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To cite this article: R Miotk *et al* 2012 *J. Phys.: Conf. Ser.* **406** 012033

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Spectroscopic study of atmospheric pressure 915 MHz microwave plasma at high argon flow rate

R Miotk[1], B Hrycak[1], M Jasinski[1] and J Mizeraczyk[1,2]

[1] *Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow
Machinery, Polish Academy of Sciences, Fiszera 14, 80-952 Gdansk, Poland*
[2] *Department of Marine Electronics, Gdynia Maritime University,
Morska 81-87, 81-225 Gdynia, Poland*

E-mail: rmiotk@imp.gda.pl

Abstract In this paper results of optical emission spectroscopic (OES) study of atmospheric pressure microwave 915 MHz argon plasma are presented. The plasma was generated in microwave plasma source (MPS) cavity- resonant type. The aim of research was determination of electron excitation temperature T_{exc} gas temperature T_g and electron number density n_e. All experimental tests were performed with a gas flow rate of 100 and 200 l/min and absorbed microwave power P_A from 0.25 to 0.9 kW. The emission spectra at the range of 300 - 600 nm were recorded. Boltzmann plot method for argon 5p - 4s and 5d – 4p transition lines allowed to determine T_{exc} at level of 7000 K. Gas temperature was determined by comparing the measured and simulated spectra using LIFBASE program and by analyzing intensities of two groups of unresolved rotational lines of the OH band. Gas temperature ranged 600 - 800 K. The electron number density was determined using the method based on the Stark broadening of hydrogen H_β line. The measured n_e ranged $2 \times 10^{15} – 3.5 \times 10^{15}$ cm^{-3}, depending on the absorbed microwave power. The described MPS works very stable with various working gases at high flow rates, that makes it an attractive tool for different gas processing.

keywords: OES, electron excitation temperature, electron number density, gas temperature

1. Introduction

In plasma sources plasma is excited by applying high electric field to a gas. Tendero et al. give an overview of the numerous atmospheric pressure plasma sources which can be classified as DC, RF and microwave sources [1]. Atmospheric plasma sources are important tools for technological applications, e.g. the treatment of critical exhaust gases, plasma chemistry and activation and cleaning of materials [2-6]. Since there is no need for vacuum components, they are mostly easy to integrate in the process line.

The microwave plasma sources (MPSs) found applications in the processing of decomposition of gaseous pollutants like freon [7-11] and also production of hydrogen via methane conversion [12, 13].

Since thermal and electron reactions play an important role in the gas pollutants decomposition, the knowledge of the neutral gas temperature and electron number density in such plasmas is crucial for understanding the chemical kinetics of the gas decomposition process and its optimization.

In our previous spectroscopic investigations, the microwave plasma devices operated at 2.45 GHz and at low gas flow rates (0.5 - 2 l/min) were used [14-16]. The gas temperature and electron number density were about 4000 K and 10^{15} cm^{-3}, respectively.

In this paper, results of spectroscopic study of microwave plasma at high argon flow rates are presented. The plasma was generated in waveguide-supplied MPS cavity-resonant type operated at 915 MHz. At this frequency the skin effect is weaker, so electromagnetic wave more deeply penetrates the plasma. It can be helpful in the gas processings.

The use of high gas flow rate in the presented device is expected to be of low cost and effective, and thus promising for applications in the treatment of gases. Moreover, the high gas flow rate cools device and protects the electrodes from erosion.

2. Theory

In this paper optical emission spectroscopic (OES) was used for diagnostics of 915 MHz microwave argon plasma. Plasma parameters were determined using the method based on the measurements of intensity and spectral line broadening.

2.1. Electron excitation temperature

Electron excitation temperature is a parameter describing a population of excited atomic levels. The excitation temperature may be determined from argon emission lines intensities. Atmospheric pressure microwave plasma are generally in partial local thermodynamic equilibrium (PLTE) [17, 18]. This suggests to use a Boltzmann plot method to determine the T_{exc}. Thus an observed light intensity I_{nm} of radiative transition between levels n and m may be given by [17-18]:

$$I_{nm} = A_{nm} \frac{hc}{\lambda_{nm}} N \frac{g_n \exp(-E_n / kT_{exc})}{Z} \tag{1}$$

where: A_{nm} is the Einstein coefficient for transition $n \rightarrow m$, h is the Planck constant, c is the light speed constant, λ_{nm} is wavelength for transition $n \rightarrow m$, g_n is the statistical weight of the upper level n, Z is the canonical partition function, N is the population of the ground state level, E_n is the energy of the upper level n and k is the Boltzmann constant.

