Spectroscopic study of hydrogen Balmer line shapes in a hollow cathode glow discharge in NH₃ and Ar/NH₃, Ar/CH₄ and Ar/C₂H₂ mixtures

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Abstract. The results of Doppler spectroscopy of hydrogen Balmer lines emitted from a stainless steel (SS) and copper (Cu) hollow cathode (HC) low-pressure glow discharge in ammonia, as well as in argon-ammonia, argon-methane and argon-acetylene mixtures are reported. The earlier results of electron beam interactions with NH₃, CH₄ and C₂H₂ were used for analysis of Balmer line shapes in HC glow discharge.

1. Introduction
The considerable interest has been shown in the shape of Balmer lines emitted from low-pressure discharges operating with hydrogen isotopes or with inert gas-hydrogen mixtures, see [1] for comprehensive literature review. The interest was triggered primarily by large excessive Doppler broadening (EDB) of hydrogen Balmer lines detected for the first time in a hollow cathode glow discharge (HCGD) run with hydrogen and hydrogen-inert gas mixtures [2].

Different broadening mechanisms were used to explain multi-component Balmer line shapes in hydrogen low-pressure gas discharge. The overall line shape was named Anomalously Doppler Broadened (ADB) Profile. The narrowest part of the line profile represents convolution of several profiles emitted by thermalized excited hydrogen atoms and H* generated by dissociative excitation in electron impact collisions with H₂ [3]. The broader middle part of the line profile is, in most cases, related to the dissociative ionization of H₂ via several reactions with the respect to the Franck–Condon principle.

The electron impact dissociative excitation of small inorganic and organic molecules containing hydrogen has been extensively studied. The electron impact dissociative excitation of ammonia molecule was studied by Kurawaki and Ogawa [4]. The Balmer line (Hα and Hβ) profiles, produced by electron beam→NH₃ collisions, have been measured precisely by means of Fabry-Perot interferometer. The translational energy distributions of H* (n=3,4) are determined from Doppler line shapes and they have five components. The peaks lie at 1, 3, 2, 4-5 and 8-12 eV. The excitation function for H* (n=4), which is very similar to the one for H* (n=3), has five thresholds at: 22.5, 22.5, 29.0, 33.3 and 40 eV, and indicate that five different processes contribute to the formation of H*.

Namely, the excitation to the Rydberg states converging to the (2a₁)¹ state of NH₃⁺ is the major process for the formation of the first and second component. Doubly excited Rydberg states play

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important role in the dissociative excitation of NH$_3$. Thus, in this experiment the translation energy distribution proved to be very useful tool for investigation of Rydberg states and their dissociation dynamics.

In the experiment [5], the Balmer H$\beta$ line profiles, induced by electron beam → CH$_4$ collisions, were also precisely recorded with Fabry-Perot interferometer. The translational energy distributions of H* (n=4) were determined from Doppler profiles and three components were detected with the peaks at 3 eV, below 1 eV and at 4 eV. The excitation function for H* (n=4), which is similar to the one for H* (n=3), has three electron energy thresholds at 21.6, 28.1 and 35.3 eV, indicating three different processes important for H* formation. Also, there seems to be the fourth peak with translational energy of 8-12 eV [5]. According to the authors [5], the excitation to Rydberg states converging to the $\tilde{A}^2A_1$ state of CH$_4^+$ is the major process for the formation of first component, while optically forbidden doubly excited Rydberg states play an important role for other components. Another detailed study of electron→CH$_4$ interaction provided list of dissociation processes responsible for production of H$^-$ (n=4) and proved that there are at least three major processes responsible for the formation of H$^-$ from methane, see Table 4 and figure 1 in [6]. This result may be extended to several other hydrogen containing molecules, see e.g. [7].

In the case of C$_2$H$_2$, Doppler profiles of the H$\alpha$ line show no structure and they became broader with an increase of electron energy [8]. For example, the electron energy increase from 40 eV to 150 eV raises the average kinetic energy of H$^-$ from 1.3 eV to 3.8 eV. The continuous kinetic energy change was explained by the fact that large number of processes contribute to the H$\alpha$ line shape due to complex molecular structure of acetylene [8].

