The effect of the introduction of small amount of H$_2$ on Ar-plasma properties

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Abstract. The impact of the introduction of small amounts (up to 3.6 %) of H$_2$ in Ar plasmas produced by a surfatron was studied. This was done in view of futures plans to measure the electron density via H$\beta$-broadening. The H$_2$ concentration was varied between 1.2 and 3.6 % while the pressure was in range from 5 to 20 mbar. While changing the H$_2$ concentration we studied the length of the plasma, the plasma wall heating and the electron temperature. The latter was measured using the method introduced in a previous study based on a combination of absolute line intensity measurements and a collisional radiative model. It was found that, for the mixture ratios we used, the electron temperature does not change but that the H$_2$-addition has a substantial impact on the gas temperature.

1. Introduction

Surface wave sustained discharges (SWD) are systematically investigated both experimentally and theoretically in recent years. The interest in such discharges is based on the fact that they are stable and good reproducible over a wide range of conditions. With the aim to refine the various applications, more insight into the properties of these plasmas is needed. This can be obtained by means of experiments, modeling or combination of both. Different diagnostic methods can be used to determine the plasma parameters – optical spectroscopy (by emission or absorption), probes (Langmuir’s techniques), and mass spectrometry. Since the plasma is generally confined in a quartz tube that is transparent for light, emission spectroscopy is a good candidate to obtain information about the main plasma parameters like the electron temperature and density.

This contribution is devoted to optical diagnostics. It will be shown that for a proper interpretation of the radiation, insight is needed in the deviations from equilibrium. It was shown how the excitation temperature $T_{13}$ of Ar is changed by transport phenomena and how this knowledge can be used to transform the excitation temperature into the electron temperature $T_e$ using a Collisional Radiative Model (CRM) [1]. In search for a good method to determine the electron density $n_e$ one might consider to introduce a small amount of hydrogen so that $n_e$ can be deduced from the H$\beta$ line broadening. However, we will show that even a small amount of H$_2$ will change the plasma considerably.
2. Theory

Plasma properties such as the electron temperature and the electron density can be deduced from the atomic state distribution function (ASDF). If the system is in equilibrium the ASDF is described by the Saha/Boltzmann equation

\[
\eta^p = \eta \eta \left( \frac{\hbar^2}{2 \pi m_e k_B T_e} \right)^{3/2} \exp \left( \frac{I_p}{k_B T_e} \right),
\]

where \( \eta^p = n_p / g_p \) is the level density (\( n_p \)) per statistical weigh (\( g_p \)) of an atom in state \( p \), \( k \) and \( h \) Boltzmann’s and Plank’s constants, \( m_e \) the mass of an electron. The ionization energy of the level is given by \( I_p = E_p - E_n \) while \( n_e = n_p / g_p \) and \( n_i = n_i / g_i \).

The natural logarithm of Saha formula gives

\[
\ln \left( \eta^p \right) = \frac{I_p}{k_B T_e} + \ln \left( \eta \right),
\]

where

\[
\eta = \eta \eta \left( \frac{\hbar^2}{2 m_e \pi k_B T_e} \right)^{3/2} .
\]

The electron temperature can be found via the slope by plotting \( \eta^p \) versus \( I_p \) in a semi-logarithmic plot and \( n_e \) can be determined by a linear extrapolation of \( \eta^p \) in the direction of \( I_p = 0 \). Assuming that \( n_e = n_i \), the electron density \( n_e \) can subsequently be deduced from \( \eta_i \).

However, in the low-pressure regime, the plasma is not in local thermodynamic equilibrium (LTE) and this method can not give the right values of \( n_e \) and \( T_e \). In our case, for plasmas under pressure 20 mbar, we expect a number of effects causing departure from LTE. First, since the electrons are heated by the electromagnetic field, while the atoms are cooled by collisions with the wall, the electron temperature is higher than the temperature of the atoms and ions. Second, due to the transport of charged particles out of the plasma (at low pressure the diffusion flux is large) the Saha balance between ionization and two electron recombination is distorted. This implies that the shape of the ASDF can no longer be described with the Saha equation; the slope is variable and it is no longer possible to define one single temperature. Furthermore, the extrapolation method to find the electron density is no longer correct. Third, the efflux of charged particles leads to a situation in which the number of forward processes like excitation and ionization are no longer equal to that of the inverse process of de-excitation and recombination. This may lead to equilibrium departures of the electron energy distribution function EEDF.

In order to take account of the equilibrium distorting phenomena we modified the well-known method of excitation temperature determination.

The ASDF of the argon system in the surfatron plasma under investigation showed several slopes (figure 1), indicating that, indeed, the system is not in equilibrium. Globally two parts of the ASDF could be distinguished: the lower energy part formed by the ground state (also named level “1”) and the \( 4p \) group (levels “3”). The upper part of the atomic systems is formed by the levels \( 5p \) till \( 8s \).
Figure 1. An ASDF for an argon surfatron plasma.