From the plot $\ln(I_{nm}\lambda_{nm} / g_nA_{nm})$ versus the energy E_u, we can estimate the excitation temperature from the slope of the best line that fits the experimental points [17-18].

2.2. Gas temperature

Gas temperature in microwave plasma is close to the rotational temperature T_{rot} of the OH radicals [19-21]. The OH ($A^2 \Sigma \rightarrow X^2 \Sigma$) transition is one of most intense systems emitted by low temperature plasmas containing even a small amount of H_2O. This band is widely used for gas temperature estimations.

The rotational temperature can be obtained by fitting the entire band in LIFBASE [22] program or more simply from the relative intensities of groups of unresolved rotational lines corresponding G_0, G_1 and G_{ref} branches of the OH ($A^2 \Sigma \rightarrow X^2 \Sigma$) band. These branches form distinct peaks at about 306.4 nm, 306.8 and 309.1 nm, respectively. This OH band has been studied thoroughly by Ch. de Izarra [21]. In order to avoid the difficulties encountered in experimental measurements of group line intensities it has been decided to only consider the maximum amplitude of the groups of lines G_0 and G_1. His research has shown that the intensity of G_0 and G_1 strongly depends on the rotational temperature. A more detailed analysis of the groups G_0 and G_1 shows that the wavelength of their maximum amplitude varies as a function of the T_{rot}. It is obvious that this amplitudes are dependent on the instrumental broadening $\Delta\lambda_I$ that must be precisely determined. Izarra publication contains a set of relations G_0/G_{ref} and G_1/G_{ref} as a function of the gas temperatures varying from 600 – 9000 K, in 200 K steps, and for $\Delta\lambda_I$ varying from 0.02 – 0.98 nm, in 0.02 nm steps. The similar method was used by Jasinski et al. in [14].

2.3. Electron number density

In plasmas with the electron number densities greater than $\sim 5*10^{13}$ cm^{-3}, spatially and temporally resolved n_e can be determined using the OES of the line shape of the Balmer transition (4-2) of atomic hydrogen at 486.13 nm (H$_\beta$ line) [15, 18, 23-26].

The lineshape of the H$_\beta$ emission is determined by Lorentzian (Stark, van der Waals, resonance, natural) and Gaussian (Doppler, instrumental) broadening mechanisms that result

in a Voigt profile. The convolution of the Gaussian and Lorentzian components results in a Voigt profile. The relation between Gaussian, Lorentzian and the resulted Voigt full-widths at half-maximum (FWHM) profiles is given by [18, 26]:

$$\Delta\lambda_V = \frac{\Delta\lambda_L}{2} + \sqrt{\frac{\Delta\lambda_L^2}{4} + \Delta\lambda_G^2}$$

$$\Delta\lambda_G^2 = \Delta\lambda_D^2 + \Delta\lambda_I^2 \tag{2}$$

$$\Delta\lambda_L = \Delta\lambda_W + \Delta\lambda_S + \Delta\lambda_N + \Delta\lambda_R$$

where the subscripts represent: V - Voigt , L - Lorentzian, G - Gaussian, D - Doppler, I - instrumental, W - Van der Waals, S - Stark, N - natural, R - resonance. Resonance and natural broadenings are usually negligible due to very low FWHM values in comparison to the Stark, the Doppler, van der Waals and instrumental broadenings [18, 26].

The random motion of the atoms in the plasma causes the Doppler broadening of the spectral lines. The FWHM of the Doppler profile is [24, 26]:

$$\Delta\lambda_D = 7{,}17 \times 10^{-7} \lambda_0 \sqrt{\frac{T_g}{m}} \quad [nm] \tag{3}$$

where T_g is the gas temperature in Kelvin, m is the atomic mass in a.m.u. and λ_0 is the wavelength.

Van der Waals broadening results from the interaction of an excited atom with neutral ground state atom of another species and is an important broadening mechanism in high-pressure plasmas. The FWHM of the van der Waals profile is [24]:

$$\Delta\lambda_W = 6{.}48 \times 10^{-22} \frac{p}{kT_g^{0.7}} \quad [nm] \tag{4}$$

where p is the pressure. One can see that the van der Waals broadening is a gas temperature dependence: if temperature is higher, the broadening is lower.

