ENERGY DISTRIBUTIONS OF NEUTRALS AND CHARGED SPECIES

IN HOLLOW CATHODE H₂ DISCHARGES. A STUDY OF FAST H ATOMS.

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Abstract

A joint study of atomic and molecular emission spectroscopy, ion mass spectrometry and Langmuir probes, is presented for a hollow cathode H₂ discharge at pressures 0.7-20 Pa, rendering energy distributions of the different groups of particles that span five orders of magnitude. The H Balmer line profiles can be decomposed in three contributions (“narrow peak”, “plateau” and “far wings”) with very different widths. The narrow peak and the plateau are largely attributed to electron impact dissociative excitation and ionization of H₂, and display Doppler temperatures of ~ 0.3 and ~ 6 eV, respectively. The energy resolved mass spectra of H⁺ confirm the assignment of the plateau region. The far wings give rise to emissions extending to Doppler shifts of 0.5 nm, which correspond to translational energies of ~ 300 eV. The dependence of the relative intensities of these components with pressure is studied. With a grounded grid before the observation window, a structure is induced in the blue shifted wing. Assuming that the structure is solely caused by dissociative excitation of H₂ upon collisions with the plasma ions (H⁺, H₂⁺ and H₃⁺), their relative concentrations can be estimated. These estimations are in very good agreement with the values derived from independent mass spectrometric measurements.

Introduction

Light emission by excited hydrogen atoms in H_2 plasmas provides most useful information about the physics of very different environments ranging from fusion reactors [1-4] to astronomical media [5-7]. In laboratory plasmas, the intensities and line-shapes of emission lines can provide a measure of the concentration of H atoms [8, 9] or can be used for the estimate of electron densities [10, 11] or to detect the presence of dust [12]. In addition, the analysis of the line profiles can unveil the main mechanisms of H atom generation.

Large broadening of hydrogen Balmer lines has been observed and discussed for decades in the emission spectroscopy of H_2 glow discharges [3,13-29]. It is generally assumed that this broadening is due to the presence of translationally hot H atoms. Various processes, either in the gas-phase or at the walls of the discharge cells, can be relevant for the production of the hot H atoms. Clues about the mechanisms at play in each case have been usually derived by decomposing the line-shape into different contributions. In most discharges the Balmer lines and, in particular, the H_α line can be divided into three components [14,15,25]: a comparatively narrow peak, a component of intermediate width, and a very wide component. Throughout the paper we will often term these three components “core”, “plateau” and “far wings” respectively, as named frequently in previous works. The first two components, which display Gaussian profiles, are largely attributed to dissociative excitation of H_2 upon electron impact. In fact, Balmer lines with contours including the central core and the plateau had been reported in low pressure hydrogen samples subjected to electron beam collisions [30-32]. The third component, which implies very fast atoms, is generally attributed to collisions of H atoms with ions accelerated in the electric field or with energetic neutrals resulting from the neutralization of the ions either in the gas phase or at the reactor walls (see refs. [15,16, 25,26, 28,29] and references therein).

In recent works [28,29] Phelps developed a model for the description of spatial distributions and profiles of H_α emission lines which incorporates the different types of relevant collisions mentioned in the previous paragraph. The model provides a good global description of the line profile measurements from a wide variety of experimental sources. As indicated by the author, H_α profiles not only reflect the velocity distributions of the excited atoms, but contain also information about the energies of the plasma species that excited them. The model was also applied to direct measurements of positive ion energy distributions, but in this case discrepancies were found between measurements [33] and calculations [29].

On the other hand, ion energy distribution measurements are especially relevant, since they give a measure of the main process of energy gain by heavy particles from the field [34, 35] and might thus hold important clues about the origin of the hot atoms responsible for the broader wings of the emission lines. In spite of their obvious interest, most studies on the line profiles of H Balmer lines do not include ion distribution measurements (see refs in [28, 29]). Exceptions to this situation are the works by Radovanov et al. [17] and Babkina et al [36] with RF discharges. In the first of these works, the authors conducted measurements of H_α emission profiles together with ion-energy distributions at the grounded electrode of an Ar/H₂ RF discharge. A qualitative analysis of the results suggested that the broad component of the line profile was most likely due to fast H atoms backscattered in the neutralization of H^+ and H_3^+ ions at the powered electrode. In the study of Babkina et al. [36] information on the neutralization processes of fast ions on a biased electrode was derived from joint measurements of the emission spectroscopy of hyperthermal H atoms and of the energy distributions of the ions formed in the electron stripping of these fast atoms through collisions with neutrals in the plasma.