Since the ASDF is a result of excitation kinetics, all the relevant processes in which the excited states are involved should be taken into account. This is the task of a CRM. The resulting distribution function of excited levels can be written as

\[ b(p) = r^+(p) + b_r r^1(p), \]  

(4)

where the equilibrium departure \( b(p) = \eta(p)/\eta^*(p) \) of a level \( p \) depends linear on the equilibrium departure of the ground state \( b_1 \), and \( r^+(p) \) and \( r^1(p) \) are the so-called relative population coefficients that reflect respectively the recombining and ionizing part of the system. The plasma under investigation are strongly ionizing so that only the second term is important. Since \( r^1(p) = b(p)/b_1 = [\eta(p)/\eta_1] \{ \eta^*_1/\eta^*(p) \} \) while \( \eta^*_1/\eta^*(p) = \exp(E_{1p}/kT_e) \) we can derive the following relation between the excitation temperature \( T_{1p} \) and the electron temperature \( T_e \)

\[ E_{1p}/kT_e = E_{1p}/kT_{1p} + \ln r^1(p). \]  

(5)

This relation will be applied to the 4p level group (level “3”). The \( r^1(3) \) value is determined by the CRM whereas the excitation temperature \( T_{13} \) defined as \( E_{13}/kT_{13} = -\ln \left[ \eta(3)/\eta_1 \right] \) can be found by measuring \( \eta(3) \) and \( \eta_1 \).

In ionizing plasma, the production (such as absorption, three particle recombination, radiative recombination) of the level population is mainly collisional while the destruction (emission, photo ionization and excitation) is a combination of radiative decay and collisional excitation to higher levels or the ion states. The plasma we study are ionizing, meaning that especially the lower energy part of the ASDF is not in partial Local Saha Equilibrium (pLSE); instead this part is overpopulated with respect to the Saha density (cf. equation (1)). The non-pLSE part of ASDF can be divided in two domains. The lower domain is ruled by the Corona balance (CB) case B, meaning that all resonant radiation is absorbed while the plasma is transparent for all other bound-bound transitions. In top of the CB case B we find the Excitation Saturation Balance ESB [2]. This part of the energy scheme is ruled by electron-induced processes. The production as well as destruction of the level population is collisional and thus proportional to \( n_e \), so the shape of the ESB part of the ASDF will not give information on \( n_e \).
Figure 2 gives a typical sketch of the ASDF for ionizing plasma. It can be seen how the population is spread over the system. The lower levels are overpopulated with respect to Saha, i.e. $\eta > \eta'$. This overpopulation ($b = \eta/\eta'$) decreases with increasing effective quantum number $p$ i.e. decreasing ionization potential $I_p$. High in the spectrum the departures from the Saha equilibrium must disappear. The levels are so close to the continuum that the excitation flow is small compared to the activity of ionizing and recombining processes. This pLSE part is not observable for strongly ionizing plasma regions. The population of the lower excited levels is determined by the $r'$ coefficient mainly. As can be seen both radiative and collisional processes are relevant although the radiation to the ground state is reabsorbed.

![Figure 2](image)

**Figure 2.** A sketch of a distribution function typical for an ionizing Ar systems; the resonant radiation is reabsorbed while the plasma is open for $4s - 4p$ radiation. The $p_{cr}$ level indicates the boundary between Case B corona and ESB. Above $p_{cr}$ the levels are completely ruled by electron collisions.

3. **Experimental setup**

The spectroscopic measurements were performed on microwave induced plasma created by a surfatron. The surfatron is an integrated surface wave plasma launcher which performs both field shaping and impedance matching. The microwaves are coupled into the plasma via the launching gap and can travel in both axial directions in the interface between plasma and dielectric (quartz tube). The generated plasma is confined in the same quartz tube (in our case with $r_{inner} = 6$ mm, $r_{outer} = 8$ mm). The frequency of the microwaves is fixed at 2.46 GHz. A Microtron 200 generator with a maximum power of 200 W has been used to generate the electromagnetic waves.

The emitted plasma light is focused by a small lens into an optical fiber, by which the optical light is guided to the entrance slit of a 1 meter monochromator. A CCD camera is connected to the monochromator and has been used to record the spectrum as a function of lateral distance. “The used” experimental setup enables to measure the emitted plasma light along a radial line of sight at a specific axial position. A schematic overview of the setup is shown in figure 3. Description, in more details, of the optical and microwave system of the setup is given in [1]. The measurements have been made under different working conditions. The pressure in the tube was in range from 5 to 20 mbar. The values of the flow rate were set at 25, 50 and 100 sccm for the argon and 0.3, 0.6 and 0.9 sccm for the hydrogen. The gas flows, gas pressure in the tube, the incident and reflected powers and the length of the discharge column have been measured for all cases. In the present work we will show results under conditions of 10 mbar gas pressure, flow rate of argon 50 sccm and different additions of hydrogen.
A schematic overview of the experimental setup