The presence of large excessive Doppler broadening (EDB) determined from the broadest part of multi-component ADB profile, explains so-called plasma-sheath “Collision Model” (CM) [9-11]. According to this model, in hydrogen, the EDB is related to hydrogen atomic and molecular ions (H*, H$_3^+$ and H$_5^+$) present always in low-pressure discharges. The main sources of fast excited hydrogen atoms in hydrogen discharges are H$^+$ and H$_3^+$ ions (exhibit an asymmetric charge-exchange reaction in collisions with H$_2$, see reactions (1) and (3) in [1], which are, as a consequence of relatively low cross-sections for collisions, efficiently accelerated towards cathode. Some of these ions on their way to cathode collide with the matrix gas producing fast excited neutrals H$. The rest of accelerated ions and newly generated H$_2$ reach cathode where they neutralize, or neutralize and fragmentize. The back-reflected particles from the cathode are fast H atoms directed back to discharge. After collisions of these fast H atoms with H$_2$ and/or with other discharge constituents, fast excited hydrogen atoms H$^-$ are produced as well. These fast excited hydrogen atoms moving towards and from cathode are detected in different discharges by means of Doppler spectroscopy of Balmer lines. In order to achieve best signal to noise ratio for this purpose first three Balmer lines are used, in particular, the H$\alpha$ and the H$\beta$ line.

The aim of this work is to study atomic hydrogen line shapes in hollow cathode glow discharge in ammonia and in argon-ammonia, argon-methane and argon-acetylene gas mixtures. The intention is to test applicability of earlier results of electron beam dissociation of CH$_4$ and C$_2$H$_2$ [5-8] for analysis of Balmer line shapes in HCGD. The EDB of hydrogen Balmer lines in all working gases is studied as well [12,13].

2. Experimental

The HCGD source [12] with two symmetrically positioned molybdenum anodes and stainless steel (SS) or copper (Cu) cathode is used. The HC tubes were 50 mm long with 6 mm internal diameter and 1 mm wall thickness. The distance between cathode and each anode was 15 mm. To operate discharge in DC mode, a current stabilized power supply is used. For all measurements, the discharge was operated between grounded HC and rear anode. During the discharge operation, the cathode was air cooled with a fan, placed 150 mm from the discharge tube. The temperature of the outer wall of the HC tube is measured by a K-type thermocouple.
For all working gases (NH₃, Ar+10%CH₄ and Ar+10% C₂H₂), discharge filled the whole volume of HC. All reported studies of HC discharge were carried out in a low-voltage (300–550 V) high-pressure (1 to 2 mbar measured by a capacitive pressure gauge) regime.

The spectroscopic measurements were realized with 2 m focal length spectrometer (reciprocal dispersion of 0.74 nm/mm in the first diffraction order with 651 grooves/mm reflection grating). The instrumental profile was very close to Gaussian, with full half-width of (0.018±0.002) nm. The end-on discharge image was projected, with unity magnification, onto the entrance slit of the spectrometer by an achromatic lens (focal length 75.8 mm). Signals from the CCD detector (3648 pixels, 8 μm pixel width) are A/D converted, collected and processed by PC.

3. Results and discussion

3.1.1. Ammonia

The experiments with ammonia were carried out under the pressure of 1.33 mbar, current 45 mA and voltage 376 V and 465 V with SS and Cu HC, respectively. Hydrogen line shape analysis was carried out using the Hα line. The typical Hα profiles with SS and Cu cathode are presented in figure 1 with the best fits composed of three Gaussians and residue plots.

As per figure 1, it is evident that two distinct Doppler temperatures are present in a line core, which is expected for our discharge conditions and line shape detection system on the basis of electron beam → ammonia experiment [5], see Introduction. This experiment indicated presence of five dissociation processes in electron energy range 25-100 eV. In our experiment the Gauss 1, representing excited hydrogen atoms with temperature below 0.5 eV, corresponds to slow component 1 (1eV) with electron threshold energy at 22.5 eV [5]. The Gauss 2 with larger temperature in the range 3 to 4 eV may be correlated either with component 2 or component 4 from latter reference. This is why it is important to clarify the origin and behaviour of these components. The threshold energy for component 2 as for component 1, is assigned also to be 22.5 eV, and, therefore, the Rydberg states converging to the (2a₁)⁻¹ state of NH₃⁺ should play also an important role for this component formation as for
component 1. The Rydberg states for component 2 and those for component 1 are most likely different in symmetry. The translational energy of component 2 is about 3 eV, and the dissociation processes for its formation should be related with dissociation limits at about 19 eV, see figure 5 in [5]. The component 4 has a peak in translational energy distribution at 4 eV for H⁺ (n=3) and a threshold energy of 33.3 eV. The doubly excited or singly excited and singly ionized Rydberg states should be intermediates for formation of this component with possible dissociation limit at 28.6 eV, see figure 5 in [5]. In addition, it has been found that this component, as the most intense one at higher electron energies, determines the behaviour of H⁺ formation at higher excitation energies [5]. In order to clarify the role and importance of component 4, an experiment with HCGD in pure hydrogen is performed under similar experimental conditions [14]. By comparison of G₂ relative contribution to the line profile in H₂ and in NH₃, a large difference in favour to later one has been detected. Thus, one can draw conclusion that due to matching energy and due to predominant influence on line profile in NH₃ discharge, the Gauss 2 is correlated with component 4 in [5].