In the present study we have simultaneously recorded Doppler broadened H_α emissions of hollow cathode H₂ discharges, and energy distributions of ions at the cathode walls. These data have been complemented with Langmuir probe measurements for the estimation of electron temperatures and densities in the plasma. Vibrational and rotational temperatures have also been determined from emission spectra of the Fulcher H₂ band. The joint analysis of the extensive set of experimental results has allowed the identification of the main processes responsible for the contours of the Balmer emission lines in the discharges.

Experimental

A diagram of the experimental setup can be seen in Figure 1. It has been described in detail in earlier works [9,37]. The hollow cathode discharge reactor used for our experimental measurements consists of a grounded stainless steel cylindrical vessel (10 cm diameter, 34 cm length), and a central anode stainless steel bar. In hollow cathode discharges, the plasma can be roughly considered to be confined into the negative glow region. The electric field in this negative glow, which fills most of the cathode volume, is close to zero [35,38], and ions diffuse inside it without a net gain of kinetic energy. The ion energy distributions are then largely determined by the acceleration of ions in the comparatively thin cathode sheath region between the negative glow and the cathode, and are mostly characterized by a narrow

maximum at energies of some hundred eV, close to that of the anode–cathode potential. In the present case, the cathode sheath surrounds in a nearly uniform way the whole negative glow (as indicated approximately by the potential contour curves represented in Figure 1), and ions move from the negative glow edge towards the cathode following trajectories practically perpendicular to the grounded cathode wall (see top and right white arrows in Figure 1-top panel and right white arrow in Figure 1-bottom panel). Slight exceptions to this behavior can be found next to the small lateral flanges that support dielectric optical windows and other testing equipment, where the contour potential curves might be somewhat distorted, and ions follow the local direction of the electric field (see the couple of white arrows at the left hand side of the reactor in Figure 1-top and bottom panels). We will return to this point later. As to the central anode, ocular inspection of the plasma emission at its surroundings through an additional optical window placed in front of it (not represented in Figure 1) allows to perceive that the anode is surrounded by a very narrow anode glow of a different color than that of the negative glow and then, very closely, by the homogeneous luminescence of the negative glow.

Steady-state plasma currents ~ 150 mA and voltages ~ 400 – 550 V (depending on gas pressure) were maintained during the experiments. An electron gun was used to ignite the discharge at the low pressures studied, and was switched off after the establishment of the discharge. A continuous flow of pure H_2 was used for plasma generation. Experiments were performed for reactor pressures from 0.7 to 20 Pa, measured with a capacitance manometer (Leybold, CTR90). The pressure was chosen by balancing the input and output gas flows using a needle valve in the gas inlet and a gate valve located at the gas exit between the reactor and its vacuum system, which consisted of a turbomolecular pump backed by a dry pump. The residual vacuum, measured with a Penning manometer, was 10^{-4} Pa.

Figure 1. Top panel: Experimental setup diagram. The location of the diagnostics (plasma monitor and optical spectrometer), hollow cathode, anode, the electrical system used to ignite the plasma (electron gun) and the gas input and output systems are shown, as well as the approximate shapes of the negative glow and the potential curves of the cathode sheath. Bottom panel: Enlarged horizontal section of the reactor at the plane of emission measurements. White arrows in both panels indicate approximately the direction of ion motion in the observation regions (see text).