Perturbation in the wave function on the excited states of hydrogen by the electric field induced by the charged particles of the plasma causes the Stark broadening of the spectral lines. The n_e can be calculated using the theory GKS [27], where Stark broadening is estimated in a quasi-static approximation using the classic Holtsmark field. The more recent Gig-Card theory is suitable to be used to determine the electron density in atmospheric pressure microware discharges and give best results that correlates $\Delta\lambda_S$ and n_e [23-26, 28]. This theory incorporates the ion dynamics to evaluate the Stark broadening of lines spontaneously emitted by the plasma.

3. Experiments

The experimental setup consisted of: microwave generator (915 MHz), isolator, rectangular waveguide (WR 975) as a feeding line, directional coupler, power meters, MPS cavity-resonant type with movable plunger, gas supply and flow control system (see figures 1, 2).To measure the plasma spectrum we used the spectrograph (DK-480 CVI with 1200 and 3600 grooves/mm) equipped with CCD sensitivity calibrated camera (SBIG ST-6 750*242). A PC computer was used to control the spectrograph and acquire the data.

In the resonant cavity two opposite electrodes were placed coaxially in the cavity axis. A gas to be treated at atmospheric pressure flows into the cavity through a gas inlet forming swirl flow round electrodes and then passes between them, so that a microwave plasma is initiated between the two electrodes. One of the electrodes has an axial hole to provide an outlet from the resonant cavity for the plasma and operating gas (based on patent rights [29, 30]).The absorbed microwave power P_A by the discharge was calculated as $P_I - P_R$, where P_I and P_R are the incident and reflected microwave powers, respectively. The incident and reflected microwave powers P_I and P_R were directly measured using directional coupler equipped with bolometric heads and HP power meters.

Window in the wall of the generator allows for observation of the microwave discharge. To measure the spectra, the light emitted by the plasma was focused with a quartz lens (50 mm in diameter, focal length – 75 mm) onto double diaphragm with pinholes of a 1 mm diameter

at the entrance slit of the spectrometer (see figure 3). The width of the spectrometer entrance slit was 50 μm (20 mm height). The double diaphragm were placed to collimate the light. Photos of microwave argon plasmas at different values of absorbed microwave power are shown in figure 4. The figure shows, that the light intensity increases with increasing the value of absorbed microwave power.
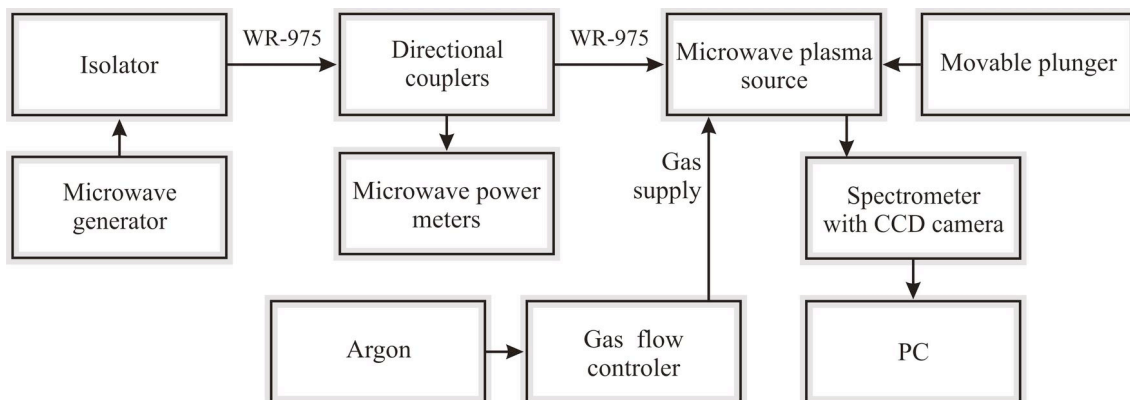

