# GAS TEMPERATURE DETERMINATION IN AN ARGON NON-THERMAL PLASMA AT ATMOSPHERIC PRESSURE FROM BROADENINGS OF ATOMIC EMISSION LINES

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# Abstract

In this work a new spectroscopic method, allowing gas temperature determination in argon non-thermal plasmas sustained at atmospheric pressure, is presented. The method is based on the measurements of selected pairs of argon atomic lines (Ar I 603.2 nm/Ar I 549.6 nm, Ar I 603.2 nm/Ar I 522.1 nm, Ar I 549.6 nm/Ar I 522.1 nm). For gas temperature determination using the proposed method, there is no need of knowing the electron density, neither making assumptions on the degree of thermodynamic equilibrium existing in the plasma.

The values of the temperatures obtained using this method, have been compared with the rotational temperatures derived from the OH ro-vibrational bands, using both, the well known Boltzmann-plot technique and the best fitting to simulated rovibrational bands. A very good agreement has been found. *Keywords:* Plasma spectroscopy, microwave discharges, gas temperature, Stark broadening parameters, atomic emission spectroscopy.

## 1. Introduction

Nowadays non-thermal plasmas sustained at atmospheric pressure are considered as a very promising technology. Their non-equilibrium properties including low power consumption and the capacity to induce physical and chemical processes at relatively low gas temperatures, are responsible for the great attention that these plasmas have gained from an applied point of view [1-2]. Their reactivity comes from their high energy electrons, while the ions and neutral species remain relatively cold. Moreover, atmospheric pressure condition simplifies the handling of plasmas, avoiding the use of complicated vacuum systems. Plasma processing at atmospheric pressure, in addition to the elimination of constraints imposed by vacuum-compatibility and reduction in the capital cost of equipment, provides clear advantages over traditional vacuum-based plasma processing, offering improvements for generation of active chemical species, high chemical selectivity, minimal ion densities (resulting in low surface damage), and surface treatment methods unachievable by other means.

The gas temperature or heavy particles temperature (neutrals and ions) is a characteristic plasma parameter related to its capacity for heat dissipation. To know it in technological applications, such as those related to plasma surface treatments (thin film deposition, sterilization, surface functionalization...), plasma with the presence of a catalyst, or plasma treatment of liquids could be crucial. Also, in the last years, the use of cold plasma technology for treatments of living being has notably increased, particularly, in the medicine area [3], where a new field of research focuses on the use of plasma technology in the treatment of living cells, tissues, and organs. In these cases, a good control of this plasma parameter is also critical.

Optical Emission Spectroscopy (OES) techniques based on the analysis of molecular emission spectra are commonly used for gas temperature determination of plasmas at atmospheric pressure. The rotational temperature derived from them is considered as a good estimation of the kinetic temperature of the plasma heavy particles [4-5] due to the strong coupling between translational and rotational energy states under these high pressure conditions. Emissions of different molecular bands of the diatomic species (such as OH, N<sub>2</sub>, N<sub>2</sub><sup>+</sup>, CN..., among others), have been traditionally employed with this purpose [6-13].

At the same time, the use of molecular emission spectroscopy is not always easy for gas temperature measurement. Indeed  $N_2$ ,  $N_2^+$ , CN emission bands are commonly overlapped in plasmas containing nitrogen [4], what often makes very difficult to get reliable values of the gas temperature. If these plasmas also contain some OH species, the OH band appears overlapped with  $N_2$  band [14].

In argon/nitrogen plasmas, the rotational temperature obtained from the analysis of ro-vibrational transitions of the N<sub>2</sub> ( $C^3\Pi_u \rightarrow B^3 \Pi_g$ ) second positive band, has a difficult interpretation because the very efficient quasi-resonant energy transfer from argon metastable atoms can populate the rotational levels of N<sub>2</sub> ( $C^3\Pi_u$ ) state [15].

In plasmas in liquids or in-contact with them (such as plasma bubbles generated in water), the emission of the OH(A-X) band suffers from significant quenching because of the big concentrations of water vapor, and the rotational population distribution of OH(A) is an image of its own formation process, having a non-Boltzmann nature [16,17]. In this case, the rotational temperature of OH(A-X) is not a good estimate of the gas temperature.

