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Investigation of $\text{H}^-$ production in plasma of dc glow discharge

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Abstract. The laser photodetachment technique was applied to investigate the negative ion dynamics in the positive column of a pure hydrogen dc glow discharge at pressures $P = 0.1 – 3$ Torr. Upon the discharge current modulation, the negative ion $\text{H}^-$ concentration decayed with the characteristic loss time of hydrogen $\text{H}(1s^2\text{S})$ atom concentration. The evolution of $\text{H}$ atom concentration was investigated by the time-resolved actinometry. The axial electric field was measured by double probe technique. The analysis of the experimental data, i.e. the dependencies of $\text{H}^-$ and $\text{H}$ concentrations as well as reduced electric field on the discharge parameters (discharge current and pressure), allowed us to determine the rate constant of $\text{H}^-$ production in the discharge, where vibrational excitation and reactions with atoms $\text{H}$ greatly influence upon $\text{H}^-$ production and loss processes. The main processes, which contribute to $\text{H}^-$ production, are discussed in detail. The vibrational excitation of $\text{H}_2$ is shown to increase the rate of dissociative attachment essentially not only via the excitation of the well-known low-threshold ($\varepsilon_{\text{th}} \approx 3$ eV) resonance of $\text{H}_2(X^2\Sigma_u^+)$, but also via the excitation of the high-threshold resonances of $\text{H}_2(^2\Sigma_u^+)$ ($\varepsilon_{\text{th}} \approx 6$ eV), $^2\Pi_u$, $^2\Pi_g$ ($\varepsilon_{\text{th}} \approx 8-13$ eV) etc). Detailed analysis of dissociative attachment via high-threshold resonances allowed us to describe experimental data in the whole range of $E/N$ being investigated, whereas taking any other mechanisms into account (attachment to Rydberg states of $\text{H}_2$ etc) failed to do that.

1. Introduction

Electronegative plasmas are widely used in various technologies, especially in microelectronics [1]. Negative ions play an important role in plasmas of electronegative gases, affecting the charge balance, the electric field and in turn electron energy distribution function (EEDF). Furthermore, they directly take part in plasma chemical reactions. So, it makes the negative ion investigation a matter of a particular importance.

In spite of the fact that hydrogen is a weakly electronegative gas, hydrogen negative ions and different ways of their production (different discharges in hydrogen) are of great interest [2, 3, 4]. It is mainly caused by the problem of fast neutral beam production for fusion experiments. Furthermore, hydrogen plasma is one of the most investigated for theoretical models object. Therefore it can be thought as of a “model” plasma for investigation of elementary processes in plasmas and for verification of models in order to apply them to the more complicated gases. It is essential for modelers to describe the processes of negative ion production and loss correctly and to know the accurate values of the rate constants of these processes.

In the present work plasma of a pure hydrogen dc glow discharge was investigated. Under the experimental conditions ($P = 0.1 – 3$ Torr, $j = 1 – 10$ mA/cm$^2$) the main process of negative ion...
production in hydrogen plasma is dissociative attachment of electrons to vibrationally excited hydrogen molecules $H_2(v)$ ($v=0, 1, \ldots$):
\[
e + H_2(v) \rightarrow H + H^- ,
\]
so that the cross section of this process violently depends on the vibrational state (vibrational excitation) of $H_2$ molecule. Therefore, even a weak vibrational excitation of $H_2$ can dramatically affect the $H^-$ production.

The main $H^-$ loss channel under the experimental conditions is associative detachment with hydrogen atoms $H$ (it has been also confirmed by our time-resolved photodetachment measurements):
\[
H^- + H \rightarrow H_2 + e .
\]

The rate constant of this process was repeatedly measured and it is well-known [5]:
\[
k_{det}=1.8 \cdot 10^{-9} \text{ cm}^3/\text{s}.
\]

In this work the rate constant of dissociative attachment of electrons to $H_2$ (R1) at different reduced electric fields $E/N$ has been experimentally determined in the discharge, where vibrational excitation of $H_2$ and reactions with atoms $H$ take place.