An optical fiber connected to a Jobin Yvon-Horiba FHR1000 dispersive spectrometer in Czerny-Turner configuration, with a focal distance of 1 m and a diffraction grating of 1800 mm⁻¹, was placed in one of the observation windows, using alternatively a charge-coupled device

(CCD) or a photomultiplier as detectors. Optical spectra were obtained using the CCD detector for large wavelength intervals (~ 300 nm), or the photomultiplier for more precise measurements, with narrower intervals (~ 1 nm). Integration times were changed among the different measurements in order to obtain a sufficient number of counts for the lines of interest. The spectral range for the system with the aforementioned grating is 300-800 nm. Spectral efficiency was calibrated using a tungsten lamp previously calibrated in the Institute of Optics (CSIC, Madrid). Instrumental resolution was calibrated for each detector and slit widths used in this work by using the Hg line at 546.07 nm from a fluorescent tube. For the photomultiplier and slit widths of 24 μm , the instrumental line width was 0.014 nm, whereas for the CCD and an input slit width of 24 μm (similar to the pixel width of 26 μm , which limits the maximum resolution with this detector), the instrumental line width was 0.020 nm. The optical fiber location was alternated between two different observation windows of the reactor: a common window ((a) in Figure 1), used for most of the measurements, and another one ((b) in Figure 1) in which a grounded metal grid was placed internally for reasons described later in the work.

A plasma monitor (Balzers PPM421) was employed to detect ions with mass and energy resolution. It uses an electron multiplier as detector and was placed in a differentially pumped vacuum chamber, sampling the plasma through a ~ 100 μm diaphragm. The plasma monitor has also an ion focalizing system into the energy analyzer, located just after the sampling diaphragm, and an electron impact ionizer that allows its alternative use to detect neutral species. During operation, the pressure in the detection chamber was kept in the order of 10^{-5} Pa by means of a turbomolecular pump and a dry pump. The residual vacuum, measured with a Bayard-Alpert manometer, was approximately 10^{-6} Pa. Total ion fluxes were obtained, as described in [39-41], by integrating the ion energy distributions obtained with the plasma monitor and applying a previously calibrated sensitivity factor to the different masses. These distributions showed in general a very narrow peak at an energy determined by the anode-cathode potential difference, and a continuum of much less amplitude extending towards lower energies [34, 35]. Relative ion concentrations in the plasma were calculated by multiplying the ion fluxes by the square root of the corresponding mass. A double Langmuir probe (not shown in figure 1) built in the laboratory [42, 43] allowed the estimation of charge densities and electron temperatures.

Results and discussion

For the H₂ discharges under study, electron densities in the $(1-3) \times 10^{10} \text{ cm}^3$ interval and electron temperatures ranging from $T_e \sim 8 \text{ eV}$ for a pressure of 0.7 Pa to $T_e \sim 2.5 \text{ eV}$ for 20 Pa were estimated from Langmuir probe measurements, in agreement with ref. [9]. Typical ionization degrees were of the order of $\sim 10^{-5}$, and typical dissociation degrees were of the order of ~ 0.1 [9]. The vibrational and rotational temperatures of H₂ were determined as in a previous work [9] by applying a collisional radiative model [44, 45] to measurements of the Fulcher- α emission lines. The results for some of the discharge pressures considered are shown in Table 1. The estimated vibrational temperatures are above 2500 K, which is consistent with a picture of efficient electron impact excitation and inefficient collisional relaxation, as expected for H₂ in the low pressure environment of our plasmas. The rotational temperatures are around 400 K, somewhat above the temperature of the reactor, which is in turn slightly higher than room temperature. Both set of values agree globally with those of ref. [9].

Table 1. Vibrational and rotational H₂ temperatures at different pressures.

