56 \pm 10\%$
	240	70	44.2	25.0	30.8		
	250	90	42.8	26.5	30.7		
Ar+0.8%H_2	290	50	3.1	0.8	96.4	$3 \pm 10\%$	$42 \pm 10\%$
	305	70	2.9	2.1	94.8		
	320	90	2.5	3.0	94.5		
Ar+3%H_2	295	50	3.1	0.9	96.0	$3 \pm 10\%$	$42 \pm 10\%$
	307	70	2.7	1.6	95.7		
	320	90	2.0	2.0	96.0		

mixture and reported in [6]. As a matter of fact, energy of H_f^* in Ne–H_2 mixture is higher than those in He–H_2 and Ar–H_2 mixtures, see Tables 1 and 2. It is proven that the temperatures of H_f^* in Ar–H_2 discharge are always lower than in other gases and gas mixtures as a consequence of the large and almost exclusive presence of H_3^+ ions in the discharge, see e.g. [2,14]. This fact, as well as large excitation cross section for the collisions of fast hydrogen atoms with argon atom can explain qualitatively, see Figure 12 in [2], large contribution of Gauss 3 to the overall H_α profile.

On the basis of earlier experiment, see Figure 9 in [2], high D_f^* temperatures are expected and they are detected in both hollow cathode discharges, see Tables 1 and 2. The presence of high energetic neutrals D_f^* in this case is related to large back scattering coefficients of D^+ from the cathode surface, which exceeds ~50% same coefficients of H^+ [17]. These ions are neutralized at the cathode and reflected back in the form of D_f, which collide with matrix gas D_2 and produce observed D_f^* [2]. High voltage in deuterium discharge, see Tables 1 and 2, plays an important role in D^+ acceleration and in this way to generation of high temperature D_f^*.

The comparison of data in Tables 1 and 2 shows also that Gauss 3 contribution to the overall profile is significantly larger in case of copper than stainless steel hollow cathode discharge, see G_3/G_{total} column in Tables 1 and 2. This result is in qualitative agreement with results from PCGD discharge, see Figure 7 in [2,3] and may be explained by larger back scattering coefficients of H^+ from Cu surface in comparison with Fe [2,3,17]. It proves that the concentrations and energies of H_f^* depends of cathode material and that, most likely, is associated with sputtering yield and characteristic back-scattering coefficients [3].

As pointed out already in Introduction, the electric field is essential for the CM to explain basic processes related to excessive Doppler broadening. The only fact in this experiment that looks in favor of RTM: the H_α line shape measurements are performed primarily by observing the negative glow region of discharge where large electric fields do not exist. Since the excessive broadening is detected in this region one may conclude that this proves validity of RTM. However, one should also bear in mind that accelerated H^+ and H_3^+ ions in a cathode fall region of discharge operated at high pressure and low-voltage regime are back-scattered towards the center of hollow cathode in the form of fast hydrogen atoms, which generate H_f^* in collisions with matrix gas. Thus, the presence of observed excess Doppler H_α broadening, Gauss 3, may be well explained within CM.

In order to examine further the importance of electric field for excessive Doppler broadening an experiment with stainless steel hollow cathode glow discharge in a low pressure, high-voltage regime is carried out. This is the case when electric field vector is coaxial with hollow cathode axis and its direction may be changed by applying rear or front anode, see Figure 1.

Table 3. Experimental conditions, relative contributions G_i/G_{total} ($i = 1, 2, 3$), shifts Δ_i ($i = 2, 3$) and energies E_i ($i = 2, 3$) of hydrogen neutrals obtained by applying three Gaussian fit to the H_α profile — low pressure high-voltage glow discharge operating with stainless steel cathode in He–H_2 mixture (89.3%:10.7%) at $p = 1$ mbar.

voltage (V)	current (mA)	anode	G_1/G_{total} (%)	G_2/G_{total} (%)	G_3/G_{total} (%)	Δ_2 (nm)	Δ_3 (nm)	hydrogen atom energy E_2 (eV)	hydrogen atom energy E_3 (eV)
1030	5	front	48.8	23.6	27.6	+0.026	+0.136	4 ± 10%	65 ± 10%
		rear	48.1	22.9	29.0	+0.023	–0.135		

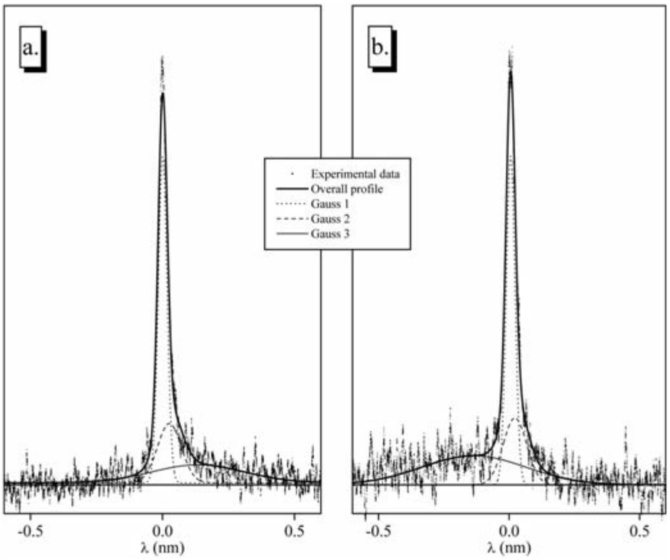

Fig. 9. Typical H_α line shapes recorded end-on from low pressure high-voltage discharge (He–H_2 mixture; stainless steel cathode) and fitted with three Gaussians: (a) front anode and (b) rear anode. Discharge conditions: $p = 1$ mbar, $U = 1030$ V, $I \approx 5$ mA.