The analysis of the obtained data has shown that the influence of vibrational excitation of $H_2$ upon $H^-$ production should be taken into account in order to describe the rate constant of (R1) correctly. It should be emphasized that vibrational excitation strongly affects $H^-$ production both via the excitation of the well-known low-threshold ($\varepsilon_{th} \approx 3$ eV) resonance of $H_2^-(X^2\Sigma_u^+)$ and via the excitation of the high-threshold resonances $H_2^-(2\Sigma_g^+ (\varepsilon_{th} \approx 6 \text{ eV}), 2\Pi_g, 2\Pi_u (\varepsilon_{th} \approx 8-13 \text{ eV})$ etc).

2. Experiment

A dc glow discharge in a long cylindrical tube (12 mm-inside diameter) was used for experimental work (Figure 1). The distance between the electrodes was 490 mm. A special feature of this configuration is the spatial homogeneity of the discharge along the tube axis in the positive column region. Experiments were carried out in pure hydrogen for pressures in the range 0.1 – 3 Torr and current densities in the range 1 – 30 mA/cm$^2$.

Negative ions were measured by laser photodetachment technique. In the traditional application of this technique, negative ions are photodetached using laser radiation of the appropriate wavelength, and the resulting electrons are collected using Langmuir probes or microwave interferometry [6, 7, 8]. In this experiment, the laser beam irradiated the whole cross section of the discharge tube, and the anode was used as the electron collecting probe. Therefore, the acquired signal was proportional to the cross section-averaged ratio of negative ion $n_\alpha^-$ and electron $n_e^-$ concentrations. Such an approach allows one to avoid the problems of calibration (the size of the volume over which electrons are collected is exactly determined) and thus to increase the accuracy of experiment. However the criteria of applicability of the given method should be mentioned.

The structure of discharge in electronegative gases is rather complicated [9, 10, 11, 12]. It is determined by the following parameters: electronegativity (i.e. a ratio of negative ion and electron densities), the relation of attachment, detachment, ionization and recombination rates [10]. Under the conditions of our experiment the following conditions were met:
\[
\alpha = \frac{n^-}{n_e^+} < 1 , \quad P = \frac{A}{Z} < 1 , \quad Q = \frac{D}{Z} \gg J = \frac{R \cdot n_e^+}{Z} ,
\]
where $A$ – attachment rate constant, $Z$ – ionization rate constant, $D$ – detachment rate constant and $R$ – recombination coefficient. This notation corresponds to the one used by Franklin and Snell in their paper [10], which gives a deep insight into the problems and peculiarities of discharges in electronegative plasmas. According to [10] if the conditions (1) are met, ion and electron concentration profiles in the plasma core are similar, so the $n^-/n_e$ ratio may be considered as constant, i.e. as independent of radial coordinate. If one takes ion heating into account and non-equilibrium ion diffusion the plasma core area will essentially expand [12]. Especially it is significant at low pressure and consequently high reduced electric fields, where ion heating is essential. It makes the above-
mentioned approach valid. However in some cases it may give slightly underestimated values of $n/n_e$ ratio.

A schematic diagram of the laser photodetachment apparatus is presented in Figure 1. More detailed information about the given approach to the photodetachment technique and about the experimental setup is presented in [13].

According to the measurements of the photodetachment signal – $H^-/n_e$ ratio – saturating with laser pulse energy the calibration was carried out, i.e. the fraction of negative ions photoionized by a laser pulse was determined. At the same time the value of photodetachment cross section can be extracted from the calibration curve. This value $\sigma_{pd} = (1.2 \pm 0.2) \times 10^{-17}$ cm$^2$ is in a good agreement with data for $H^-$ absorption cross section [14]. The negative ion dynamics after a fast switching of a discharge voltage (leading edge ~ 0.2 – 0.3 $\mu$s) was observed by time shifting the laser pulse with respect to the modulation pulse and measuring the $H^-/n_e$ ratio as a function of laser pulse delay. The evolution of the $H^-/n_e$ ratio followed the evolution of H atom density.