H ₂	2 Pa	8 Pa	20 Pa
T_{vib} (K) $\pm$ 50 K	2760	2570	2510
T_{rot} (K) $\pm$ 50 K	380	400	410

Atomic emission spectra were measured for H $_{\alpha}$, H $_{\beta}$ and H $_{\gamma}$ lines of the Balmer H series. A typical spectrum of the H $_{\alpha}$ line in 8 Pa H₂ plasma, as recorded with the CCD camera through the window without the grounded grid, is shown in Figure 2. The three regions of the line profile mentioned in the introduction are immediately apparent in this logarithmic representation. As can be seen, the broadest and less intense component (far wings) of the profile extends over a width of $\sim 1 \text{ nm}$, and the velocities of the H atoms causing this broadening correspond to energies that can reach $\sim 300 \text{ eV}$. The relative contributions of the three regions to the global emission can be very variable depending on the physical characteristics and geometry of a given discharge, as well as on the detection arrangement [28,29]. As we shall see below, in our case the emission comes largely from the extended negative glow filling most of the space

within the cylindrical cathode; and the intensity of the far wings, which are attributed to processes taking place in the narrow sheath, is comparatively small.

Figure 2: Experimental line profile (blue-widest line) showing the three different broadenings of the H_{α} emission of the Balmer series in semi-logarithmic scale: the narrowest one or “core” (a), the medium one or “plateau” (b), and the widest one or “far wings” (c). The Doppler fit to each profile and the global fit are shown.

Higher resolution spectra of the central part of the H_{α} and H_{β} lines in the 8 Pa H_2 plasma, recorded with the photomultiplier over a narrower wavelength range, are displayed in Figure 3. The H_{γ} profile, not shown for brevity, is similar to H_{β} . In the same figure, the line profile is separated in two (Gaussian) Doppler components corresponding respectively to the core and plateau regions.

Figure 3. Emission line profiles and Doppler fits for the narrowest (a) and medium (b) profiles of the Balmer H_{α} and H_{β} lines. The overall fits are also shown.

The Doppler temperatures associated with the individual profiles are also indicated in the figure. Note that for both lines the Doppler temperatures of the core are lower than 0.35 eV whereas those of the plateau are larger than 5 eV. Table 2 lists the temperatures derived from Doppler fits to the core and plateau regions of the H_{α} , H_{β} and H_{γ} lines for four of the discharge pressures investigated. The Doppler temperatures of the core (0.19-0.35 eV) are found to be narrower by a factor 15-30 than those of the plateau region (5.4-7.1 eV). The behavior is similar for the other pressures studied. A Gaussian profile could be also fitted to the broadest far wings components shown in Figure 2. In this case, the corresponding effective mean energies are typically larger than 100 eV. However, these values have not been included in Table 2, since this part of the line profile is made up by of the contributions of various groups of atoms giving rise to different Doppler shifted emissions, as discussed below.

Table 2. Temperatures (in eV) for the core and plateau regions of the H_α , H_β and H_γ lines of the Balmer series, at different discharge pressures. Estimated uncertainties are ~ 10 -15%.

H₂ pressure	T_{Doppler} Core (eV)			T_{Doppler} Plateau (eV)		
	H_α	H_β	H_γ	H_α	H_β	H_γ
<i>0.7 Pa</i>	0.23	0.23	0.19	5.9	5.5	5.5
<i>2 Pa</i>	0.33	0.23	0.24	7.1	5.8	6.9
<i>8 Pa</i>	0.34	0.24	0.34	5.4	5.5	6.7
<i>20 Pa</i>	0.32	0.30	0.35	6.1	5.8	6.3

The relative intensities of the three individual components of the line profiles, obtained from their respective areas, are represented in Figure 4 as a function of pressure. For the three Balmer lines studied, the contribution of the plateau decreases with increasing pressure, whereas that of the far wings grows. As to the central peak, a global tendency to increase with pressure can be observed, in a less regular way than that of the far wings.

Figure 4. Relative intensities of the three components of the H_α , H_β and H_γ lines for different H_2 pressures. The corresponding discharge voltages are: 540 V at 0.7 Pa, 450 V at 2 Pa, 450 V at 8 Pa and 480 V at 20 Pa.