Typical line shape recordings of the H_α are presented in Figure 9. The experimental conditions of this experiment are given in Table 3.

The results and Figure 9 clearly show that Gauss 3 may be shifted into blue or red wavelength direction by simply changing the direction of electric field vector. Similar experiment with hollow cathode glow discharge operated with higher voltages in pure hydrogen is reported in [11,16]. The dependence of shift direction of high temperature component upon electric field vector is the same as in Figure 9. Both experiments, [11] and this one, undoubtedly prove the importance of electric field for the excess Doppler broadening. The RTM in contrast to CM does not depend upon electric field and can't be used to explain results in Table 3.

Finally, we draw attention to the fact that our data on electrical parameters of studied hollow cathode glow discharge at a constant pressure in different gases and gas mixtures differ considerably one from another, see Tables 1 and 2. In contrast, all results reported in Table 1 [6] in a hollow cathode discharge are carried out at the pressure of 2 torr, at the constant current, 0.2 A, and constant voltage, 275 V. These electrical parameters are not possible to keep in all gas mixtures, since it is well-known that V-I characteristics of hollow cathode discharge depend strongly upon gas composition, see e.g. [17].

4 Conclusions

The reported hydrogen Balmer alpha line profiles, recorded end-on from the negative glow region of high pressure low-voltage in stainless steel and copper hollow cathode glow discharges operated in pure hydrogen and deuterium and in noble gas-hydrogen mixtures are symmetric with characteristic multicomponent structure. The presence of excessive Doppler broadening of hydrogen Balmer lines is detected in pure gases, see Figures 2–5, as well as in He–H_2, Ne–H_2 and Ar–H_2 mixtures, see Figures 6 and 7, see also Tables 1 and 2.

The detected large excessive broadening in pure hydrogen and in Ne–H_2 mixture is in agreement with CM and other experimental results, see e.g. [2]. These results can't be explained by RTM and they disagree with experiments [5,6]. Furthermore, it is shown that the energies of H_f^* in Ne–H_2 is higher than those in He–H_2 and Ar–H_2 mixtures, where, according to RTM, resonance transfer catalysts He^+ and Ar^+ are present, see Tables 1 and 2.

The study of the H_α line profiles with stainless steel and copper cathodes shows that contributions of H_f^* to the overall H_α profile as well as energies of H_f^* depend upon cathode material, see Tables 1 and 2. This dependence may be related to the back-scattering coefficients of H^+ and, most likely, is associated with sputtering yield as well [3].

The importance of electric field for excessive Doppler broadening is examined in an experiment with stainless steel hollow cathode glow discharge operating in a low pressure and high-voltage regime. It is shown that the pedestal part of the line profile may be shifted towards blue or red wavelength by simply changing the direction of electric field vector, see Figure 9 and Table 3.

This work within the Project 1736 "Plasma and discharges: radiation properties and the interaction with surfaces" is supported by the Ministry of Science and Environment Protection of the Republic of Serbia.

References

1. G. Baravian, Y. Chouan, A. Ricard, G. Sultan, J. Appl. Phys. **61**, 5249 (1987)
2. M.R. Gemišić Adamov, B.M. Obradović, M.M. Kuraica, N. Konjević, IEEE Trans. Plasma Sci. **31**, 444 (2003)
3. M.R. Gemišić Adamov, M.M. Kuraica, N. Konjević, Eur. Phys. J. D **29**, 393 (2004)
4. Z.Lj. Petrović, B.M. Jelenković, A.V. Phelps, Phys. Rev. Lett. **68**, 325 (1992)
5. R.L. Mills, P.C. Ray, B. Dandapany, R.N. Mayo, J. He, J. Appl. Phys. **92**, 7008 (2002)
6. R.L. Mills, P.C. Ray, M. Nansteel, X. Chen, R.N. Mayo, J. He, B. Dhandapani, IEEE Thans. Plasma Sci. **31**, 338 (2003)
7. W. Benesh, E. Li, Opt. Lett. **9**, 338 (1984)
8. E.Li Ayers, W. Benesh, Phys. Rev. A **37**, 194 (1988)
9. C. Barbeau, J. Jolly, J. Phys. D **23**, 1168 (1990)
10. M. Kuraica, N. Konjević, Phys. Rev. A **46**, 4479 (1992)
11. B.P. Lavrov, A.S. Mel'nikov, Opt. Spectrosc. **75**, 1152 (1993)
12. M. Kuraica, N. Konjević, Phys. Scripta **50**, 487 (1994)
13. I.R. Videnović, N. Konjević, M.M. Kuraica, Spectrochim. Acta **51B**, 1707 (1996)
14. S. Jovićević, M. Ivković, N. Konjević, S. Popović, L. Vušković, J. Appl. Phys. **95**, 24 (2004)
15. B.I. Moskalev, *Hollow-Cathode Discharge* (Energy, Moscow, 1969)
16. B.P. Lavrov, A.S. Mel'nikov, Opt. Spectrosc. **79**, 922 (1995)
17. T. Tabata, R. Ito, Y. Itikawa, N. Itoh, K. Morita, At. Data Nucl. Data Tables **31**, 1 (1984)