The temperatures derived from Gauss 3 line component, see figure 4 in [12], are almost constant (within an estimated uncertainty of measurement of 5%) across HC radius what is characteristic for EDB [1]. In addition, if one takes into consideration large values of temperatures, 46 eV and 55 eV measured with SS and Cu HC, respectively, the only conclusion is that one is dealing with EDB here.

3.2. Argon-ammonia mixture

The experiments with argon-ammonia mixture (≈1:1 mixture ratio) were carried out under the same pressure of 1.33 mbar, and current 45 mA; voltage of 325 V and 435 V with SS and Cu HC is applied, respectively. The typical Hα line profiles recorded with Cu HC and their best fits composed of three Gaussians are presented in figure 2.

![Figure 2. The Hα line profile recorded at: (a) the HC axis; and (b) the vicinity of HC wall in Ar-NH₃ mixture fitted with three Gaussians. Line profiles are normalized to unity area. Discharge conditions: copper HC, Ar/NH₃ at p = 1.33 mbar, U = 435 V and I = 45 mA.](image)

As for ammonia, three Gaussians are required for the best fit of experimental profiles recorded with both hollow cathodes in argon-ammonia mixture. The average Doppler widths of approximately 0.4 eV and 3-4 eV are found to be in good qualitative agreement with electron beam → NH₃ experiment [5].

The values of EDB temperature T_{EDB}, derived from the half width of Gauss 3, of 35 eV (SS) and of 42 eV (Cu) indicate that Gauss 3 is related to EDB [1,14]. Here, it should be noted that all earlier reports of EDB temperature with SS HC in various Ar/H₂ (0.5% - 3.0% H₂ vol.) quoted T_{EDB} = 36 eV.
[1,14], which is close to 35 eV measured in this experiment. Also, the previous results with Cu HC (TEDB=42 eV) [14] match well the 42 eV in this study. The contribution of fast excited hydrogen atoms H\(^{+}\) to line intensity in Ar/NH\(_{3}\) gas mixture, however, considerably decreased for both hollow cathodes: compare contributions of Gauss 3 to line intensity in Table 2 (\(\approx 95\%\)) in [14] and \(\approx 14\%\) in present work. It is known that the origin of the fast H\(^{+}\) in Ar/H\(_{2}\) mixtures is always related to the dominant role of H\(_{3}\)\(^{+}\). It seems that the discharge in Ar/NH\(_{3}\) has smaller concentration of this molecular ion. This is, most likely, tentative explanation for considerably higher discharge voltage in Ar/NH\(_{3}\) in comparison with Ar/H\(_{2}\) mixture.

3.3. Argon-methane mixture

The experiments with argon-methane mixture were carried out under the pressure of 1.33 mbar, current 45 mA and voltage 310 V and 370 V with SS and Cu HC, respectively. The H\(_{\alpha}\) line shape was used throughout for profile analysis. This profile was fully consistent with the one of H\(_{\beta}\) line, but with better signal to noise ratio. The typical H\(_{\alpha}\) line profile recorded with SS HC and best fit composed of three Gaussians are presented in figure 3. The residue plot is shown as a lower part of the same figure.

![Figure 3. The H\(_{\alpha}\) line profile recorded at the HC axis Ar-CH\(_{4}\) mixture fitted with three Gaussians. The line profile is normalized to unity area. Discharge conditions: stainless steel HC; Ar + 10% CH\(_{4}\) at p = 1.33 mbar, U = 310 V, I = 45 mA and T\(_{wall}\)=65\(^\circ\)C. The lower graph displays the residual between best fit and experimental data.](image)

It is evident that three distinct components are present in the ADB profile. The narrowest and the middle one are expected after electron beam→CH\(_{4}\) experiments [5-7], see Introduction, where in electron energy range 25-150 eV at least three dissociation processes and their products are expected. However, our results indicate again presence of only two processes related to Gauss 1 and Gauss 2. In our experiment the Gauss 1, excited hydrogen atoms with temperature below 0.5 eV, corresponds to slow component (1 eV) in electron beam→CH\(_{4}\) experiment [5]. The Gauss 2 with larger temperature of around 2 eV may be correlated either with first component (3 eV; threshold at 21.6 eV) or less likely with the third component (4 eV; threshold at 35.3 eV) from [5]. The largest expected Doppler temperature in the range 8-12 eV [5] is not detected in our HCGD experiment. The detection of two Doppler temperatures, instead of expected four, is most likely consequence of low spectral resolution of our line shape recording system and electron energy distribution, which is not monoenergetic as in electron beam experiments [5-7].