Finally, in some plasma under certain specific experimental conditions, none of the abovementioned diatomic species can be detected for reliable gas temperature estimation. For all these reasons, alternative OES methods based on the measurement of the gas temperature from the broadenings of some atomic lines have been developed. In this way, the van der Waals broadening of some argon atomic lines (425.9, 522.1, 549.6 and 603.2 nm Ar I) have been used for this purpose [18-21]. These techniques are based on Ar I lines detection, and require sometimes the additional detection of  $H_{\beta}$  (Balmer series hydrogen line) for electron density determination [22] (from its Stark broadening contribution). But in plasmas in contact with the air, so containing nitrogen (Ar/N<sub>2</sub>, He/N<sub>2</sub>, Ar/He/N<sub>2</sub>...), argon and hydrogen atomic lines are often highly quenched [23-25], what limits the applicability of abovementioned techniques.

In the present work, we propose a new method allowing gas temperature determination, based on the measurements of Lorentzian profiles for pairs of argon atomic lines. In applying this method, there is no need of knowing the electron density - so no additional measurements of this parameter are necessary-, neither assumptions on the degree of thermodynamic equilibrium among excited states (unlike gas temperature methods based on rotational temperature determination) are made.

The values of the temperatures obtained using this method have been compared to the rotational temperatures derived from the OH ro-vibrational bands, using both, the well known Boltzmann-plot technique and the best fitting to simulated ro-vibrational bands.

## 2. Gas temperature determination method.

As already mentioned, Optical Emission Spectroscopy techniques based on the analysis of molecular emission spectra can be used for gas temperature determination of plasmas at atmospheric pressure. Emissions of molecular bands of the diatomic species OH,  $N_2$ ,  $N_2^+$ , CN, NH, NO, CH, C<sub>2</sub> and SiH, are usually employed with this purpose. Using either a Boltzmann-plot representation [20] or through comparisons between the experimental spectrum and its theoretical simulation one, the rotational temperature can be derived. In this work, the values of gas temperatures measured from the spectra of the OH specie (existing as impurity in the plasma) have been considered as a point of reference to discuss results derived from the new method we present below.

For plasmas generated at atmospheric pressure, experimentally measured line profiles can be fitted to a Voigt function, characterized by a full-width at half-maximum (FWHM),  $W_V$ , resulting from the convolution of a Gaussian function ( $W_G$ ) with a Lorentzian function ( $W_L$ ) (see e.g. Ref [26] and [27]). Indeed, the profiles of atomic lines emitted by plasma can be assumed as a function resulting from different broadening mechanisms leading to Gaussian or Lorentzian profile shapes, briefly described below.

The motion of emitter atoms with respect to the detector, with a continuous velocity distribution depending on their temperature, leads to the so called *Doppler broadening* and a Gaussian-shaped line profile with a FMHW  $W_D$  (in nm) given by

$$W_D = 7.16 \cdot 10^{-7} \lambda \sqrt{T_g / M}$$
 (1)

where  $T_g$  and M are the temperature (in K) and mass of the radiating atom (in a.m.u.).

The experimental line profile is also affected by the instrumental function of the spectrometer used for diagnosis. Usually, this instrumental function can be well approximated by a Gaussian profile with a FWHM  $W_I$ , as shown in the next section.

The *van der Waals broadening* is due to dipole moment induced by neutral atom perturbers in the instantaneous oscillating electric field of the excited emitter atom and

generates line profiles with a Lorentzian shape (with a FWHM  $W_W$ ), according to the Lindholm-Foley theory [28].

The *resonance broadening* of spectral lines is due to dipole-dipole interactions of the emitter with ground-state atoms of the same element [29] and also contributes to the Lorentzian part of the profile with a FWHM  $W_R$ .

The *Stark broadening* of a line is due to interactions of the emitter atom with the surrounding charged particles, perturbing the electric field it experiences. In the case of a non-hydrogenic atom, the profiles of isolated spectral lines broadened by collisions with electrons and ions have a Lorentzian shape.