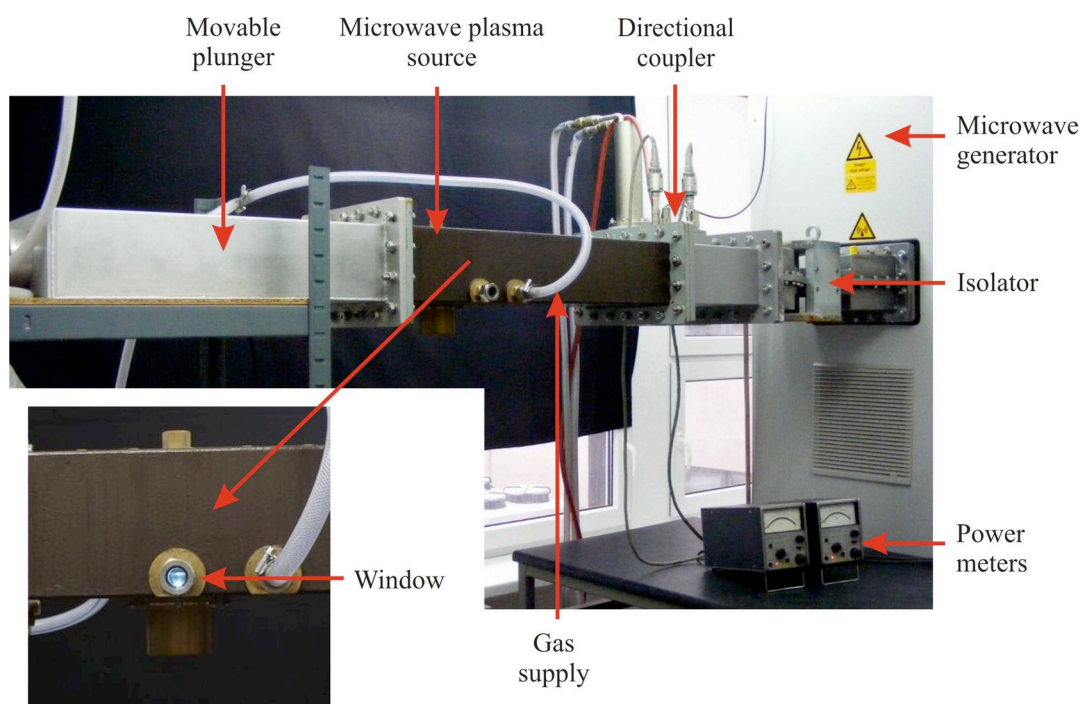Figure 1. Diagram of the experimental setup.
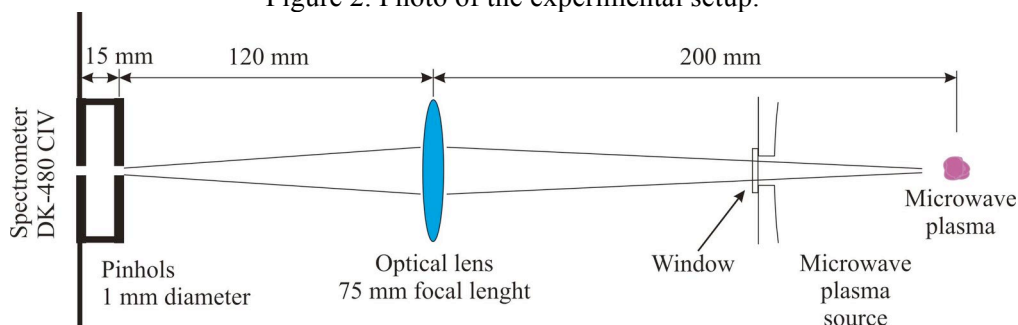

Figure 2. Photo of the experimental setup.

Figure. 3. The experimental setup used for the spectroscopic investigation.
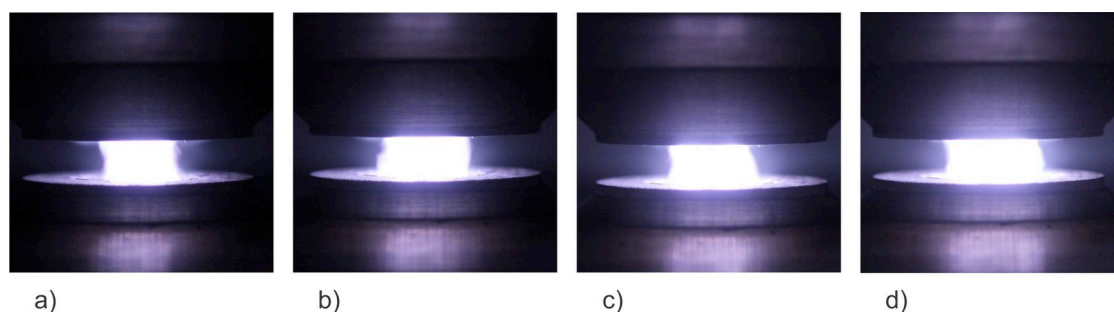
Figure 4. Photos of the microwave argon plasma at P_A: a) 0.3 kW, b) 0.4 kW, c) 0.5 kW, d) 0.6 kW. Flow rate - 200 l/min, distance between electrodes - 4.6 mm.

