# Line shapes of atomic hydrogen in a plane-cathode abnormal glow discharge

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Hydrogen Balmer lines were observed in the plasma of a plane-cathode abnormal glow discharge in mixtures of argon or neon with hydrogen and in pure hydrogen. Intense spectral-line wing development was detected whenever argon was present in the plasma. This effect is related to the formation of $H_2^+$ ions in a charge-transfer reaction between metastable $Ar^+$ and $H_2$ molecules.

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## I. INTRODUCTION

Recent studies of shapes of atomic-hydrogen lines in an electric hollow-cathode discharge [1,2] has shown hydrogen line shapes with an extraordinary wing development not observed in the positive column of the same discharge. The extensive wings indicate the presence of excited hydrogen atoms with very high velocities. The overall line profile consists of two parts: one very narrow part induced by Stark and Doppler broadening in the plasma, and the second much broader part (usually with a considerably smaller amplitude). Similar hydrogen-atom line shapes were detected in rf [3,4], and multicusp discharges [5–7]. Recently, Barbeau and Jolly [8] investigated energetic atoms in a dc hydrogen glow discharge using complex hydrogen line profiles while Vrhovac *et al.* [9] studied dissociative excitation of hydrogen in both rf and dc glow discharge. The widths of the far wings observed in the glow discharges are much larger than the widths that can be expected from dissociative excitation by electrons detected in beam experiments [10–12].

Here one should notice that these gas-discharge experiments [1–9] all have in common that they are performed at relatively low electron densities, $10^9$–$10^{11}$ cm$^{-3}$. In this paper we report the results of a study of the influence of the gas mixture in a plane-cathode abnormal glow discharge on hydrogen line shapes at electron density $\simeq 10^{14}$ cm$^{-3}$.

## II. EXPERIMENT

For the light source we selected a plane-cathode glow discharge (PCGD) of the Grimm type [13,14]. This type of the PCGD has been successfully used for surface analysis of some metals and alloys using emission spectrometry (see, e.g., Refs. [15] and [16] and references therein). Our PCGD was constructed locally following the design of Ferreira, Human, and Butler [16]. A schematic diagram of the side view of the lamp is given in Fig. 1 of Ref. [16]. The exchangable hollow anode 30 mm long with inner and outside diameters 8 and 13 mm, respectively, has either a longitudinal (15 mm long, 1.5 mm wide) or transversal slot (8 mm long, 0.5 mm wide) for plasma observations. The water-cooled cathode holder has an exchangable carbon or metal electrode 18 mm long and 7.6 mm in diameter which screws tightly onto its holder to ensure good cooling. All spectra recordings were performed side-on, 1 mm from the cathode in the region of negative glow; see Fig. 1 of the present paper and Fig. 3 in Ref. [15]. The gas flow through the discharge of about 200 cm$^{-3}$/min was sustained at a pressure of 150 Pa by means of a needle valve and two-stage mechanical vacuum pump. To run the discharge a 0–2 kV, 0–100 mA dc voltage stabilized power supply was used. In series with the discharge and power supply a ballast resistor of 10 kΩ is placed. Typical voltages applied directly to the PCGD electrodes range from 500 to 750 V.

For spectral measurements two spectrometers were used. For the qualitative analysis of spectra a 4-m Hilger-Watts-Ebert-type spectrometer (reciprocal dispersion of 2.42 Å/mm) with an optical multichannel analyzer (model O-SMA, Spectroscopy Instruments) was used. The array consisted of 1024 pixels, each 25 μm wide with effective dispersion of 0.0605 Å per pixel. This spectrometer with a 10-μm entrance slit and with an array detector has a measured instrumental half width at half maximum (HWHM) of 0.20 Å. The size of the pixels

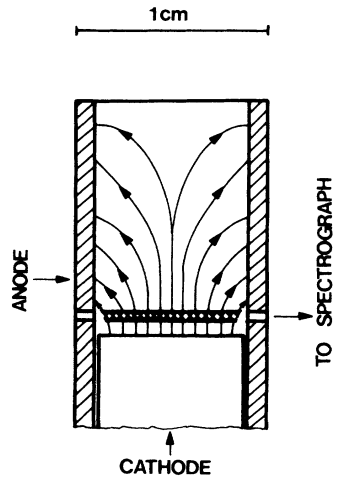


FIG. 1. Schematic diagram illustrating the discharge. The shaded area represents the region which was observed side-on with spectra-recording equipment.

