On the mechanism of Doppler broadening of H_β after dissociative excitation in hydrogen glow discharges

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The analysis of the Doppler profile of the Balmer β (H_β) line emitted from the low current, low pressure H_2 dc, and low and high frequency rf discharges was used to get additional data on the fast excited hydrogen atom production in the cathode sheath region. The results show very broad line profile in both dc and low frequency discharges, due to the excited particles of several hundred electrovolt moving towards and away from the cathode. The effect of different heavy particle collisions on dissociative excitation and ionization in the cathode region for different discharge conditions is discussed.

1. Introduction

The purpose of this communication is to present Doppler shift measurements of Balmer β (H_β) radiation for hydrogen discharges over a range of frequencies from dc to 13.56 MHz. We shall comment on the possible dissociation processes in the cathode sheath including the observed energy distribution of the product atoms. This work is an extension of our earlier studies on dissociative excitation of hydrogen in rf and dc glow discharges [1]. Recently Barbeau and Jolly [2] observed asymmetric Balmer β profiles in dc hydrogen discharges where they propose ion charge transfer excitation for atoms going towards the cathode and surface neutralization and backscattering for atoms leaving the cathode.

We have tested the relative contribution of gas-phase charge exchange collisions producing fast H* and reflection of the particles on the cathode surface leading to the energetic atoms in dc glow discharges. As our results for different dc currents in hydrogen discharges gave quite different spectral profiles, we attempted to establish the correlation between the kinetic energy distribution of H* atoms and ion energies at the cathode of different dc glow discharges. We have done measurements for both constricted cathode glow, sometimes called normal discharge, with operating current density of 0.15 mA/cm^2 and high current diffuse discharge, or abnormal discharge, with current density of about 0.75 mA/cm^2 [1–9]. In the following text these discharges will be called normal and abnormal discharge respectively.

Comparison of spectroscopic data from various rf frequency discharges is important because the observed differences can be an additional test of some suggested mechanism. In this experiment we tried to find out the phase correlation between the density of excited atoms and the rf voltage. Therefore, we present the results of Doppler shift measurements in the rf discharges for four different frequencies 50, 200, 300 kHz and 13.56 MHz. The parameters such as frequency, pressure and power were monitored throughout the experiment. In particular the effect of frequency, for constant pressure and power in the discharge, on kinetic energy distribution of excited hydrogen atoms could be derived.

Such parametric studies of discharge properties can provide a valuable information on the mechanism of the fast atom production after the dissociation of H_2, and could be useful to show how the discharge properties evolve when frequency is changed. Finally, we compared our results for the effect of rf frequency with the two electron group model [10–12] and experimental results of several authors [13–16].

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2. Experimental

The discharge was maintained between two parallel plate electrodes, 4 cm in diameter and spaced 2.0 cm apart. The rf system was capacitatively coupled and highly asymmetric, with one of the electrodes and the wall chamber grounded. For dc discharges the electrode set was placed in a glass tube to prevent breakdown towards the walls of the vacuum chamber. The pressure range covered in this experiment was from 0.3 to 0.7 Torr and the flow rates from 1 to 10 sccm. Pressure was determined to better than 1% and flow rates to 0.5%.

The operating glow discharge current in dc measurements was 2 and 10 mA and corresponding voltages 500 and 850 V. The rf power was applied from a 13.6 MHz CVC model KR-1 generator through an impedance matching network model KR-30. Typical power was in the range from 20 to 50 W, with peak to peak voltage 300–500 V and a bias voltage of about 100 V. The low frequency 50–300 kHz linear amplifier (with the built in matching circuit) was used to run the rf discharges at lower frequencies. The power was in the range from 1 to 40 W with peak to peak voltage 800–1900 V. The power was determined by multiplying the voltage and current waveforms point by point and then averaging over a cycle.

The spectral profiles and the time-resolved optical emission were obtained by detecting the light in a direction parallel to the electric field, through a 0.4 mm slit in the electrode (grounded electrode in rf experiments and the cathode in dc glow experiment). The detection angle was 7°. The spatial profiles of Balmer β emission were obtained detecting the light in the direction perpendicular to the electric field. The radiation was analyzed by means of a SPEX monochromator, using a cooled photomultiplier and photon counting system controlled by computer. The spectral and spatial resolution of the optical system were 0.02 nm and 1 mm respectively. In order to obtain the time dependence of the optical signal relative to the rf voltage (for the frequency range 50–300 kHz) the signal from the photomultiplier was fed into the charge sensitive amplifier, and then in the storage oscilloscope.