4 Results and discussion

In this section we present OES measurements of electron excitation, gas temperature and electron number density. Spectra were recorded and then corrected according to the wavelength sensitivity of CCD camera. The wavelength sensitivity of CCD camera was determined using a tungsten halogen calibration lamp. Using a Hg-Ne low-pressure calibration lamp (λ = 365.02 nm, 435.84 nm and 546.07 nm, Hg I) we measured that the Gaussian instrumental line profile FWHM was about 0.134 nm and 0.06 nm for 1200 and 3600 grooves/mm grating, respectively. Typically, spectra were measured with 1200 grooves/mm grating. Only for OH ($A^2 \Sigma \rightarrow X^2 \Sigma$) rotational band measurements the 3600 grooves/mm grating was used. All experimental tests were performed with the argon flow rate of 100 and 200 l/min.

4.1. Electron excitation temperature measurements

The electron excitation temperature can be determined using the Boltzmann-plot method from the selected argon $4p-4s$ and $5p-4s$ transition lines (figure 5). The list of selected argon lines with spectroscopic parameters: g_n, A_{nm}, λ_{nm} and E_n are shown in table 1. Electron excitation temperature can be estimated from the best linear fit of plot $\ln(I_{nm}\lambda_{nm}/g_nA_{nm})$ versus the energy E_u [17-18] (figure 6a). Figure 6b shows electron excitation temperature as a function of absorbed microwave power. Obtained T_{exc} at level 7000 K is independent of absorbed microwave power and flow rate.
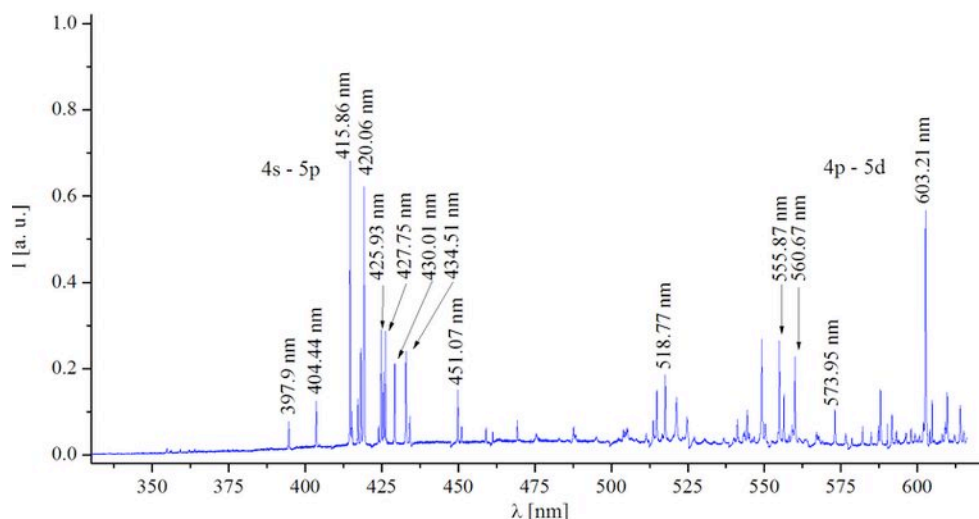

Figure 5. Emission spectrum of argon plasma with selected argon $4p-4s$ and $5p-4s$ transition lines for Boltzmann-plot method. Absorbed microwave power - 0.4 kW, flow rate - 200 l/min.

Table 1. Spectroscopic parameters of argon lines for Boltzmann plot method [31].