Finally, the finite lifetime of the excited levels give rise to the *natural broadening*, which is typically very small ( $\sim 0.0001$ nm) and can be neglected in the case of atmospheric pressure plasma spectroscopy.

The broadening contributions with a Gaussian shape will lead to a profile with a FWHM ( $W_G$ ) given by

$$W_G = \sqrt{\left(W_D\right)^2 + \left(W_I\right)^2} \tag{2}$$

and those ones having a Lorentzian shape, give rise to a profile also Lorentzian having a FWHM ( $W_L$ ) given by

$$W_L = W_R + W_S + W_W \tag{3}$$

In the present method, we consider atomic lines with a negligible resonant broadening. Thus, the Lorentzian part of a line profile is only due to Stark and van der Waals broadenings, and the full width at half maximum (FWHM) of the Lorentzian profile,  $W_L$ , can be written as follows:

$$W_{L}(T_{e}, T_{g}, n_{e}) = W_{S}(T_{e}, T_{g}, n_{e}) + W_{W}(T_{g})$$
(4)

In this expression it has been considered the dependency of  $W_S$  on electron density  $(n_e)$ , electron temperature  $(T_e)$  and gas temperature  $(T_g)$ ; on the other hand,  $W_W$  is determined by the gas temperature. These dependencies are justified here bellow.

Several studies of Stark broadening for atomic and singly charged ion lines were carried out by Griem and co-workers, and the obtained Stark broadening parameters are available in [27]. New calculations for neutral atom lines were extended by other authors [30-34]. Provided that the impact approximation for both ionic and electronic contributions to the Stark broadening of the atomic lines is valid, the eq. (4) can be written as:

$$W_{S}(T_{e}, T_{g}, n_{e}) \cong \left[ w_{S}^{e}(T_{e}) + w_{S}^{i}(T_{g}) \right] \frac{n_{e}}{10^{16}}$$
(5)

where parameters  $W_s^e$  and  $W_s^i$ , are the full-width at half-intensity maximum given for an electron density equal to  $10^{16}$  cm<sup>-3</sup>. From eq. (5), a linear dependence of  $W_s$  on electron density is observed.

In non thermal-plasmas having  $T_g$  is much lower than  $T_e$ , in eq. (5) the ionic contribution  $w_S^i(T_g)$  can be neglected. Also,  $W_S$  can be considered to have a weak dependence on  $T_e$  in our small range 6000–7000 K [31], so to only depend on  $n_e$ .

Thus, eq. (5) can be approximated as follows:

$$W_L(T_e, T_g, n_e) \approx W_L(T_g, n_e) = w_s \frac{n_e}{10^{16}} + W_W(T_g)$$
 (6)

On the other hand, van der Waals broadening has a full width at half maximum  $W_w$  in nm given by [28]:

$$W_{W}(T_{g}) = 8.18 \cdot 10^{-12} \lambda^{2} \left( \alpha \left\langle \overline{R^{2}} \right\rangle \right)^{2/5} \left( T_{g} / \mu \right)^{3/10} N$$
(7)

where

$$\left\langle \overline{R}^{2} \right\rangle = \left\langle \overline{R}_{U}^{2} \right\rangle - \left\langle \overline{R}_{L}^{2} \right\rangle \tag{8}$$

is the difference of the squares of coordinate vectors (in  $a_0$  units) of the upper and lower level,  $\lambda$  the wavelength of the observed line in nm,  $\alpha$  is the polarizability of perturbers interacting with the excited radiator in cm<sup>3</sup>,  $T_g$  is the temperature of the emitters (coincident with the gas temperature) in K,  $\mu$  is the atom-perturber reduced mass in a.m.u., and N is the density of perturbers in cm<sup>-3</sup>.