The physical mechanisms responsible for the distinct components of the Doppler broadening observed can be now analyzed. The Doppler temperature of ~ 0.3 eV obtained for the core peak is similar to that reported in previous publications [14, 30]. Light emission in this region is attributed to the dissociative excitation of H_2 molecules according to the following scheme:

Where H_2^* represents H_2 molecules in Rydberg levels, “nl” denotes excited states of the hydrogen atom, and E is the energy transferred to each fragment. The Balmer series emissions correspond to transitions $n \geq 3 \rightarrow n=2$ and the estimated E values, derived from the energies of the likely dissociative molecular states implied are in the 0.25-0.5 eV range [14, 46]. Direct excitation of H atoms through electron impact, which does not result in a large momentum transfer to the atom, could also contribute to the narrow central peak. Threshold electron energies for these processes through Frank-Condon molecular transitions or direct excitations are ~ 14 -16 eV [46] and ~ 11 -12 eV [47], respectively.

The plateau broadening is also assumed to be due to electron impact. In this case the likely channels would be dissociative excitation (equation 1) to doubly excited states, or dissociative ionization via:

with threshold electron energies above 30 eV [14,46]. Dissociation through doubly excited states would lead to atoms with an energy of 7.5 eV [15] whereas dissociative ionization would produce excited atoms with $E=5$ -8 eV [14]. The width of the plateau region in our plasmas corresponds to energies within this range (see Table 2).

Additional evidence for the contribution of the ionization channel (equation 2) to the plateau region of the Balmer lines can be derived from the measurement of ion energy distributions. Three ions: H^+ , H_2^+ and H_3^+ are detected in our plasmas. As commented on in elsewhere [9,35] the first two are mostly produced through electron impact. Besides the dissociative process reflected in reaction 2, direct ionization of H and H_2 can also take place:

Protonated hydrogen, which clearly dominates in the plasmas under study, except for the lowest pressure (0.7 Pa), is generated in the reaction:

The values of the rate coefficients of reactions (3-5) and a more extensive set of reactions involved in the ion H_2 plasma chemistry is given in [9].

The energy distributions of the ions reaching the cathode are displayed in Figure 5. In general, the distributions have a dominant narrow peak at an energy corresponding roughly to that of the voltage fall in the cathode sheath, followed by a long weak tail extending to lower energies. The relative intensity of the tail increases with growing pressure. As discussed in a previous work [35] the tail of the distributions is due to sheath collisions and, in the specific case of H_2^+ , this tail is due to efficient symmetric charge transfer processes, which dominate the distributions for the higher pressures. Most interesting for the purpose of the present discussion are the energy distributions of H^+ ions, which present a secondary peak or shoulder with a maximum at an energy $\sim 6-7$ eV higher than that of the main peak. This higher energy peak, which is more prominent at the lower pressure shown in Figure 5 (0.7 Pa), corresponds to H^+ ions generated in reaction 2, as discussed in ref. [35], where the process was analyzed in detail and the measurements were compared to previous electron beam data [48]. With growing pressure, the intensity of this high energy peak decreases due to the decrease in the electron temperature and to the growth of the collision frequency in the reactor, which results in a lower production rate and a higher thermalization of the H^+ ions reaching the detector. Note that the present measurements combining emission spectroscopy and energy resolved mass spectrometry of the plasma ions allow the detection of the two products of reaction 2, medium energy (plateau) H atoms and H^+ ions, and highlight the relevance of this process in the plasma.

Figure 5. Ion energy distributions for several of the different H_2 pressures investigated. The discharge voltages are the same that in Figure 4.

Although reaction 2 is the most favoured explanation for the emission corresponding to the plateau region, other possibilities have also been suggested. We will leave aside the heterodox interpretation given in [27] (see comments in [25] and [29]) and will mention briefly the work of Loureiro and Amorim [24]. These authors suggested that the broad plateau region extending to both sides of the peak of the H_α line should not be interpreted as indicative of the presence of relatively fast H atoms (with energies up to 8 eV) but rather as a non-Gaussian profile associated with the non-Maxwellian distribution of excited H atoms produced in reaction 5, which is exoergic by ~ 1.6 eV. However, the direct detection in our experiments of ions produced through reaction 2 supports the concomitant presence of the associated fast H atoms and thus the validity of the decomposition of the H Balmer lines in various Gaussian components due to groups of H atoms with very different “temperatures”, which was questioned by these authors. In addition, if reaction 5 were the main mechanism determining the emission in the plateau region, the relative importance of this component in the global profile should increase with pressure over the range studied, since in this pressure interval bimolecular processes (like reaction 5) become faster than direct electron impact ionizations (like reaction 2) [49]; however precisely the opposite is observed (see Fig. 4).