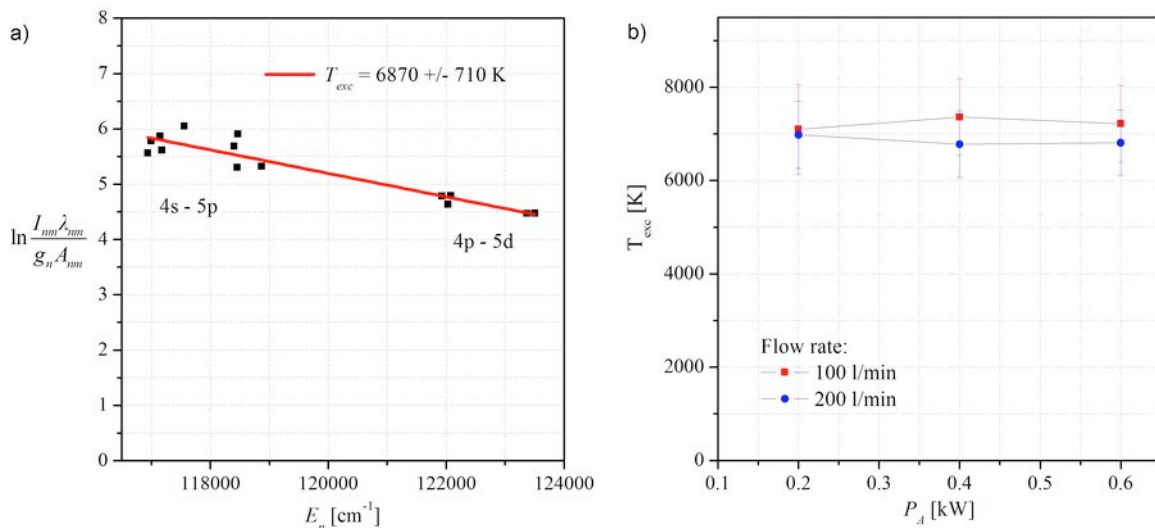| λ_{nm} [nm]	Radiative transition	A_{nm} [10^7 s^{-1}]	g_n	E_n [cm^{-1}]
394.9		0.0333	3	118459
404.44		0.0455	2	118469
415.86		0.1400	5	117183
420.06		0.0967	7	116942
425.93	4s - 5p	0.3980	1	118870
427.75		0.0797	3	117151
430.01		0.0377	5	116999
434.51		0.0297	3	118407
451.07		0.1180	1	117562
518.77		0.1380	5	123372
555.87		0.1420	5	122086
560.67	4s - 5d	0.0333	3	121932
573.95		0.0455	2	123505
603.21		0.1400	5	122036

Figure 6. a) Boltzmann plot for argon $4p{-}4s$ and $5p{-}4s$ transition lines (P_A = 0.4 kW, Q = 200 l/min), b) Electron excitation temperature as a function of absorbed microwave power P_A for two values of argon flow rate 100 and 200 l/min.

4.2. Gas temperature measurements

To determine rotational temperature the emission spectra at the range of 305.5 - 309.5 nm were recorded (figure 7). The OH radical emissions are results of water vapor naturally present as impurity in the gas, so the intensity of the ($A^2 \Sigma \rightarrow X^2 \Sigma$) rotational band was very low. According to this in measurements the width of the entrance slit of the spectrograph was set at 100 μm. Due to the low light intensity, the double diaphragm (at the entrance slit) was not used.

