Spectroscopy of the discharges created and maintained by a surface-wave

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Abstract. The discharges created and maintained by a surface-wave are being used in an increasing number of applications in different fields of science and technology. Knowing the processes which take place in the plasma is essential if we want that these applications being done correctly. These processes are related with the characteristic parameters of plasma such as temperatures and densities. For that, it is necessary to measure them. Different methods can be used with this purpose. Among them, the methods of passive spectroscopy do not disturb the discharge because they utilise the intensities and the broadenings of the spectral lines emitted by the plasma. In this work, the methods to measure the gas and electron temperatures, the electron density and the metastable and resonant atom populations are described, including the experimental values of the plasma parameters obtained from them.

Key words. Microwave plasma-Spectroscopic diagnosis methods-Plasma parameters-Spectral line broadening

1. Introduction

The discharges created and maintained by a surface-wave (SWD) are of a special type of microwave discharge, characterized by having dimensions higher than the wavelength of the electromagnetic field that is maintaining them, and the coupler device of the microwave energy. From an experimental point of view, the surface wave discharge has several characteristics that make it especially useful in the research of basic plasma physics, and can also be applied in different fields of science and technology. These characteristics are: a) the wide range of pressure (mTorr-some atmospheres) and frequency (MHz-GHz), b) the use of different atomic (Ar, He, Kr, Xe) and molecular (N₂ and O₂) gases and their mixtures, with flows lower than 0.5 l/min against several l/min that another plasma type such as the ICP needs (~ 10 l/min), c) the discharge extension outside the exciter device and, in this way, long plasma columns, and d) also, to point out, the absence of the significant fluctuations and instabilities and a very good reproducibility.

In recent years, SWDs are used in an increasing number of applications such as surface treatment (formation and deposition of thin material films, in the manufacturing of, for example, electronic devices), light sources, emission of laser radiation, sterilization and spectrochemical analyses (Stafford et al. 2002, Hubert & Sing 1998, Kudela et al. 1998, Calzada et al. 2002). Knowing the processes (internal kinetics) which take place in the plasma is essential if we want correctly to carry out these applications. The processes in the
plasma depend on the parameter values of the discharge such as temperatures and densities. The electron density \( n_e \) is one of the most important parameter. Knowing its value is basic if we want to understand the kinetics of the discharge because the electrons transfer the energy from the microwave field to the plasma, through their collisions with the rest of the particles which constitute it.

Metastable atoms play an important role in the microscopic mechanisms (internal kinetics) that take place in the plasma due to their high energy and their long mean life. They constitute a reserve of chemical energy which can produce endothermic reactions of excitation, ionization and dissociation of the other atoms and molecules. Depending on the discharge conditions, the contribution to the ionization from the metastable levels to the total ionization rate may be very important, influencing the population distributions of the excited states of the plasma atoms (and, therefore, the degree of thermodynamic equilibrium). Besides, the stepwise ionization from them permits a decrease in the necessary energy to sustain the discharge.

On the other hand, the possibility of the different processes (excitation and ionization) in the plasma being carried out will depend on the energy available in the discharge, fundamentally in the form of the kinetic energy of the electrons (electron temperature, \( T_e \)) and the heavy particles such as atoms and ions (gas temperature, \( T_g \)).

For measuring these parameters we can use techniques of passive spectroscopy, because the wide range and intensity of the spectral lines emitted by the atoms and ions into the discharge. Starting from intensities and broadenings of the spectral lines we obtain information about the basic parameters of the plasma named above.

2. Broadening effects on a spectral line

The shape and width of the spectral lines emitted by the plasma are governed by the processes which happen in the plasma perturbing the emitting atoms and molecules. Moreover, the optical device used in the laboratory to register the lines introduces additional broadening on their profile. The width of the lines is measured at half-way of the height (full width at half maximum, FWHM), and it is represented by \( \Delta \lambda \) in the case where de profile of the line is given as a function of the wavelength. The different causes which contribute to the line broadening are briefly described below.

**Natural broadening** is due to the fact that each quantic state of an atom is not perfectly defined but presents a dispersion of energy because of the perturbations exercise by the electromagnetic fields of the photons on the atom, with an intensity distribution fitting a Lorentz profile (Mitchell & Zemansky 1971).

**Doppler broadening** is caused by the movement or the thermal agitation of the emitting particles. The velocity distribution of these particles originates a distribution of frequencies due to the Doppler effect, giving rise to a Gaussian type profile. When the particle velocity distribution is Maxwellian, this broadening \( \Delta \lambda_D \) depends on the translational (kinetic) temperature \( T_g \) of the particles originating it (Mitchell & Zemansky 1971).