In the Coulomb approximation,  $\left\langle \overline{R_i^2} \right\rangle$  can be calculated from:

$$\left\langle \overline{R_i^2} \right\rangle = \frac{1}{2} n_i^{*2} \left[ 5n_i^{*2} + 1 - 3l_i(l_i + 1) \right]$$
 (9)

being  $n_i^*$  is the effective quantum number, which can be obtained from the hydrogen approximation as

$$n_i^{*2} = \frac{E_H}{E_P - E_i}$$
(10)

where  $E_P$  is the ionization level of the radiating atom,  $E_H$  is the Rydberg constant and  $E_i$  is the excitation energy of the upper or lower level of the transition line.

Considering the ideal gas equation  $N = P/K_BT_g$ , the expression for the FWHM due to van der Waals broadening can be written as,

$$W_{W}(T_{g}) = \frac{C}{T_{g}^{\frac{7}{10}}}(\text{nm})$$
 (11)

with *C* being determined by the type of gas in the discharge and the nature of the atom emitters:

$$C = \frac{8.18 \cdot 10^{-19} \lambda^2 \left( \alpha \left\langle \overline{R^2} \right\rangle \right)^{2/5} P}{k_{\beta} \mu^{3/10}} \qquad (\text{nm} \cdot \text{K}^{7/10})$$
(12)

For an argon plasma at atmospheric pressure, when considering the van der Waals broadening of argon atomic lines ( $\mu = 19.97$  and  $\alpha = 16.54 \cdot 10^{-25} \text{ cm}^3$ ), *C* can be written as

$$C = 7.5 \cdot 10^{-7} \lambda^2 \left( \left\langle \overline{R^2} \right\rangle \right)^{2/5} (\text{nm} \cdot K^{7/10})$$
(13)

Eventually, eq. (3) can be expressed as

$$W_L(T_g, n_e) = w_S \frac{n_e}{10^{16}} + \frac{C}{T_g^{\frac{7}{10}}}$$
(14)

On this basis, we propose in this work a new method for gas temperature determination based on the measurement of the Lorentzian contribution to the whole FWHM for two atomic lines, *L1* and *L2*:

$$W_{L}^{L1}(T_{g}, n_{e}) = w_{S}^{L1} \frac{n_{e}}{10^{16}} + \frac{C^{L1}}{T_{g}^{\frac{7}{10}}}$$

$$W_{L}^{L2}(T_{g}, n_{e}) = w_{S}^{L2} \frac{n_{e}}{10^{16}} + \frac{C^{L2}}{T_{g}^{\frac{7}{10}}}$$
(15)

The dependency on the electron density can be eliminated from these expressions, and a lineal dependence between the FWHM of the Lorentzian part of the total profile of these two lines,  $W_L^{L1}$  and  $W_L^{L2}$ , is obtained:

$$W_{L}^{L1} = \frac{W_{S}^{L1}}{W_{S}^{L2}} W_{L}^{L2} + \left( C^{L1} - C^{L2} \frac{W_{S}^{L1}}{W_{S}^{L2}} \right) T_{g}^{-0.7}$$
(16)

Finally, the gas temperature is given by

$$T_{g} = \left(\frac{C^{L1} - C^{L2} \frac{W_{S}^{L1}}{W_{S}^{L2}}}{W_{L}^{L1} - \frac{W_{S}^{L1}}{W_{S}^{L2}}}\right)^{\frac{1}{0.7}}$$
(17)

Thus, knowing the Stark parameters for two lines and their C parameters, the gas temperature can be determined from full Lorentzian FWHMs of these lines. Nevertheless, the applicability of this method depends on the knowledge of these

parameters, with a certain degree of accuracy. It will be shown in this paper that theoretical estimation of these parameters existing in the literature can lead to significant errors in gas temperature values derived from this method. In this paper, an experimental way to determine more realistic parameters is also presented.

#### 3. Experimental setup

In this work we measured the gas temperature of an argon microwave (2.45 GHz) induced plasma column sustained at atmospheric pressure and generated inside a quartz tube (1.5-4 mm of inner and outer diameter, respectively), described elsewhere [35]. This plasma had been previously characterized in [36], being its electron density in the order of 10<sup>14</sup> (cm<sup>-3</sup>). Also, its electron temperature was estimated from the excitation temperature obtained considering a partial Local Thermodynamic Equilibrium among argon excited levels, being in the range from 6000 K to 7000 K [36].

