Spectral characteristics of inductively coupled plasma of water vapor

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Abstract. The paper presents the results of experimental measurements of the emission properties of water plasma in an inductive discharge. The power of the inductive discharge was 600 W at a frequency of 27 MHz and a pressure from 0.25 to 4 mbar. Plasma temperature was estimated from the Balmer hydrogen series using relative intensities method. It is shown that in this pressure range, the plasma is not in equilibrium and the energy difference between individual excited states increased with distance from the tube axis. The plasma heating time was estimated from the dynamics of the spectral line intensities to be 200 ms.

1. Introduction

Electrodeless plasma of water vapor is used in a number of applications [1–7]. Water vapor is a relatively cheap raw material whose dissociation in an inductive discharge produces oxygen atoms and hydroxyl (OH) radicals, which have high chemical reactivity. This makes water plasma attractive for use in applications such as decontamination, oxidation, etching, etc. The presence of atomic hydrogen in the plasma allows the plasma temperature to be relatively easily estimated from the spectra of the hydrogen Balmer series. However, the high thermal conductivity of hydrogen [2] and the energy deposit to the dissociation of water molecules complicate the obtaining of sufficiently heated plasma at the level of inert gases (e.g., argon) [3].

Despite a number of studies addressing water inductively coupled plasma (ICP), the task of studying the energy and spectral characteristics and searching for regularities that can help to estimate the parameters of water ICP remain important challenges.

2. Experimental setup

The figure 1 shows the experimental arrangement. Inductively coupled plasma 1 was ignited in a quartz tube 2 of diameter $D$ from 20 to 45 mm. Inductor 3 was made from copper and had $N$ from 1 to 5 coils. The inductor was supplied from CESAR 2710 RF power source with a frequency of 27.12 MHz. The RF power source has output power 600 ± 30 W. The vacuum was made by a vacuum pump, which has been installed on one side of the quartz tube. A vessel with distilled water 4 was placed on the other side. The metering valve 5 was placed near the vessel 4 and a check valve 6 was installed near the vacuum pump.
Prior to the switching the generator on, air was evacuated from the discharge tube 2 by the pressure of \( \sim 0.1 \) mbar. Then, the valve 5 was closed and the valve 6 opened. After that, water vapor was supplied to the system using the metering valve 5. After that, the RF supply was switched on, and the plasma was ignited. The pressure \( p \) was measured by a vacuum gauge 8 (Testo 552). The discharge time was from 0.1 to 0.5 sec.

The discharge spectrum was detected from the side of the quartz tube using a Solar LS S150 Czerny–Turner spectrometer (spectral range \( \lambda \) from 180 to 1100 nm and a spectral resolution of 0.3 nm) through an optical fiber cable 7. The exposure time during spectrum acquisition was varied depending on the brightness of the detected lines.

The spatial temperature distribution was measured using a tube with a flat end (figure 2) connected to optical fiber 7. The fiber was enclosed in a metal tube 9 (having dark inner wall) with a length of 10 cm and a diameter of 3 mm to record the light flux from a narrow plasma layer.

Stable discharge in water vapor at a power of 600 W existed at a pressure \( p \) of up to 5 mbar. When the pressure of water vapor was higher than 10 mbar, the plasma was extinguished due to insufficient power.

3. Results and analysis

Figure 3 shows comparative spectra of the inductive discharge in water vapor for \( D = 45 \) mm and \( N = 2 \) at pressures \( p = 0.25 \) mbar (figure 3a) and \( p = 4 \) mbar (figure 3b). It is seen that with increasing pressure,
the intensity of the OH molecular band increases (309 nm) and the intensity of the Hγ line decreases. This indirectly indicates a decrease in temperature with increasing pressure. As the temperature increases, the concentration of the OH radical decreases: it dissociates into hydrogen and oxygen [2]. In experiments [3] at a pressure of 0.05 mbar and a heating power of 200 W, the OH molecular band was almost invisible, suggesting almost complete dissociation of the molecules in the plasma.

![Figure 3. Discharge spectra in a tube of diameter $D = 45$ mm. a) $p = 0.25$ mbar, b) $p = 4$ mbar.](image)

The plasma temperature concept makes sense only when the condition of local thermodynamic equilibrium is satisfied. In this case, a convenient method for determining the temperature is the Boltzmann plot method described in [8]. To use this method, it is necessary that the plasma be optically thin and the local temperatures of all particles be equal. These conditions are satisfied only at sufficiently high pressures (> 0.1 bar) [9].