The far wings of the line profile require much more energetic processes than those considered thus far and, as mentioned in the introduction, are usually attributed to collisions of high energy ions with H_2 or to hot atoms reflected from the wall upon ion neutralization. In our hollow cathode reactor, ions gain energy from the field as they are accelerated through the sheath region toward the metallic walls of the cathode. The excited atoms produced in these collisions will travel more or less in the direction of the colliding ion, and the corresponding emission will be Doppler shifted and can contribute to the wings depending on the ion energy. It should be noticed that this energy depends on the discharge voltage, which varies between some 400 and 550 V for the range of pressures investigated. On the other hand, the sheath width can also change slightly with voltage and discharge pressure [35].

A clear structure in the wings of the H_α emission was found formerly in hollow cathode H_2 discharges with a special design leading to highly directional ion flows [22,23]. The cathode voltages used in these experiments were in the kV range. The structure, which was clearly more marked at the blue wing of the line, consisted of three peaks that were assigned to excited hydrogen atoms, H^* , produced in charge transfer collisions of hydrogen molecules with the three types of ions present in the plasma:

In these experiments, the energy is carried essentially by the colliding ion and is transferred to the products, which share it mostly as kinetic energy between the various product species. For a given ion energy (with a maximum value determined by the voltage fall in the cathode sheath) three groups of H^* atoms with decreasing kinetic energies, corresponding respectively to reactions 6, 7 and 8, are produced. From their well resolved wing profiles, Fitzgerald et al. [23] could estimate the concentrations of H^+ , H_2^+ and H_3^+ ions in their plasmas employing a simple model that takes into account the energy-dependent reactive cross sections (taken from [49]) for the respective reactions.

In our reactor, the ions are not attracted towards the dielectric observation windows used for optical spectroscopy, but follow rather more or less oblique trajectories toward the metallic grounded walls in the vicinity of these windows, as represented by two white arrows in the left hand side of the reactor shown in Figure 1 (window (a)). This effect is due to the distortions of the potential contour curves in their surroundings. In order to enhance the directionality of the ions towards the optical observation region, a metallic grid connected to the cathode was placed in front of one of the windows (window (b) in Figure 1) and emission spectra were recorded alternatively through the two opposite windows, with and without the grid. The results for the two experimental configurations are displayed in Figure 6 for the H_α line at three of the pressures investigated. For comparison, the two sets of measurements have been scaled at the maximum of the central peak.

Figure 6. Detail of the far wings ((c) component) of the H_{α} line for different pressures and for the two observation windows: with and without the grounded grid.

As can be seen, the line profiles are very similar, except at the blue shifted wing for the higher pressures, where weak secondary maxima appear in the spectra recorded with the grounded grid in front of the observation window. Our experimental arrangement leads to less distinct and, hence, relatively lower resolved peaks than those of [23], where the ion accelerating potential reached 6 kV (equivalent H_{α} Doppler shift > 1 nm); but the contribution of the different groups of H^* atoms can also be assigned by fitting the partially resolved profile to a sum of three Gaussians, as shown in Fig. 7 for the blue far wing of our 8 Pa discharge.

Figure 7. Detail of the resolved components of the H_α line emission at 8 Pa, 450 V, as measured with a grounded grid placed before the observation window. The labels H^+ , H_2^+ and H_3^+ on the three peaks indicate the parent ion that contributes to the corresponding energetic H atom, through charge exchange reactions with H_2 .