 

and pixel-to-pixel blooming across the array limited the spectral resolution of our 4-m spectrograph and did not permit a precision study of the hydrogen line shapes. For this purpose a photomultiplier-spectrometer (model PGS-2 spectrograph, Carl Zeiss, Jena) system with a reciprocal dispersion of 3.70 Å/mm was used. To scan spectral lines it was necessary to mount an exit slit on the PGS-2 spectrograph. With 20-$\mu$m entrance and exit slits, the measured instrumental profile was 0.20 Å. All scannings of hydrogen lines were performed with 20-$\mu$m slits.

## III. RESULTS AND DISCUSSION

First, side-on recordings of hydrogen Balmer lines in the PCGD with copper cathode and an argon-hydrogen mixture showed line shapes similar to those detected in pure hydrogen in Refs. [1] and [2], although with a much more intense lower and broader part of the line profile [see the example in Fig. 2(a)]. However, the narrow core of the $H_\beta$ profile is still much broader than the nearby Ar II line, see Fig. 2(a), illustrating the well-known effect: Stark and Doppler broadenings are larger for hydrogen lines than for heavy-ion lines with the quadratic Stark effect.

For comparison, the $H_\beta$ profile recorded in pure hydrogen is given in Fig. 2(b). Although electric power input in the PCGD was the same in both cases the lower part of $H_\beta$ profile is considerably more intense in the Ar-$H_2$ mixture, indicating the important role of argon in the process. However, one should notice that the width of the low-intensity part of the $H_\beta$ profile in pure hydrogen, Fig. 2(b), is larger than in the Ar-$H_2$ mixture. To be able to measure HWHM in this case it was necessary to increase sensitivity of spectra recording and to analyze the lower part of the profile. Similar procedure is applied in Ref. [2] (see Figs. 3–5 of Ref. [2]).

It is important to underline that $H_\beta$ profiles presented in Fig. 2 represent side-on integral intensity recordings in the region of negative glow, 1 mm from the surface of the cathode. In order to recover hydrogen line profiles from the radial intensity measurements at different wavelengths, the Abel procedure is applied. In the further analysis of $H_\beta$ line profiles we followed a procedure already described, see, e.g., Refs. [2] and [4]. Since it was difficult to determine whether the lower part of the profile consists of more than one Gaussian profile, the fittings of this part of the experimental profiles were performed with a single Gaussian profile. A hydrogen-atom temperature of 95 eV at the axis, 1 mm from the cathode of the 15-W PCGD in the Ar-$H_2$ mixture is derived. Under the same power input in pure $H_2$, the hydrogen-atom temperature of 125 eV is detected. Other plasma parameters in the Ar-$H_2$ mixture were determined from (i) the relative intensities of Ar I and Ar II lines for electron temperatures; (ii) the width of the 6965-Å Ar II line for plasma gas temperature; (iii) the Stark width of the narrow part of the $H_\beta$ line profile for electron density. Typical results [17] at the axis 1 mm from the cathode of the 15-W PCGD discharge in the argon-hydrogen mixture (97:3) were (a) the electron temperature from Ar II lines 4700 K, (b) the electron temperature from Ar II lines 25 800 K, (c)