In practice, the ICP parameters are unevenly distributed in the plasma coil. Near the walls of the discharge chamber, the temperature and electron density decrease due to thermal conductivity [10]. On the axis of the chamber, there is also a decrease in temperature due to RF shielding if the radius of the chamber exceeds the depth of the skin layer.

![Figure 4. Temperatures calculated from the relative intensity of the hydrogen Balmer series lines at different distances from the axis of the discharge tube for $p = 1$ mbar, $D = 40$ mm and $N = 1$.](image)

Figure 4 shows the experimental temperatures calculated from the relative intensity of the hydrogen Balmer series lines using the formula [8]:

$$T_e = \frac{h \nu}{k} \ln \left( \frac{I_\alpha}{I_\beta} \right)$$

$$T_i = \frac{h \nu}{k} \ln \left( \frac{I_\alpha}{I_\beta} \right)$$

$$T_m = \frac{h \nu}{k} \ln \left( \frac{I_\alpha}{I_\beta} \right)$$

$$T_r = \frac{h \nu}{k} \ln \left( \frac{I_\alpha}{I_\beta} \right)$$

where $T_e$ is the electron temperature, $T_i$ is the ion temperature, $T_m$ is the macroscopic temperature, and $T_r$ is the radiation temperature.
where $E$ is the energy of the upper (excited) level, $I$ and $\lambda$ are the intensity and wavelength of the corresponding spectral line, $A$ and $g$ are the probability of transition and the statistical weight of the excited level, respectively, $k$ is the Boltzmann’s constant, the subscripts $m$ and $n$ correspond to the transitions from the $m^{th}$ and $n^{th}$ excited levels to the same lower level ($n > m$), and $r$ is the distance from the axis of the discharge tube (figure 2). The subscripts correspond to the names of the lines whose relative intensity was used to determine the temperature ($H_\alpha$, $H_\beta$, $H_\gamma$).

It can be seen that the temperatures do not coincide, i.e., the plasma is not in thermodynamic equilibrium. This may be caused by self-absorption of the $H_\alpha$ line (which occurs in a plasma consisting mainly of hydrogen [11, 12]) or by overpopulation of the third energy level of hydrogen. Thus, the real temperature of the atoms is between the values of $T_{\gamma\beta}$ and $T_{\gamma\alpha}$. It can be seen that it is much lower than the temperature for argon plasma with the same input power, which is explained by the high thermal conductivity of hydrogen and the loss of energy due to the dissociation of water molecules [2].

It can be seen (figure 4) that the difference of the temperatures $T_{\beta\alpha}$, $T_{\gamma\alpha}$, and $T_{\gamma\beta}$ of different excited plasma atoms increases with increasing $r$. This suggests that the difference of the kinetic energies increases with increasing $r$.

Figure 5 shows curves of the normalized intensity of the $H_\alpha$, $H_\beta$, $H_\gamma$ lines versus time obtained by sequential spectrum acquisition with an exposure of 50 ms at a pressure $p = 1$ mbar. Zero time corresponds to the moment of turning on the RF generator. The moment of turning off the RF power was 500 ms.
It can be seen that the plasma does not immediately reach a stationary mode, with the intensity of different lines increasing at different rates: the Hα line reaches a stationary level within ~ 100 ms, and the Hγ line within ~ 200 ms. The different times for the spectral line intensities to reach stationary levels correspond to the process of plasma heating. It can be concluded that the heating time in this case is about 200 ms.

In addition, it can be seen in figure 5 that with an increase in $r$, the line intensities sooner reach stationary levels and the decline after turning off the RF generation is longer. In the axial region (figure 5c,d), during the discharge time (500 ms), a stationary mode does not have time to establish, and the decline is faster, indicating insufficient heating due to the small thickness of the skin layer (3 mm) and rather slow heat transfer.

In plots a)–c) in figure 5, the Hγ line has a dip in the range from 300 to 400 ms. This dip is equal in magnitude to the spectrum acquisition noise (since the Hγ line is weak compared to the Hα and Hβ lines) and is therefore not analyzed in this paper. For a detailed analysis, it is required to record the time dependence of the Hγ line with better dynamic resolution.

Conclusions
As a result of the study, some characteristics of water ICP such as temperature and heating time were determined.

It is shown that at a pressure of 1 mbar, the plasma is not in local thermodynamic equilibrium. At an input power of 600 W and a diameter of the discharge tube from 20 to 45 mm, the temperature is from 1500 to 2500 K.

It is shown that the temperature and the degree of plasma nonequilibrium increase with distance from the axis of the discharge tube and with decreasing pressure. The plasma heating time estimated from the time of increase in the intensity of the Balmer series lines is 200 ms.

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