In our case, only two maxima are clearly visible, corresponding to H^* atoms generated in collisions of H_3^+ and H^+ ions with H_2 . A small contribution of H_2^+ must be included to recover the whole profile. An approximate estimate of the relative proportion of the three ions can be made using the same procedure applied by Fitzgerald et al [23]. Within this approximation, the ratio between the densities of H^* atoms produced through reactions 7 or 8 and those of reaction 6 can be expressed as [23]:

$$\frac{n_{H_x^+}}{n_{H^+}} = \frac{\sigma_{H^+} \Delta\lambda_{H^+} I(H_x^+)}{\sigma_{H_x^+} \Delta\lambda_{H_x^+} I(H^+)} \quad (9)$$

Where n are the densities, σ the cross sections, $\Delta\lambda$, the Doppler shifts, and $I(H_x^+)$, the intensities obtained from the area under the peaks. As indicated in the introduction, equations 6-8 are not the only pathways for the production of fast H^* atoms in hydrogen plasmas. Alternative mechanisms are provided by collisions of H_2 with hyperthermal H atoms backscattered from metallic walls upon neutralization of fast ions, or produced by collisions of H_2 with H^+ ions accelerated in the sheath. Depending on the system, these mechanisms, with

relatively high excitation cross sections [28], can be determinant for the recorded emission profile [28,29,36]. However, in our experiments, possible collisions with fast atoms backscattered from metallic walls would not have a high directionality and are not expected to contribute significantly to the structured emission reflected in Figure 7. On the other hand, generation of H^* in a two-step mechanism starting with the production of fast H atoms through $H^+ + H_2$ collisions, followed by subsequent collisions of these fast atoms with H_2 in the sheath, is unlikely under the low pressures of our experiments. We have not considered these mechanisms in our analysis. The consistency of the data on far wing profiles and mass spectrometric ion distributions (see below) justifies this assumption.

For the calculation of the ion ratios in equation 9, we have used the recent cross section values proposed by Phelps [28, 50] for an energy of 300 eV, which are: $\sigma(H^+) \sim 4 \times 10^{-19} \text{ cm}^2$ for reaction 6; $\sigma(H_2^+) \sim 1.5 \times 10^{-19} \text{ cm}^2$ for reaction 7, and $\sigma(H_3^+) \sim 3 \times 10^{-19} \text{ cm}^2$ for reaction 8 (strictly speaking, one should consider cross section values over the $\sim 0\text{-}300 \text{ eV}$ range of the whole sheath, but the cross section ratios, which are the relevant magnitudes for the quotient expressed by equation 9, hardly change with energy, and the cross section values at the high energy end of the interval are by far the largest). The relative concentrations of the three ions are listed in Table 3 for discharge pressures of 4, 8 and 20 Pa. The method could not be applied to the emission measurements at pressures of 2 Pa and below, since for these low pressures the collision probability of the ions accelerated in the sheath is too low and the small blue shifted peaks are very weak and poorly resolved. In the same table, the results are compared to the direct mass spectrometric values, which are derived from an integration of energy resolved spectra like those portrayed in Figure 5.

Table 3: Relative H^+ , H_2^+ and H_3^+ ion concentrations, determined by ion mass spectrometry (MS) with the Plasma Process Monitor (PPM) and analysis of the H_α far wings emission. The estimated uncertainties in the relative ion concentrations with the PPM are $\sim 10\%$. Absolute errors in the estimations from emission measurements are given together with the data.

H ₂ Pressure	4 Pa		8 Pa		20 Pa	
Relat. Ion Concentrat.	Ions (MS)	H _α far wings	Ions (MS)	H _α far wings	Ions (MS)	H _α far wings
H ⁺	0.03	0.06 ± 0.03	0.10	0.13 ± 0.05	0.18	0.16 ± 0.02

H_2^+	0.10	0.10 ± 0.04	0.07	0.08 ± 0.04	0.06	0.05 ± 0.03
H_3^+	0.87	0.85 ± 0.05	0.83	0.80 ± 0.07	0.77	0.79 ± 0.04

The very good agreement between the two sets of values, derived independently with different experimental methods, indicates that ion collisions in the sheath are indeed largely responsible for the far wings emission and the whole blue-shifted far wing can be accounted for by this mechanism. The results of table 3 support also the consistency of the cross sections proposed by Phelps [28] for reactions 6-8 up to 300 eV. The evolution with pressure of the relative ion concentrations obtained in the present experiments confirms the results from ref. [9]. The concentration of H_3^+ is found to be clearly the highest one for the pressure interval shown in Table 3, and that of H^+ increases slightly with pressure at the expense of H_2^+ and H_3^+ . A possible candidate for the production of additional H^+ could be the reaction [35]:

with estimated cross sections [48] of 10^{-16} – 10^{-17} cm² for the collision energies of the plasma sheath, but other inelastic and charge transfer processes are probably involved too.