4. Results and discussion

The method of absolute line intensity (ALI) measurements has been used as a diagnostic tool to determine absolute intensities of optical thin lines of argon plasmas. The transition-integrated line intensities (for lines of levels $4p$, $5p$, $5d$, $6s$, $6d$, $7d$) were obtained from line intensity measurements that were calibrated absolutely with the known intensity of a Ribbon lamp. Measurements of the density per statistical weight of several atomic lines have been used to construct the ASDF. This has been done by plotting the population densities of the excited states as a function of the ionization energy. The density of the ground state $n_1$ has been found ($n_1 = 1.6 \times 10^{23}$ m$^{-3}$ for 10 mbar at 450 K gas temperature) using the ideal gas law (combined with an estimate value for the gas temperature and measured gas pressure). So the excitation temperature of the lower part, thus the $4p$-levels and the atom ground state, could be determined with a precision, in the order of 6% or better (this is mainly based on the fact that the energy gap between the ground state and the excited state is large). With the method sketched in equation (5) we can transform $T_{13}$ into $T_e$.

Levels high in the atomic system have been used to determine an estimate value of $\eta_e$ by extrapolation the ASDF to the continuum (this corresponds with $E_p = 15.76$ eV for argon). From $\eta_e$ a $n_e$ value was deduced in order of $10^{19}$ m$^{-3}$. However, this method of $n_e$-determination is very inaccurate since, as stated above, the slope of the ESB part of the ASDF does not depend on $n_e$. Therefore other methods should be applied to find $n_e$. One possibility is to introduce H$_2$ into the plasma and to deduce $n_e$ from the broadening of H$_2$ line. In the present study we will look in how far this introduction changes the properties of the Ar plasma. More specifically we will investigate how the $T_e$ as determined with the $r^f$ method on Ar, will change due to the small addition of H$_2$. Moreover we will investigate whether the same ASDF shape as formed by the ESB can be found in the H system and what consequences the H$_2$ addition has on general plasma features such as the plasma size and the heat generation.

In order to find the influence of the addition of hydrogen on the top of the Ar-ASDF several measurements with Ar-H$_2$ gas mixture were performed. The following concentrations of hydrogen were used: 1.2, 2.4, and 3.6 %. It was found that the introduction of hydrogen has several consequences: more addition of hydrogen gives more heat, the plasma becomes warm. The wall temperature changes in range of 50 to 130 °C. With increasing the content of hydrogen the plasma decreases in length. For the case of pure argon the plasma length is of approximately 38 cm; for case
of Ar-H_2 mixtures the plasma length ranges from 8 to 29 cm, depending on the hydrogen concentration and gas pressure (5, 10, 15, 20 and 25 mbar). Some test measurements were done with the purpose to investigate the stability of the plasma tip. It was found that above 3.6% of H and 20 mbar gas pressure, the system is not stable. The plasma is very hot and short in length. In order to avoid melting of the tube we could not go to higher H_2 concentrations.

**Figure 4.** ASDF for Ar-H_2 mixture. Gas pressure 10 mbar, gas flow rate – 50 sccm of Ar and 0.3, 0.6, 0.9 sccm of H_2, axial position – 2 cm.

**Figure 5.** ASDF for H_2. Gas pressure 10 mbar, gas flow rate – 50 sccm of Ar and 0.3 sccm of H_2, different positions

Figures 4 and 5 present the (constructed) ASDF respectively for the cases of Ar-H_2 mixture and H_2 (measuring the lines: 656.2, 486.1, 434.0 and 410.1 nm from the Balmer series). The measurements, presented in this work, have been done under conditions: 10 mbar gas pressure, 50 sccm of Ar gas flow and 0.3, 0.6 and 0.9 sccm of H_2. Figure 4 shows the influence on the Ar system with introduction of different amount of H_2 at axial position 2 cm from the launcher. It can be seen that the ASDF for Ar does not change for small additions of H_2, which means that the electron temperature _T_e_ is constant. At the same time it was found that the wall of the quartz tube becomes hotter (_T_wall_ increases) and the plasma length shorter. That leads to higher gas temperature _T_g_ (ergo the gas temperature _T_g_ is increasing) which indicates that the kinetic energy exchange from electrons to heavies particles is much better if H_2 is present.

From figure 5 it can be seen that the ASDF of H_2 differs both in absolute value and shape for different axial positions (2, 10, 20 cm). It was found in [3] that the hydrogen system in a pure hydrogen plasma, driven by the TIA, is ruled by the ESB, i.e. that the overpopulation of excited states depends on the effective quantum number _p_ (for the hydrogen equal to the principal quantum number _n_) via the _p^x_ law with _x_ close to 6. It is remarkable for the surfatron plasma (under our experimental conditions) that the _p^6_ law based on the hydrogen rates [2, 4] is present in the Ar but not in the H system.

In a future study a more profound analyses will be done to find the reasons of that different behavior of the H system. The reason can be that apart from electron excitation also other processes like charge and excitation transfer between the Ar and H might be of importance.

**References**

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