The average energy of fast excited hydrogen atoms TEDB, derived from the width of Gauss 3, ranges between 28 eV and 29 eV with SS and between 29 and 30 eV with Cu HC. The magnitude of these
temperatures proves that the excessive broadening of the H$_\alpha$ line is present in both HC discharges under studied experimental conditions. The Gauss 3 contribution to the line profile differs for SS (62-83%) and Cu (75-92%) HC.

3.4. Argon-acetylene mixture
The experiments with argon-acetylene mixture were carried out at the pressure of 1.33 mbar, current 45 mA and voltage 475 V and 515 V with SS and Cu HC, respectively. Typical experimental profile of the H$_\alpha$ line recorded at the axis of Cu HC is presented in figure 4. As for argon-methane mixture, three Gaussians are required for the best fit of experimental profiles. The average Doppler widths of Gauss 1 and 2 are $\approx 0.4$ eV and $\approx 2$ eV, respectively. The latter value is in agreement with results of electron beam$\rightarrow$C$_2$H$_2$ experiment (for electron energy range from 50-100eV) [8]. The slow component, which would correspond to Gauss 1 in our glow discharge, was not observed in the electron beam$\rightarrow$C$_2$H$_2$ study [8]. The temperature determined from the half width of Gauss 3 ranges from 28.5 to 31.5 eV for both HC, which indicates that Gauss 3 with excessively large half width is related to EDB [1,14]. The contribution of fast excited hydrogen atoms H* to line intensity is lower for SS (46-67%) than for copper (63-95%) HC.

![Figure 4.](image)

**Figure 4.** The H$_\alpha$ line profile recorded at HC axis in Ar-C$_2$H$_2$ mixture fitted with three Gaussians. Line profile is normalized to unity area. Discharge conditions: copper HC; Ar+10%C$_2$H$_2$ at p = 1.33 mbar, U = 515 V, I = 45 mA and T$_{wall}$=956°C. The lower graph displays the corresponding residual.

Here, it should be noted that T$_{EDB}$ measured in this experiment are lower than those reported in earlier studies with Ar-H$_2$ gas mixtures (0.8% and 3.0% H$_2$ vol.) [1,14]. In latter study T$_{EDB}$ values were 36 eV for SS HC and 42 eV for Cu HC. Apart from T$_{EDB}$, the contribution of excited hydrogen atoms H* to the H$_\alpha$ line intensity is considerably decreased in this experiment as well. However, there are several processes, which may influence T$_{EDB}$ and G$_3$ contribution to the line intensity in argon-hydrocarbon discharge. One of these processes may be related to collisions of H$_3^+$ with matrix gas. It seems that H$_3^+$ ions and relevant products for EDB, fast H and H*, loose more energy in collisions with matrix gas than in Ar-H$_2$ mixture and, consequently, the energy of fast H* atoms in both HC is smaller. This results in decrease of T$_{EDB}$ in argon-hydrocarbon discharge. Another more likely reason for decrease of T$_{EDB}$ in argon-hydrocarbons mixtures is production of soot and its deposition on the HC wall. The soot layer at HC surface decreases both, number and energy reflection coefficient of fast reflected H atoms, which are of great importance for generation of fast H* in collisions with matrix gas. Considerable decrease of T$_{EDB}$ values has been already detected in argon-water vapour mixture with same HC materials [15] and it was explained by the presence oxide layers at HC surface.
4. Conclusion
The study of the Hα line shape in a DC, low-pressure, continuous flow, HCGD operated with ammonia, argon-ammonia and argon-hydrocarbon gas mixtures shows multi-component ADB profiles, which can be well fitted with three Gaussians. The narrow and the medium width Gaussian have half widths: 0.3 to 0.4 eV and 3 to 4 eV, respectively, in ammonia and argon/ammonia mixture; and below 0.5 eV and about 2 eV, respectively, in argon-hydrocarbon gas mixtures. The origin of these components has been related to dissociative excitation and dissociative ionization and excitation of ammonia, methane or acetylene in collision with discharge electrons. For all studied working gases, the third Gaussian, having one order of magnitude larger width than the preceding two is related to the presence of EDB. The large energy gain and excessive H⁺ energy is explained within collision model [9-11] in relation to asymmetric charge exchange.

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