After having the experimental spectrum of OH, a simulation of this band was carried out using LIFBASE program. The simulated OH ($A^2 \Sigma \rightarrow X^2 \Sigma$) band was fitted to the experimental one by variation of the rotational temperature. Figure 7 shows the comparison of the both spectra: experimental and simulated fitted to the experimental one. Figure 8 presents obtained T_{rot} as a function of absorbed microwave power. The temperature slowly increases with increasing absorbed microwave power and with decreasing the working gas flow rate (figure 8). The second way to determine T_{rot} was maximum amplitude relations G_0/G_{ref}, G_1/G_{ref} from the measured spectrums.
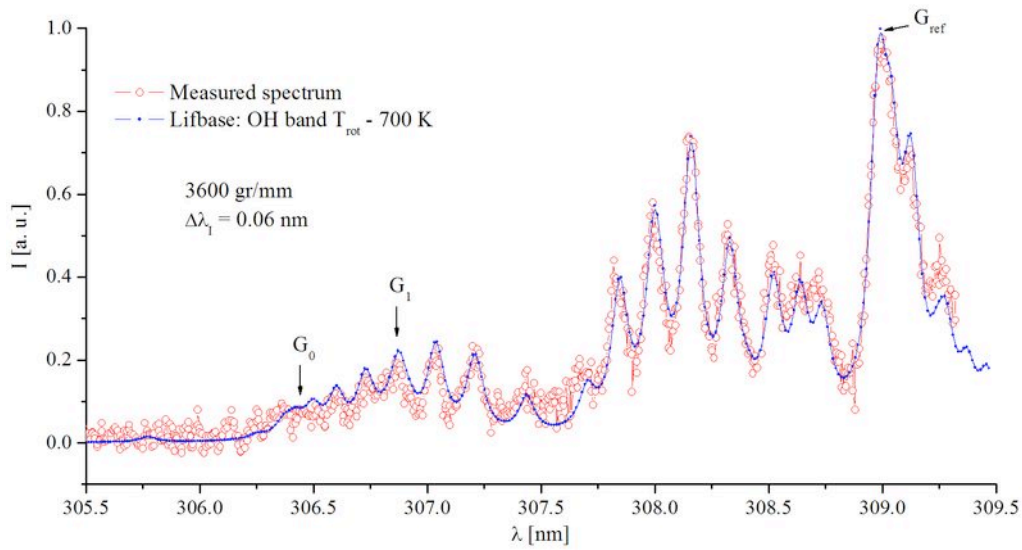
Figure 7. Comparison of the measured and simulated in LIFBASE emission spectra of OH rotational band in argon plasma (P_A = 0.6 kW, Q = 200 l/min).
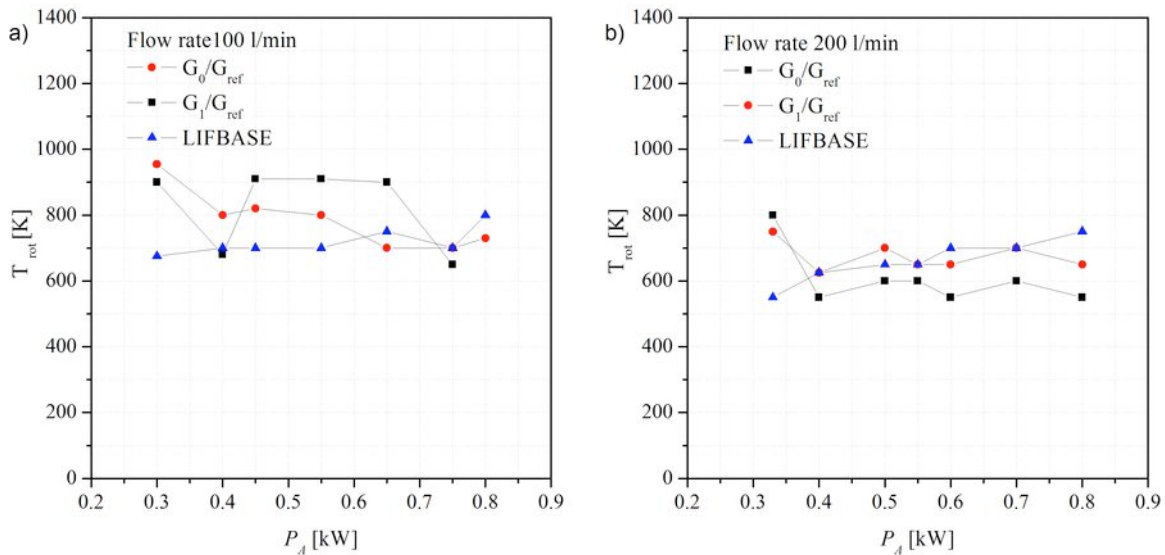

Figure 8. Measured rotational temperatures of OH radicals as a function of absorbed microwave power for two values of argon flow rate: a) 100 l/min, b) 200 l/min.

4.3. Electron number density measurements

To obtain a detectable intensity of H_β emission spectral line a small addition of H_2 (0.5%) was introduced to argon flow. Assuming that the gas temperature in discharge is constants (absence dependence of the absorbed microwave power, figure 8) and is at the level of 700 K for Q = 100 l/min and 650 K for Q = 200 l/min, respectively. For this values, dependence (3) allows to estimate the value of the Doppler broadening for the H_β line. From equation (2) the FWHM of Gaussian profile can be determine. The FWHM values of the Gaussian profile of H_β line is given in table 2. The parameters presented in table 2 are independent of the absorbed microwave power.

Table 2. H_β line Gaussian broadening effect FWHM.

Q [l/min]	$\Delta\lambda_I$ [nm]	$\Delta\lambda_D$ [nm]	$\Delta\lambda_G$ [nm]
100		0.009	
200	0.134	0.008	0.134

Figure 9 shows an example of H_β spectral line profile measured in microwave argon plasma and the Voigt profile fitted to the experimental points.
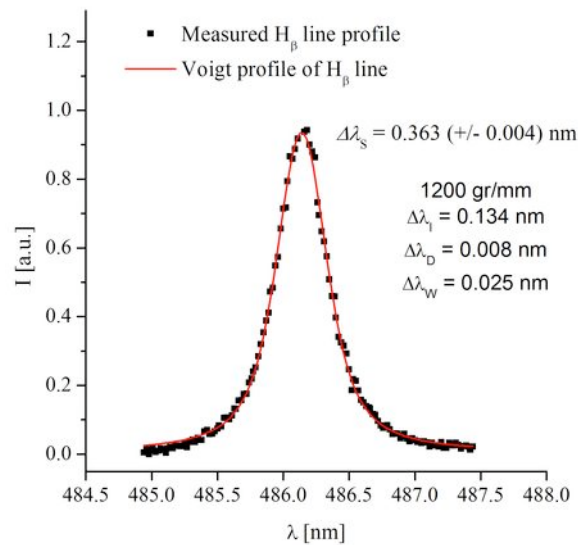