Figure 1 includes a scheme of the optical detection assembly and data acquisition system to process spectroscopic measurements. A *surfaguide* was employed as coupling device, injecting a microwave power of 100 W to the plasma. A movable plunger and several stubs allowed the impedance matching so that the best energy coupling could be achieved, making the power reflected back to the generator ( $P_r$ ) negligible (< 5%). The argon flow rate was set at 0.5 slm (standard liters per minute) and adjusted with a calibrated mass flow controller.

Light emission from the plasma was analyzed by using a Czerny-Turner type spectrometer of 1m focal length, equipped with a 2400 grooves/mm holographic grating and a photomultiplier (spectral output interval of 200-800 mm) as a detector. The light emitted by the plasma was side-on collected using an optical fiber at different axial positions along the plasma column (z = 4, 6, 8, 10 and 12 cm measured from the end of

the column). A UV-VIS collimating beam probe was coupled to the optical fiber giving a  $0^{\circ}$ -45° of field of view and 3mm of aperture.

To measure the gas temperature from Ar I lines, lines without resonance broadening and with an appreciable dependence on the electron density were used. It was shown in a previous work [19], that lines corresponding to the  $nd \rightarrow 4p$  transitions with n > 4 (such as Ar I 603.2 nm, Ar I 549.6 nm and Ar I 522.1 nm) can be considered as a good option.

The instrumental function of the spectrometer was measured from the FWHM of the line Ne I 632.8 nm emitted by a helium-neon laser (this line is a good option to make this estimate as it has a wavelength close those of the Ar I lines considered in this work). When using equal entrance and exit spectrometer slit widths, this function had a approximately triangular shape, which could be well fitted with a Gaussian function (see Fig. 2). In this way, a instrumental broadening with  $W_I = 0.024$  nm was measured when using slit widths of 50 µm.

On the other hand, measurements of the light absorption have shown that the plasma studied can be considered as optically thin in the direction of observation chosen (transversally) for the Ar I lines detected.

The Ar I line profiles experimentally measured were fitted to a Voigt profile. The Lorentzian contribution to the whole broadening in each case was obtained from the Voigt FWHM measured for each line using the following formula [37, 38]:

$$W_V \approx \frac{W_L}{2} + \sqrt{\left(\frac{W_L}{2}\right)^2 + W_G^2}$$
(18)

and considering  $W_G \approx W_I$ , since according to eq. (1), the Doppler contribution can be considered as negligible when compared to the instrumental one, under the experimental conditions in our plasma (for  $T_g \leq 2500$  K,  $W_G {}^{ArI603} \leq 0.0034$  nm;  $W_G {}^{Ar549} \leq 0.0031$ nm;  $W_G {}^{ArI522} \leq 0.0030$  nm).

### 4. Results and discussion

Figure 3 shows a typical spectrum emitted by the plasma column at some specific axial position. It exhibited a relatively strong emission of Ar I lines, and a moderate emission of H I Balmer system ( $H_{\alpha}$ ,  $H_{\beta}$ ) and OH ro-vibrational band (3060 Å system, A-X). Both, H and OH species resulted from the dissociation water present as impurity in the feed gas.

## 4.1. The rotational temperature

OH (A-X) ro-vibrational band was used for  $T_g$  determination. Table I includes the spectroscopic features of Q<sub>1</sub> branch lines employed for the Boltzmann-plot method. Table II shows the axial gas temperature ( $T_g^{BP}$ ) profile obtained in this way. On the other hand, Table II also includes the values of  $T_g^{LB}$  derived from comparisons between the experimental spectrum and its theoretical simulation. LIFBASE code developed by Luque and Crosley [39] was used for simulation of OH bands.

At each axial position, LIFBASE was used to generate simulated spectra over a broad temperature range at coarse temperature increments of 20 K using a resolution of 0.024 nm. For each incremented temperature the residual is calculated as a value defined to be the sum of the differences between experimental and predicted intensity peak values across the entire spectral range. The smallest residual of the full temperature range provided the rotational temperature according this code. Rotational and gas translational temperatures were assumed to be in equilibrium.