3. Results and discussion

3.1. Radio-frequency discharges

Spatial dependence of H_β light gave strongly asymmetric profiles, with the light detected dominantly in the vicinity of the rf powered electrode [1,8]. We have also found that such spatial profiles depend on the wavelength. The spatial emission at wavelengths corresponding to red and blue wings decay faster than the emission at the center of the line. Fig. 1 shows an example for 100 kHz discharge.

Although spatial profiles are rather similar for high and low frequency rf discharges, the voltage and current waveforms and time and spectrally dependent emission profiles are different.

In low frequency rf discharges the phase shift between current and voltage is close to zero and the discharge impedance is mostly resistive. It can be assumed that during the cathodic part of the cycle the main component of the current on the electrode is the ion current and the electron current during the anodic part.

The observed phase shift between current and voltage at 13.6 MHz is close to $\pi/2$, so the discharge impedance was mainly capacitive. The dominant current is the displacement current and the time variations of the total current density correspond fairly well to experimental [17–19] and numerical [20] results for the wave riding regime. According to the investigations done by several authors [10–16]

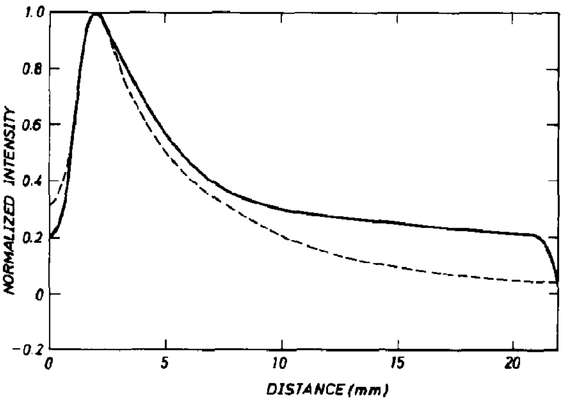

Fig. 1. Spatial profile of Balmer β radiation in 100 kHz discharge at $p=0.65$ Torr; peak radiation (solid curve); wing radiation (dashed curve).

and the time variations of the current measured in this experiment during the cathodic part of the cycle (when the powered electrode is negative), the ion and electron current densities have the same sign, corresponding to the collection of ions and to the emission of secondary electrons leaving the cathode. In the anodic part of the cycle the higher number of electrons reaches the electrode so the electron conduction current increases.

In fig. 2 the dependence of the Balmer β Doppler profile on discharge frequency is presented. Different behavior of discharges at lower (50–300 kHz) and higher frequencies is demonstrated via the spectral profiles of Balmer β line. At lower frequencies ions have time to cross the sheath during a cathodic half cycle and to create very fast H*, e.g. 300 eV for 300 kHz and even higher for 50 kHz.

Moreover, the time-resolved emission profile for the far wings of H_β line in the 100 kHz discharge has shown (see fig. 3) that most of the H_β radiation is emitted during the cathodic part of the cycle (at the potential maximum) when ion current dominates. These measurements prove that besides electron impact collisions (dissociative excitation and ionization of H_2) which are responsible for low (0.2–1 eV) and medium (5–10 eV) energy H* atoms [1] the heavy particle collisions are rather important. According to the data in fig. 2 the fraction of the fast H* atoms is increasing with decreasing rf frequency, while their mean energy remains unchanged. These

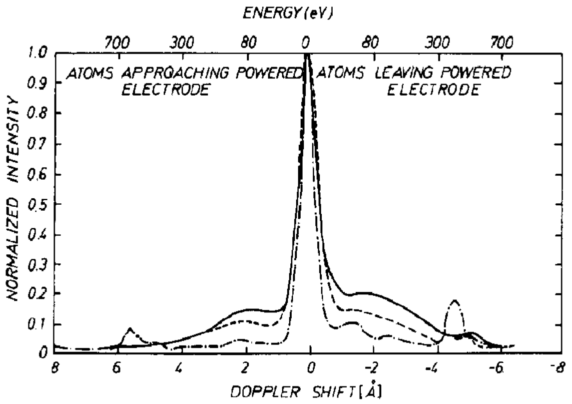

Fig. 2. Balmer β Doppler shift observed in rf glow discharge in H_2 at different frequencies at the same pressure $p=0.55$ Torr; 50 kHz (solid curve); 300 kHz (dashed curve); 13.56 MHz (chain curve).