Figure 9. Measured H_β line profile and the Voigt function fitted to the experimental points for argon plasma. Absorbed microwave power P_A - 0.4 kW, flow rate - 200 l/min.

The fitting was made using the Voigt function with a Gaussian line width of 0.134 nm (table 2) in Origin software. Deconvolution the Voigt profile return value of the FWHM Lorentzian profile (Stark and van der Waals). The van der Waals broadening can be calculated from equation 4. Obtained $\Delta\lambda_W$ at the level of 0.051 nm for 650 K and 0.046 nm for 700 K, respectively. The difference between the measured FWHM of Lorentzian profile and calculated the van der Waals broadening gives the Stark broadening (2).

The electron number density calculated from Gig-Card and GKS theory is shown in figure 10. Obtained electron number density n_e ranged 2×10^{15} – 3.5×10^{15} cm^{-3} depending on the absorbed microwave power and flow rate. Generally, Gig-Card theory always gives lower values of the electron number density than GKS theory.
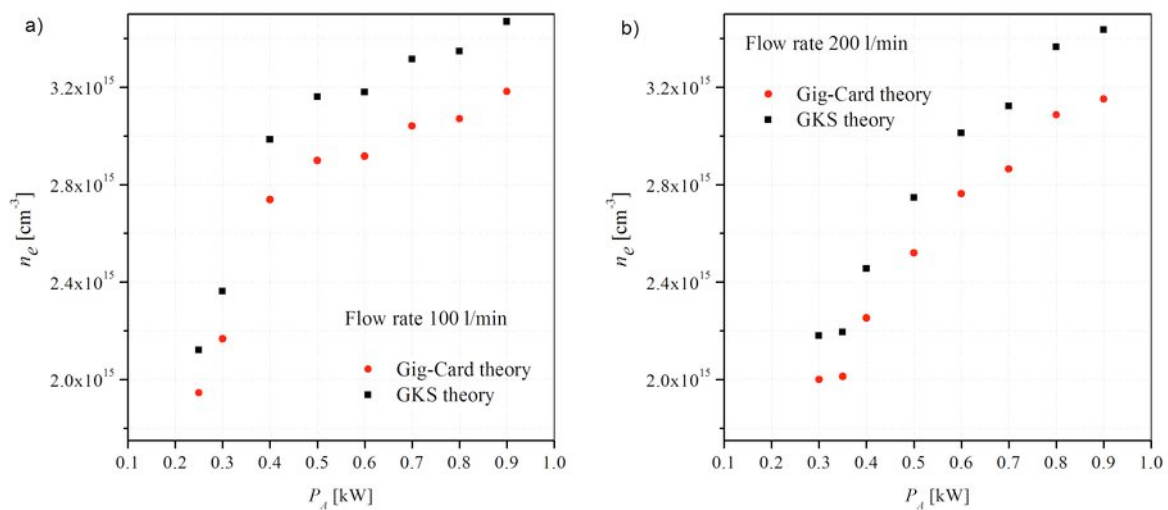

Figure 10 Electron density as a function of absorbed microwave power for two values of argon flow rate: a) 100 l/min, b) 200 l/min.

5. Conclusions

Spectroscopic study of microwave 915 MHz argon plasma at atmospheric pressure and high flow rate was presented in this work. The study concerns to determine electron excitation, gas temperature t and electron number density. The results showed that:

- Electron excitation temperature obtained at level 7000 K is independent of absorbed microwave power and argon flow rate,
- The rotational temperatures of OH radical ranged from 600 up to 800 K, depending on absorbed microwave power and argon flow rate,
- Electron number density was from $2\times10^{15} - 3.5\times10^{15}$ cm^{-3}, depending on the operating parameters (absorbed microwave power, argon flow rate) and theory that was used (GKS or Gig-Card theory).

The investigated microwave plasma source cavity-resonant type works very stable with various working gases. The parameters (flow rate, absorbed microwave power) can be changed in wide range that makes MPS an attractive tool for different gas processing at high flow rates.

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