The axial gas temperature profiles obtained from both methods were quite similar and constant, within the experimental accuracy range of measurements. Analogous results were also reported by for other microwave plasmas maintained under similar experimental conditions [19, 36].

# 4.2. Gas temperatures derived from atomic lines broadenings

Table III gathers the values of FWHM of the Lorentzian profile of the lines Ar I 603.2 nm, Ar I 549.6 nm and Ar I 522.1 nm, measured at different axial plasma positions. For each pair of lines, these values allow for  $T_g$  determination using eq. (17), provided *C* coefficients and Stark broadening parameters are known.

Table IV includes values of *C* coefficients calculated for these lines from eq. (13), and the Stark broadening parameters theoretically determined by Dimitrijevic *et al.* [31] for electron temperatures of 5000 and 10000 K (as in the plasma studied the electron temperature was expected to range from 6000 to 7000 K). Tables V and VI show the  $T_g$ values obtained using these parameters for electron temperatures of both 5000 and 10000 K, respectively.

Clearly, the values of  $T_g$  obtained in this way were far from those measured using OH ro-vibrational band. This discrepancy was particularly high for the cases in which the pairs Ar I 603.2 nm/Ar I 522.1nm and Ar I 549.6 nm/Ar I 522.1nm were employed. This disagreement pointed out that theoretical values of Stark broadening parameters used in  $T_g$  calculations might not be valid for the experimental conditions of the discharge studied in the present work. This was not a very surprising result as the values of excitation temperature given in [36] were just an estimation of the electron temperature of this plasma; in fact, some authors have found higher electron temperature values for argon microwave plasmas sustained at atmospheric pressure, when using other optical techniques, such as the Thomson scattering [40].

In order to circumvent this issue, the values of  $\frac{W_S^{L1}}{W_S^{L2}}$  appearing in eq. (17) were also determined experimentally. According eq. (16),  $W_L^{L1}$  has a linear dependency on  $W_L^{L2}$  provided that  $T_g$  is constant, being the ratio  $\frac{W_S^{L1}}{W_S^{L2}}$  the proportionally factor. As the axial profile measured for  $T_g$  in this plasma column was constant, this condition was fulfilled, and the slope of the linear fitting of the experimental values of  $W_L^{L1}$  vs.  $W_L^{L2}$ throughout the column could be used to obtain  $\frac{W_S^{L1}}{W_S^{L2}}$ .

Figure 4, 5 and 6 show the results from the linear fitting  $W_L^{L1}$  vs.  $W_L^{L2}$  for each couple of lines. Table VII includes the values of  $\left(\frac{W_S^{L1}}{W_S^{L2}}\right)_{exp}$  obtained using this procedure, and their comparison to the theoretical ones.

At this point we are able to recalculate the values of  $T_g$  using eq. (17) with the new values of  $\left(\frac{W_S^{L1}}{W_S^{L2}}\right)_{exp}$ . Table VIII gathers these results and their corresponding errors.

The new values of  $T_g$  are very close to those obtained from rotational temperature methods in Table III, even for the pairs of lines Ar I 603.2 nm/Ar I 522.1nm and Ar I 549.6 nm/Ar I 522.1nm. In general, results from the pair Ar I 603.2 nm/Ar I 549.6 nm were the most accurate ones, as shown in Table VIII. We ascribed this result to both the fact that these lines were both intense enough, and to lower errors in the determination of their FWHMs,  $W_L^{L1}$  and  $W_L^{L2}$  in eq. (17).

Finally, Figure 7 summarizes the main results from this work. It includes the gas temperature values obtained from the three pairs of lines using theoretical and experimental Stark parameters ratios, and compares them to the values obtained using OH ro-vibrational band (from both LIFBASE and Boltzmann-plot procedures). From this figure, we can conclude that gas temperature values obtained from the new method have a very good agreement with those obtained from OH band, as long as the experimental Stark parameters ratios measured for this plasma are employed. Theoretical Stark parameters for 5000 K and 10000 K seemed to lead to an overestimation of the gas temperature, particularly high in the 5000 K case.