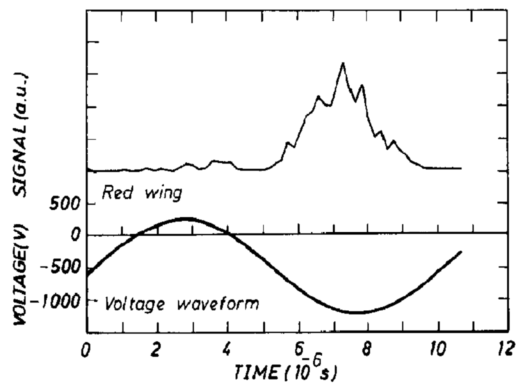

Fig. 3. Time-resolved emission profile of Balmer β red wing $\lambda=4863$ Å, together with the voltage waveform in 100 kHz discharge at $p=0.65$ Torr.

findings are in a rather good agreement with the results obtained with a two electron group fluid model [10]. The blue wing of the Balmer line here represents excited hydrogen atoms going away from the cathode (i.e. powered electrode). These atoms are produced after the ion or neutral species bombardment of the cathode and are less directed than those moving towards the cathode. They can be responsible for the same rate of spatial decay of light at both red and blue wings as shown in fig. 1.

At 13.56 MHz the ions do not respond to the instantaneous electric field but to its average value and are accelerated by the average electric field of the cathode sheath. Therefore, in the sheath region the electron impact dissociative excitation and ionization collisions dominate. The profiles obtained at 13.56 MHz show no sign of extensive red or blue wings and just a small fraction of H* atoms of 25 eV energy. Small peaks on the blue wing of the H_β are weak molecular transitions. This is in accordance with our previous investigations [1] of the spectral profiles in same experimental conditions, in direction perpendicular to the discharge axis. There we did not find any difference between the kinetic energy distribution function (EDF) of H*($n=4$) atoms evaluated in the sheath and in the bulk. It is reasonable to assume that under these conditions the energy of atoms and ions arriving at the surface of the powered electrode is mainly determined by fluxes of electrons and ions in the plasma bulk.

We have also examined the effect of pressure on the spectral profile at lower rf frequencies. The result

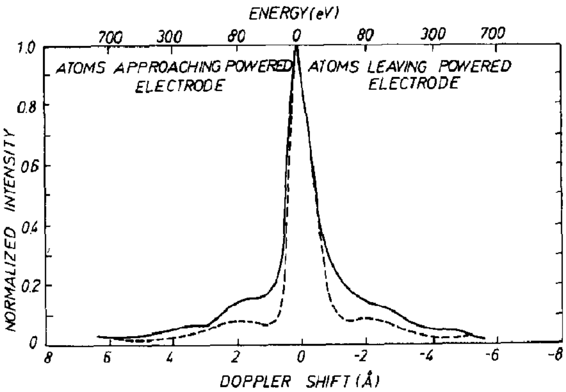

Fig. 4. Balmer β Doppler profiles observed in 200 kHz discharge in H_2 at two different pressures; 0.3 Torr (solid curve) and 0.55 Torr (dashed curve).

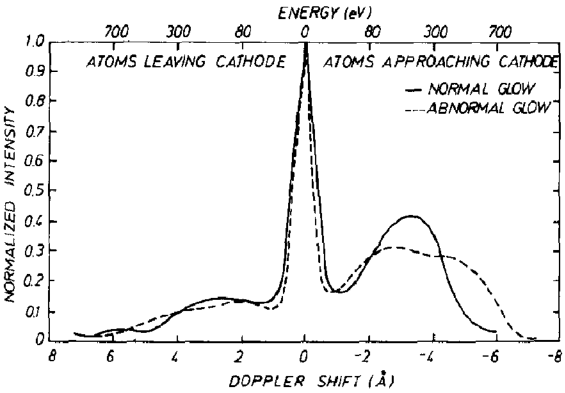

Fig. 5. Balmer β Doppler shift observed in hydrogen dc normal and abnormal glow discharge at the same pressure $p=0.65$ Torr. (——) $I=2$ mA, $U=510$ V; (---) $I=10$ mA, $U=856$ V.

for 200 kHz is shown in fig. 4. Essentially the effect of lowering the pressure is similar to decreasing the frequency, but with the wings extended to higher energies. According to Toups and Ernie [21] the ratio of the frequency and the gas pressure is a critical parameter. At lower pressure the effective value of E/N (electric field to gas density ratio) had increased and so did the mean energy of ions and fast neutrals in the sheath region.