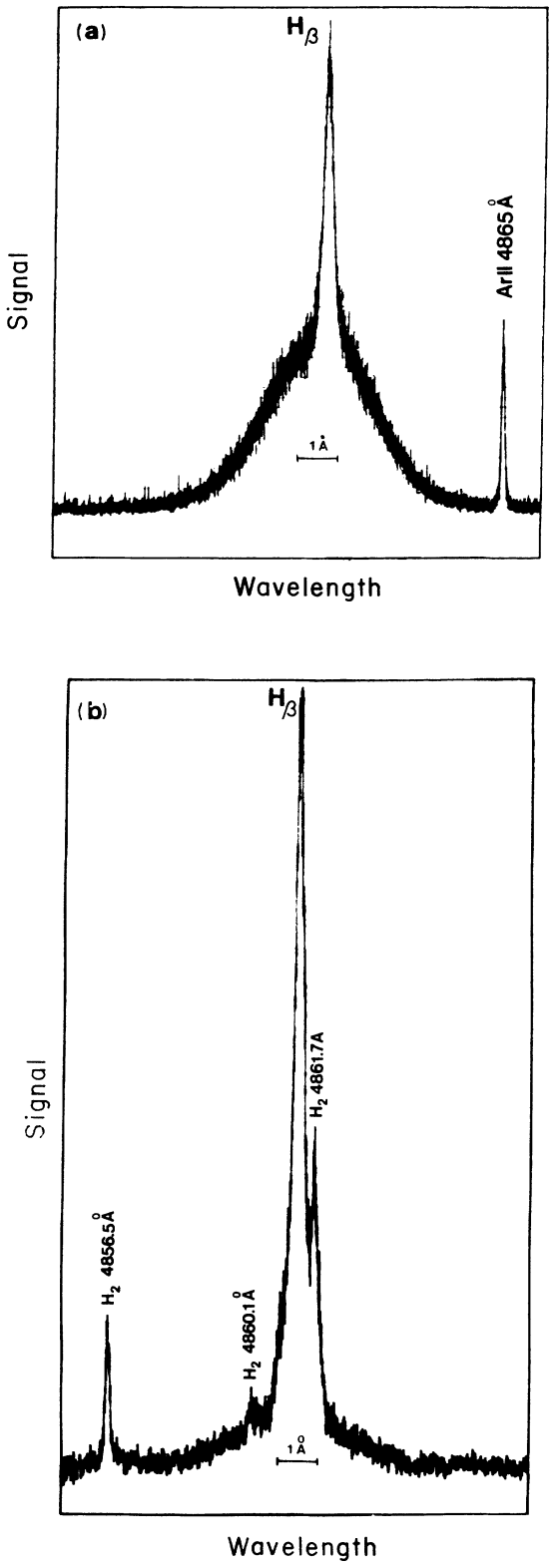


FIG. 2. $H_\beta$ line profiles recorded with a spectrometer-photomultiplier detection system; method of observation: side-on, 1 mm from the copper cathode of the PCGD (a) in an argon-hydrogen mixture (97%: 3%); discharge current 30 mA, voltage 500 V and (b) in pure hydrogen; discharge current 20 mA, voltage 750 V.

the gas temperature 1100 K, and (d) the electron density $\cong 1\times10^{14}$ cm$^{-3}$. Further spectra analysis was performed with the 4-m spectrograph. Due to the lower dispersion of this system profiles were distorted [compare $H_\beta$ profiles in Figs. 2(a) and 3]; these spectra were used for a qualitative analysis only. Profiles of $H_\alpha$, $H_\beta$, and $H_\gamma$ from the Ar-$H_2$ mixture in the PCGD with copper cathode are given in Fig. 3. All three hydrogen line profiles recorded under the same experimental conditions are widely broadened.