#### 5. Final remarks

In this paper we propose a new spectroscopic tool for determination of the gas temperature in non-thermal plasmas, based on the measurement of the Lorentzian part of the profile of a pair of atomic emission lines. The lines chosen in this work were Ar I 522.1 nm, Ar I 549.6 nm and Ar I 603.2 nm, although the method applies for any pair of atomic lines (of argon or any other atomic specie), as long as they fulfil the following conditions:

- (i) Their Stark parameters must be known as accurate as possible;
- (ii) They have a negligible resonance broadening (or they do not have any at all). To choose lines with upper and lower levels not having electric dipole transitions (resonance line) to the ground state, is a way to ensure this condition is going to

be met. Also, analytical expressions for resonant FWHM in the literature [41-42] can be used to evaluate the importance of this broadening.

(iii) Their Stark and van der Waals broadenings should not be very different from each other, in order to avoid big errors in  $T_g$  determination (see eq. 17); this condition applies for plasmas with a gas temperature relatively low (van der Waals broadening not negligible) and moderate electron densities (significant Stark broadening).

This new method can be considered as a good alternative to the traditional ones based on the measurement of rotational temperatures. In the application of this method, no assumptions on the degree of thermodynamic equilibrium existing in the plasma are needed, being this its main advantage compared to others. Possible errors related to plasma separation from thermodynamic equilibrium are avoided in using it.

Additionally, as other optical emission spectroscopy techniques, it is non plasma perturbing diagnosis method, easy to implement.

On the other hand, in this paper experimental values of the ratios of Stark broadening parameters for selected pairs of argon atomic lines have been also determined. These values were more realistic than the theoretical ones (only available for specific values of electron temperatures 5000 K, 10000 K, 20000 K...) under the experimental conditions of our discharge, and they could be employed in forthcoming measurements using this technique.

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	$\lambda$ (nm)	$A (10^8  \text{s}^{-1})$	$E (\mathrm{cm}^{-1})$
$Q^4$	308.3	33.7	32779
$Q^5$	308.5	42.2	32948
$Q^6$	308.7	50.6	33150
$Q^8$	309.2	67.5	33652
$Q^9$	309.5	75.8	33952
$Q^{10}$	309.8	84.1	34283

Table I. Spectroscopic features of  $Q_1$  branch lines of the OH (A-X) ro-vibrational band.

**Table II.** Gas temperature values obtained from the Boltzmann-plot method  $(T_g^{BP})$  and using LIFBASE  $(T_g^{LB})$  measured at different axial plasma positions.

<i>z</i> (cm)	$T_{g}^{BP}(\mathbf{K})$	$T_{g}^{LB}(\mathbf{K})$
4	$1390 \pm 70$	$1570 \pm 20$
6	$1490 \pm 70$	$1690 \pm 20$
8	$1330 \pm 70$	$1600 \pm 20$
10	$1300 \pm 120$	$1650 \pm 20$
12	$1520 \pm 70$	$1690 \pm 20$

**Table III.** Lorentzian FWHM of lines Ar I 603.2 nm, Ar I 549.6 nm and Ar I 522.1 nm, measured at different axial plasma positions.

<i>z</i> (cm)	$W_{L}^{603}$ (nm)	$W_{L}^{549}$ (nm)	$W_{L}^{522}$ (nm)
4	0.0394±0.0002	0.0607±0.0023	0.1044±0.0022
6	0.0415±0.0012	0.0657±0.0009	0.1112±0.0024
8	0.0429±0.0009	0.0689±0.0008	0.1190±0.0012
10	0.0458±0.0002	0.0741±0.0015	0.1309±0.0024
12	0.0463±0.0005	0.0768±0.0005	0.138±0.001

**Table IV.** *C* coefficients calculated from eq. (9), and the Stark broadening parameters due to electron impacts theoretically determined by Dimitrijevic *et al.* [31] for electron temperatures of 5000 and 10000 K and electron density of  $10^{16}$  cm<sup>-3</sup>