3.2. Direct current discharges

As in rf discharges the spatial dependences of optical emission observed from dc discharges show that most of the light is emitted in the cathode vicinity. In order to estimate the role of charge exchange collisions in dc discharges and to compare the data for dc and rf discharges we have measured the Doppler shift of the Balmer β line in a dc normal and abnormal glow as defined in refs. [22,23]. Typical profiles obtained in the cathode fall of the normal (2 mA) and abnormal (10 mA) glow are shown in fig. 5. The lines are very broad, showing that some particles, accelerated before the collisions, can acquire energies almost equal to the total applied voltage. It is interesting to mention that the structure on the blue wing in the abnormal glow is reproducible and can indicate the presence of different channels for $H^*(n=4)$ excitation.

The main channels for the H_2^+ destruction in hydrogen glow discharges are:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \,,$$

$$H_2^+ + H_2 \rightarrow H_2 + H_2^+ \,,$$

$$H_2^+ + H_2 \rightarrow H^+ + H + H_2 \,.$$

The first channel is the formation of H_3^+, and is dominant for ion energies less than 10 eV. At higher H_2^+ energies, e.g. in gas discharges with $E/N > 1$ kTd, the charge transfer cross section becomes dominant and H_2^+ behaves as in swarm conditions [5]. Unlike H_2 the velocity of H_3^+ as well as H^+ increase rapidly with E/N [24]. Measurements of the energy distribution of different ions from H_2 discharge by Davis and Vanderslice [8] have shown that H^+ and H_3^+ can get energy nearly equal to the discharge voltage. Using the single beam model [25], Phelps had shown that both ions can runaway [5]. The data of Williams et al. [26] show that the fraction of the H_α emitted by fast H atoms upon the $H_3^+ + H_2$ collision is 50%. On the other hand high energy of excited particles going away from the cathode, as shown in fig. 5, can only be explained by reflection of the high energy light particles, e.g. H^+ or fast H from the surface.

Like in Townsend discharges at $E/N > 1$ kTd [27], we have observed a large fraction of fast excited atoms going away from the cathode. As the reflected particles are less directed than the incoming particles [8], the broadening of Balmer β profile observed perpendicular to the field axis is due to emission of particles going away from the cathode. The probability for the reflection of particles from the electrode depends on the electrode material, and the measurements are on the way to determine the effect of atomic number on the reflection probability.

4. Conclusion

We have investigated the H_β line broadening in dc and rf hydrogen discharges. Common for all these discharges is the asymmetric spatial profile with the light emitted predominantly at the cathode (powered electrode) vicinity.

In rf discharges the dominant emission occurs during the cathodic part of the rf cycle. We have shown that both rf frequency and gas density influence the Balmer line profiles when the light is detected through the grounded electrode. Lowering the frequency (from 13.56 MHz down to 50 kHz) has the same effect as lowering the gas density (from 3×10^{22} to 6×10^{21} m^{-3}) on the energy of ions and neutrals impinging on the powered electrode. We found that both red and blue components of the H_β profile are increasing relative to the central peak with decreasing the frequency and pressure. There is a similar fraction of fast particles going towards and away from the powered electrode in low frequency (below 300 kHz) and practically no heavy particle effect on H_β excitation in high frequency (13.56 MHz) discharge.

Characteristics of the H_β spectral profile in dc glow discharges include a very large component of fast H^* going both towards and away from the cathode with the energy very close to the voltage applied across the gap for atoms going towards the cathode. Therefore we have concluded that conversion of H_2^+ into H^+ must precede the formation of fast $H^*(n=4)$. Impact and reflection of H^+ and fast H at the surface is the most important for the production of fast excited H atoms going away from the electrode.

These experiments can provide a good test of the models developed to explain the collisional processes in H_2 glow discharges. We are still not aware of any model suitable to our experimental observations and therefore the work is in progress to establish such a model.

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