As indicated above, in the absence of grid the ion directionality is lessened in the observation direction and the peak structure in the H_α wing becomes blurred (dashed line in Figure 6). The same effect is found, also for the same reason, in the red wing of the experiments with grid, which is caused by ions travelling through the (gridless) sheath opposite to that of the observation window (see Figure 1). A certain contribution of excitation by backscattered fast H atoms produced at the wall neutralization of energetic H_x^+ ions cannot be excluded, but is expected to be small.

After the elucidation of the mechanisms responsible for the three components of the H Balmer line emissions, the evolution with pressure of their relative contributions (see Figure 4) becomes clear. An increase in pressure results in a cooling of the electron temperature and thus to a decrease in the plateau, which is caused by impact of electrons from the high energy tail of the electron energy distribution, which lead to dissociative excitation to doubly excited states and dissociative ionization (reaction 2). The central peak benefits indirectly from the T_e decrease and can grow with growing pressure, since electrons leading formerly to dissociative ionization have now lower energies and are only available for dissociative excitation (reaction

1). Finally, the relative weight of the far wings caused by atoms produced in reactions 6-8 increases with the growing collision frequency associated to the pressure increase.

Summary and conclusions

Very different energy distributions of distinct groups of neutral and charged species have been identified in plasmas generated in a H_2 hollow cathode discharge by means of visible emission spectroscopy, energy-resolved ion mass spectrometry and double Langmuir probes. In fact, the spectroscopic measurements of the H_2 Fulcher band and the H Balmer series line-profiles are sufficient to determine that the energies of the different groups of neutrals span five orders of magnitude, from the rotational (or gas) H_2 temperature, which is close to the room temperature (~ 0.03 eV), to the group of the fastest excited atoms, which reaches ~ 300 eV and proceeds mainly from collisions with H_2 molecules of ions accelerated in the sheath.

Even the excited hydrogen atoms giving rise to the Balmer lines exhibit very different translational energies that can be grouped into three distinct energy distributions, reflected as three components in the line profiles. The first two components, which are mostly assigned to electron impact dissociation and dissociative ionization of H_2 molecules, correspond to Doppler temperatures of some 0.3 eV (narrow peak) and 6 eV (plateau), respectively. Energy resolved mass spectra of H^+ ions support the assignment of an important part of the plateau region to electron impact dissociative ionization of H_2 . The third, much broader component (far wings) of the Balmer lines, attributed largely to ion collisions in the sheath, includes very fast atoms leading to Balmer emissions Doppler shifted up to 0.5 nm (corresponding to translational energies of ~ 300 eV). The relative weights of these components change with pressure in opposite forms, due to the different formation paths of the different groups of atoms.

The far wings of the H_α emission show a resolved structure when the ion directionality is improved by placing a grounded metal grid before the observation window. The analysis of this structure employing a simple model [22, 23] and recent cross sections values of the H dissociative excitation in $\text{H}_2 + \text{H}_x^+$ collisions [28,51] allows to infer the relative H^+ , H_2^+ and H_3^+ ion concentrations, which are in very good agreement with independent ion mass spectrometric measurements. Our results support the consistency of the just mentioned cross section data of Phelps [28] for energies up to ~ 300 eV.

The present study has certainly some limitations, like the assumptions of the potential fall shape and of the ion directions of motion close to the sampling flanges; as well as the fact that optical and mass spectrometric measurements are not performed at the same position. The consistency between the ion and optical measurements suggests however that these shortcomings are not too relevant for our experiment. As a general conclusion, the great advantage of combining emission spectroscopy and energy resolved ion mass spectrometry for the elucidation of relevant kinetic processes in glow discharges should be emphasized.

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