Time-resolved actinometry was applied for H atom measurements. The transitions $H(3p^2P \rightarrow 2s^2S)$ ($H_\alpha$) $\lambda = 656.3$ nm and $Ar(2p^1s \rightarrow 1s^2)$ $\lambda = 750.4$ nm frequently applied for hydrogen atom actinometry were used. Modulation of discharge current allows one to determine the contribution of dissociative excitation of $H_2$ to the intensity of $H_\alpha$ line directly and thus to measure the H atom concentration at a very low discharge current and in turn at a low dissociation degree $H/H_2$ (up to $10^{-3}$) [15].

Upon a step change in the discharge current (10-20% increase of the current value) the intensities of H and Ar atom radiation rapidly change because of fast discharge parameter alteration. The radiative lifetime of the $H^+$ and $Ar^+$ emitting states, as well as the relaxation times of the EEDF and electron density, are much shorter than the H-atom lifetime. Therefore, after a fast plasma relaxation, the time evolution of the actinometric signal follows the time evolution of $\delta H$.

If the contributions of both dissociative excitation of $H_\alpha$ and background radiation at the radical’s emission band is already taken into account (and taken away from $H_\alpha$ line intensity), the relative change of atomic hydrogen density upon discharge modulation is given by [15]:

$$1 + \frac{\delta H(t)}{H_0} = \frac{1 + \delta H(t)/I^0_H}{1 + \delta A(t)/I^0_A},$$

(2)

where index “0” refers to the initial values (before the step change). Thus, in order to represent the dynamics of the ratio $\delta H(t)/H_0$ properly, it is important to use the normalized emission, i.e., $I_H/I_A$.  

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**Figure 1.** Schematic diagram of the laser photodetachment experiment
Dissociative excitation of Hα results in renormalization of the right-hand member of (2). However it does not influence upon the time characteristics of the actinometric signal, i.e. the loss frequencies of hydrogen atoms. The experiments revealed that the contribution of dissociative excitation is important only at low pressure and low current, i.e. at \( E/N > 150 \text{Td} \) (\( E/N [\text{Td}] = \frac{E [V/cm]}{N [\text{cm}^{-3}]} \cdot 10^{17} \)) and \( n_e \sim 10^9 \text{ cm}^{-3} \).

The dissociation degree H/H₂ in a stationary discharge is presented in Figure 2. The upper left insert provides the reduced electric field in stationary discharges (in the range of low currents \( E/N \) is almost independent of current). H/H₂ ratio is independent of gas temperature radial profile, because the radial profiles of H atoms and H₂ molecules are similar due to low loss probability of atoms on a silica wall.

At low current hydrogen dissociation degree is a linear function of discharge current.

### 3. Results and discussion

Figure 3 provides the results of measurements of negative ion concentrations at different stationary discharge parameters.

Investigation of negative ion dynamics upon discharge current modulation has revealed that H⁻ concentration decays with the characteristic time of H atom evolution. It directly indicates that the main H atom loss channel is reaction (R2).

Thus the following expression is valid:

\[
\frac{H^-}{n_e} = \frac{K_{att}}{k_{det} \cdot \frac{H}{H_2}},
\]

where \( K_{att} \) – total rate constant of dissociative attachment to H₂ molecules, i.e.\( K_{att} = K_{att}^0 \cdot \frac{H_2 (v = 0)}{H_2} + K_{att}^1 \cdot \frac{H_2 (v = 1)}{H_2} + ... \).
It should be emphasized that the dissociation degree of H$_2$ (see Figure 2) at low current is a linear function of discharge current density $j$. Therefore (3) can be presented as follows:

$$\ln \left( \frac{H^-}{n_e} \right) = \ln \left( \frac{K_{att}}{k_{det} \cdot a(P)} \right) - \ln(j),$$

(4)

where $a(P)$ was taken from linear fittings of dissociation degree H/H$_2$ at different pressures (see Figure 2). In this case H$^-$/ne ratio in a log-log scale is a linear function of discharge current shifted according to pressure (see expression (4)). Indeed, the parallel lines can be seen in Figure 3 at low current. (The slopes of these lines are constant and the intercepts depend on pressure).