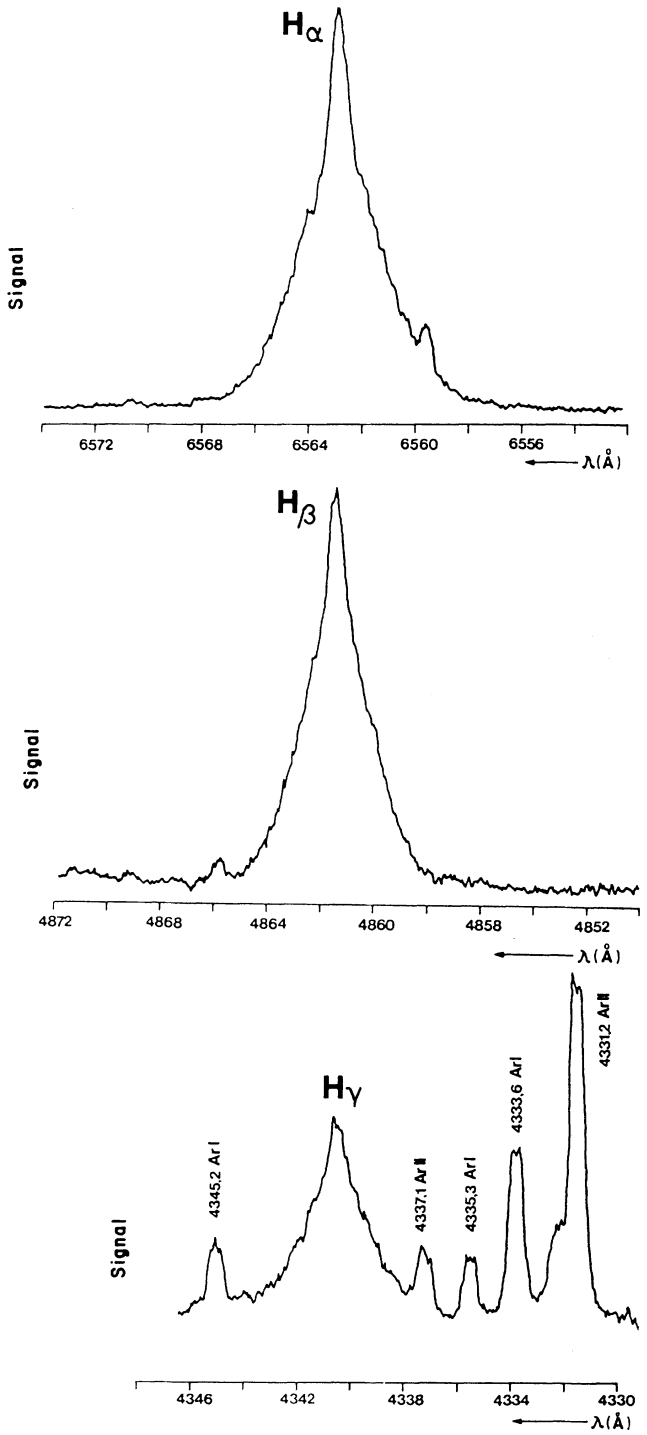


FIG. 3. $H_\alpha$, $H_\beta$, $H_\gamma$ profiles recorded with a spectrometer optical multichannel analyzer, side-on to the discharge, 1 mm from the copper cathode in the argon-hydrogen mixture (97%:3%); discharge current 30 mA, voltage 500 V.

Profiles of the $H_\alpha$ line obtained with a carbon electrode in argon and neon mixtures with hydrogen and in pure hydrogen are given in Fig. 4. Similar spectra recordings were obtained with a silver cathode. Comparison of hydrogen spectra in Figs. 2–4 and results for the silver cathode clearly illustrate the role of argon in gas mixtures with hydrogen irrespectively of the cathode material. Namely, whenever argon is present in the plasma, the lower part of hydrogen lines is very intense, indicating the presence of a very efficient interaction between an argon atom or ion and a hydrogen molecule. Here, in further discussion one should distinguish between intensity and width of the lower part of the hydrogen line profiles. Whenever hydrogen is present in the plasma the lower part of the hydrogen line profiles is broadened. In the case of pure hydrogen, Fig. 2(b), this effect is hardly visible while in the mixture of hydrogen and neon, with the low concentration of $H_2$, it is impossible to detect this broader part of the line profile with the sensitivity of the detection system used for the recording of Fig. 4. To analyze this lower part of the line profiles it is necessary to increase sensitivity considerably.