Ar I line (nm)	С	$T_{e}\left(\mathbf{K} ight)$	$w_{S} = w_{S}^{e} (\mathbf{nm})$
603.2	4.2	5000	0.126
		10000	0.149
549.6	4.9	5000	0.251
		10000	0.305
522.1	5.9	5000	0.474
		10000	0.588

<i>z</i> (cm)	$T_{g}(\mathbf{K})$	$T_g(\mathbf{K})$	$T_g(\mathbf{K})$
	Ar I 603 nm/ Ar I 549 nm	Ar I 603 nm/ Ar I 522 nm	Ar I 549 nm/ Ar I 522 nm
4	$1900 \pm 400$	$2300 \pm 210$	$4000 \pm 2000$
6	$2000 \pm 500$	$2200 \pm 500$	$2900 \pm 1000$
8	$2100 \pm 400$	$2400 \pm 400$	$3500 \pm 1000$
10	$2000 \pm 300$	$2500 \pm 300$	$2800 \pm 2400$
12	$2300 \pm 300$	$2700 \pm 400$	$6900 \pm 2100$

**Table V.** Gas temperature obtained using the eq. (12) with theoretical Stark broadening parameters at electron temperatures of 5000 K.

<i>z</i> (cm)	$T_{g}\left(\mathbf{K}\right)$	$T_{g}\left(\mathbf{K}\right)$	$T_{g}\left(\mathbf{K}\right)$
	Ar I 603 nm/	Ar I 603 nm/	Ar I 549 nm/
	Ar I 549 nm	Ar I 522 nm	Ar I 522 nm
4	$1800 \pm 300$	$2060 \pm 170$	$3200 \pm 1400$
6	$1800 \pm 400$	$2000 \pm 400$	$2400 \pm 700$
8	$1900 \pm 400$	$2100 \pm 300$	$2800 \pm 700$
10	$1800 \pm 240$	$2130 \pm 180$	$3500 \pm 1500$
12	$2000 \pm 300$	$2490 \pm 220$	$3400 \pm 1000$

**Table VI.** Gas temperature obtained using the eq. (12) with theoretical Stark broadening parameters at electron temperatures of 10000 K.

**Table VII.** Values of  $\left(\frac{w_s^{L1}}{w_s^{L2}}\right)_{exp}$  obtained using the method proposed in this work and their comparison to the theoretical ones ( $T_e$  range = 10000K-5000K).

	$\left(\frac{W_S^{L1}}{W_S^{L2}}\right)_{\rm exp}$	$\left(\frac{W_S^{L1}}{W_S^{L2}}\right)_{Th}$
$w_{S}^{603}/w_{S}^{549}$	$0.466 \pm 0.004$	0.489-0.502
$w_{S}^{603}/w_{S}^{522}$	$0.208 \pm 0.004$	0.253-0.266
$w_{S}^{549}/w_{S}^{522}$	$0.448 \pm 0.008$	0.519-0.530

**Table VIII.** Recalculated values of  $T_g$  using eq. (12) and the new values of



<i>z</i> (cm)	<i>T<sub>g</sub></i> (K) Ar I 603 nm/ Ar I 549 nm	<i>T<sub>g</sub></i> (K) Ar I 603 nm/ Ar I 522 nm	<i>T<sub>g</sub></i> (K) Ar I 549 nm/ Ar I 522 nm
4	$1600 \pm 300$	$1500 \pm 300$	$1400 \pm 300$
6	$1600 \pm 400$	$1400 \pm 400$	$1200 \pm 300$
8	$1600 \pm 300$	$1500 \pm 300$	$1200 \pm 300$
10	$1500 \pm 400$	$1400 \pm 400$	$1200 \pm 300$
12	$1700 \pm 300$	$1500 \pm 300$	$1300 \pm 300$



Figure 1. Yubero et al.



Figure 2. Yubero et al.



Figure 3. Yubero et al.



Figure 4. Yubero et al.



Figure 5. Yubero et al.



Figure 6. Yubero et al.



Figure 7. Yubero et al.