**Figure 3.** H$^-$/ne ratio as a function of discharge current at different pressures in stationary discharge

The rate constant of dissociative attachment to H$_2$ as a function of E/N was extracted from fittings of experimental data (H$^-$/ne ratio) at low current by formula (3) (see Figure 4). To analyze the mechanisms of H$^-$ production the calculation of the rate constant of dissociative attachment to the ground state of H$_2$(v=0) has been carried out. The rate constant was calculated from the cross section [16], which took into account the main resonances of H$_2^-$: the low threshold one – H$_2^-$(X$^2\Sigma_u^+$) ($\epsilon_{th} = 3$ eV) and the high threshold ones – H$_2^-$(3$^2\Sigma_g^+$) ($\epsilon_{th} = 6$ eV), H$_2^-$(3$^2\Pi_g$), H$_2^-$(1$^2\Pi_u$) ($\epsilon_{th} = 8-13$ eV) etc; and from the EEDF, obtained by solving the Bolzmann’s equation in the two-term approximation. The obtained rate constant of H$^-$ production is about one order lower than the measured one (see Figure 4, black dashed curve). But the rate of dissociative attachment to H$_2$ is known to increase significantly with vibrational excitation of H$_2$ (for example [16, 17, 18]). It has motivated us to analyze vibrational excitation of H$_2$ in order to take its influence upon the rate of H$^-$ production into account.

In order to estimate the population of vibrational levels the following approach was applied. A steady-state vibrational distribution function was assumed to be Boltzmann’s. It may be assumed because of very low discharge currents being considered, so that the population of high vibrational levels (v>3) is supposed to be negligible. Moreover, the vibrational distribution function in H$_2$ is known to be close to Bolzmann’s for the first 3-4 vibrational levels [17, 18]. The following factors were taken into account: both electron impact excitation of vibrational levels (up to v=3) and populating by the excitation of the bound singlet states (H$_2$(B$^1\Sigma_u^+$, C$^1\Pi_u$)) with their subsequent
radiative decay to the ground vibrationally excited state; V-T relaxation with H atoms (dominating relaxation channel under the experimental conditions), H₂ molecules and on the wall [19]. According to that one can estimate the vibrational temperature of H₂ molecules as a function of discharge parameters. The vibrational temperature slightly increases with discharge current and decreases with increasing pressure from 4500 K at P=0.1 Torr to 2000 K at P=2 Torr. The cross sections of dissociative attachment to vibrationally excited H₂(v) molecules via low-threshold resonance (εₜₐₜ=3 eV) were taken from [20].

![Graph](image)

**Figure 4.** Rate constant of dissociative attachment to H₂ as a function of reduced electric field E/N. Circles – experimental data, grey solid curve and dashed curves – calculation results (see text).

The rate constant calculated from the cross sections [20] with taking into account vibrational excitation of H₂ does not agree with the measured one as well (see Figure 4, grey dashed line). If one takes attachment to Rydberg states into account, it will raise the rate curve only at high reduced electric field. But at intermediate reduced electric field the agreement cannot be achieved.

The only way to fit the calculated rate constant to experimental data is to revise the approach to the high threshold resonances. The point is that although the low threshold resonance is known to increase rapidly with vibrational number, the high threshold resonances are believed to increase slightly with vibrations [16]. But, as we know, there is no direct experimental support of this assumption. Thus, we assumed that high threshold resonances rapidly increase with vibrations similar to the low threshold one. It allowed us to fit the calculated rate constant to the experimental data in the whole range of reduced electric field (see Figure 4, gray solid curve).

Summing up, we would like to emphasize that the given analysis cannot be considered as a kind of some measurement of dissociative attachment cross sections from the experimental data. The main aim was to show that only suggested mechanism could describe the experimental data in the whole range of reduced electric field. *Ab initio* calculations of H₂ and H₂⁻ excited states can be considered as an indirect support of above-stated approach [21].

We hope that these results will motivate the researchers to pay rapt attention to the high threshold resonances.
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