It has been shown [18] already that certain vibrational

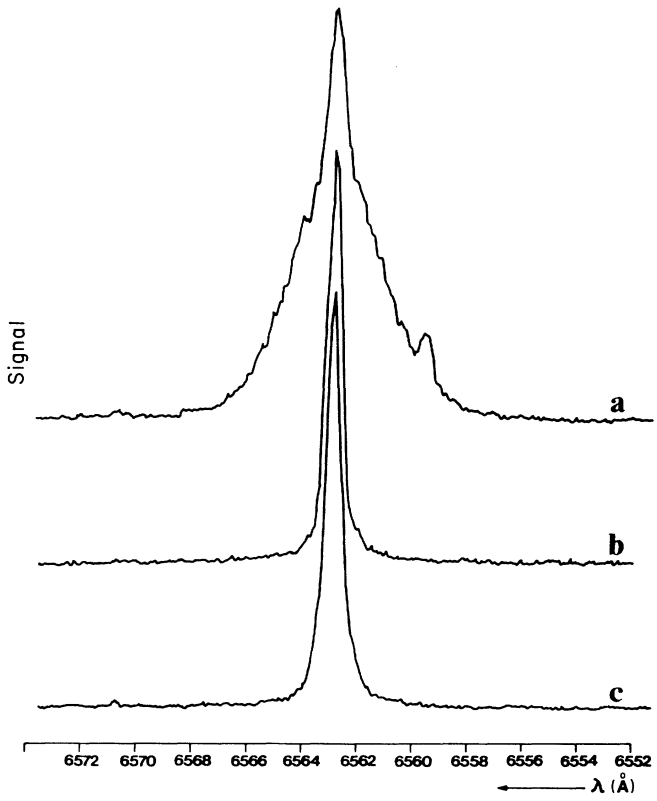


FIG. 4. $H_\alpha$ profiles with the carbon cathode recorded as in Fig. 2. *a*, argon mixtures; *b*, neon-mixtures with hydrogen (3%); *c*, pure hydrogen.

states of the $H_2^+$ molecular ion are in near resonance with the $Ar^+$ ion: the $v'=1$ state lies 63 meV below $Ar^+(^2P^\circ_{3/2})$ and the $v'=2$ state is only 13 meV below $Ar^+(^2P^\circ_{1/2})$. Thus, the charge-transfer process

$$Ar^{+(m)} + H_2 \rightarrow Ar + H_2^+ \quad (1)$$

may be considered as quasiresonant [18]. Another reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H \quad (2)$$

is very likely to occur in our plasma (see the cross-section data in Ref. [19]). However, in either case, it is essential that the $H_2^+$ or $H_3^+$ ion must gain energy in the electric field of the discharge before the dissociation. Otherwise, the large energy of excited hydrogen atoms (on the average 50 eV per atom) cannot be explained.

Recently a mechanism for the generation of high-energy excited atomic fragments in pure $H_2$ and Ar-$H_2$ mixtures has been proposed by Petrović, Jelenković, and Phelps [20]. It consists of excitation by fast neutral atoms produced in charge-exchange collisions of ions and by reflection of the fast neutral atoms in the ground state from the cathode surface. This model has been successfully applied to low-current discharges in the Townsend regime and it is in a qualitative agreement with the results of this experiment obtained at much higher electron densities. However, there is another basic difference between this experiment and those in Ref. [20]. Here hydrogen line shapes were studied in the presence of singly ionized argon atoms [see the spectra recording in Fig. 2(a)] and, as a result of reaction (1), a large concentration of $H_2^+$ ions is present in the plasma. Since the amount of reflected energetic hydrogen atoms from the cathode surface depends upon the reflectivity of the surface and upon the concentration of incident ions, in our case the effect on the hydrogen line shape is much larger than in pure hydrogen or in hydrogen-neon mixture. The half-width at half maximum of the Doppler-broadened lower part of the profile, however, is largest in pure hydrogen and it is proportional to the cathode fall potential. This is in a good agreement with the model presented in Ref. [20].

## IV. CONCLUSIONS

The observations of hydrogen Balmer lines in argon- and neon-hydrogen mixtures and in pure hydrogen revealed intensive wing developments in the presence of argon in the plasma of negative glow of a plane-cathode abnormal glow discharge at an electron density $\cong 10^{14}$ $cm^{-3}$ irrespectively of cathode material (carbon, copper, and silver). A tentative explanation for hydrogen line shapes in the presence of argon is related to the quasiresonant charge transfer between metastable argon ions $Ar^+(^2P^\circ_{3/2}, ^2P^\circ_{1/2})$ and hydrogen molecules and the formation of a $H_2^+$ ion, see reaction (1). The results of this study are in qualitative agreement with the model presented in Ref. [20] recently.

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