**Collisional broadening (Stark, pressure and resonant)** has its origin in the interactions of the emitting particles with the plasma particles. These interactions cause a random perturbation in the energy of the states of the particle emitting the radiation, which produces a broadening of the corresponding emission line. The collisional broadening may be due to various causes independent of each other. On one hand, the Stark broadening \( (\Delta \lambda_S) \), originated by the long range interaction with the charged particles of the plasma (electrons and ions), has a value which basically depends on the value of the electron density and temperature (Griem 1974; Konjević 1999). On the other hand, the so-called pressure or van der Waals broadening \( (\Delta \lambda_W) \) is due to the interaction of the excited atoms with the dipole induced in the neutral perturbers and depends on the value of the discharge gas temperature (Konjević 1999); this broadening is larger for spectral lines proceeding from the more external levels, which correspond to higher value of the effective quantum number of those lev-
els ($n^*$) (Griem [1974]); this quantum number is equal to $Z(E_{HH}/E_p)^{1/2}$, where $Z$ is the core charge, $E_{HH}$ is the Rydberg constant or hydrogen ionization energy and $E_p$ is the ionization energy of this level. Finally the so-called resonant broadening ($\Delta \lambda_R$) is a special case in which the perturbers are excited neutral atoms of the same species connected with the ground state (Konjević [1999]). Each of these collisional broadenings gives rise to a Lorentz type profile (Mitchell & Zemansky [1971]).

Broadening from self-absorption is due to the absorption of the radiation emitted by an atom by another of the same species present in the plasma. The self-absorption process reduces the spectral line intensity, basically in the central part of the profile, which leads to an effective broadening of it being the halfwidth of the self-absorbed line greater than in the case in which there is no self-absorption (Konjević [1999]; Christova [2004]; Cowan & Dieke [1948]).

Instrumental broadening ($\Delta \lambda_I$) is caused by the measuring optical device and being added to the broadening mechanisms related to the processes in the discharge atoms. In many cases the instrumental profile can be approximated to a Gaussian profile without committing any important error.

The profile of the spectral lines in plasmas generated at pressures higher than 100 Torr can be approached by using a Voigt function, characterized by its broadening as $\Delta \lambda_V$. This function type is the result of the convolution of a Gaussian function with a Lorentzian function, their broadenings being $\Delta \lambda_G$ and $\Delta \lambda_L$, respectively. Under this pressure condition ($>100$ Torr), some broadenings can be neglected and consequently, the Gaussian part of the profile is due to two Gaussian broadenings, the Doppler ($\Delta \lambda_D$) and the instrumental ($\Delta \lambda_I$) ones; the Lorenztzian part to the Stark ($\Delta \lambda_S$) and de van der Waals ($\Delta \lambda_W$) ones. All these broadenings are connected through the following expressions:

$$\Delta \lambda_L = \Delta \lambda_S + \Delta \lambda_W$$
$$\Delta \lambda_G^2 = \Delta \lambda_D^2 + \Delta \lambda_I^2$$

To unfold the Voigt profile into its Lorentzian and Gaussian components it should be used an adequate software.

3. Experimental device

In this section a schematic description of the plasma source and the optical detection and data acquisition systems for emission spectroscopy measurements is presented in Fig. [1].

The discharge was created in a quartz tube with one of its end open to the atmosphere, obtaining a plasma column. The dimensions of the discharge tube inner and outer diameter were 1-1.5 and 4-8 mm, respectively. The value of the inner diameter was chosen so that the plasma occupied almost the whole cross section of the discharge tube and, in this way, avoids the effect of radial contraction that appears in plasmas generated at a pressure higher than 10 Torr. In the case of microwave discharges, different from DC discharges, the plasma filament can be broken into two or more filaments depending on the operative conditions; among these conditions the radius of the discharge tube is (Kabouzi et al. [2002]).

The microwave power for the creation and maintenance of the plasma was between 100 and 250 W and was provided by a SAIREM generator GMP 12 kT in continuous mode at a frequency of 2.45 GHz. This power was supplied to the plasma by different exciter devices such as a surfaguide (Moisan et al. [1998]) and a surfatron (Moisan et al. [1976]). A stub system was also provided in order to adjust the impedance and ensure that the reflected power was less than 5% of the incident power.

The plasma gas was argon with a purity of about 99.99% at a flux of 0.25 l/min measured by a mass-flow controller.

The optical system consisted of two Czerny Turner monochromators, one of them with a focal length of 1 m and equipped with a holographic diffraction grating of 1200 grooves/mm (Jobin-Yvon THR-1000S) and another one with a grating of 2400 grooves/mm (Jobin-Yvon Horiba1000M). The slit widths used were 100 $\mu$m for the line spectra and 30 $\mu$m for the molecular band spectra. The detectors were two photomultiplier, R636-10 and R212-UH, of company Hamamatsu designed for the interval 180-900 nm. The radiation emitted by the plasma was collected by an optical fiber at different positions along the
plasma column, \(z = 0\) being the end of the discharge column.

4. Methods to measure the plasma temperatures

4.1. Gas temperature

The gas temperature \((T_g)\) is a measurement of the energy acquired by the heavy plasma particles (atoms and ions) of the discharge, essentially by means of electron collisions. In particular, being responsible for the atomization of the molecules of the substances introduced in the plasma, in order to analyze them. In many cases, the gas temperature is considering equal to the rotational temperature obtained from the ro-vibrational spectra of thermometric molecules present as a trace level in the plasma, assuming that these molecules are in equilibrium with the argon atoms. In this way the rotational temperature is obtained from the slope of the plot of \(\log(I/A)\) as a function of the transition upper state energy; \(I\) is the maximum value of the line intensity and \(A\) the corresponding transition probability. The molecules considered with this purpose are namely the OH radicals when, for instance, water vapor is already present as impurity in the carrier gas.

The corresponding axial distribution of the gas temperature obtained from the OH radical spectra is almost constant along the plasma column, with a value between 1200-1500 K. This result has also been reported by several authors under similar experimental conditions (Levésque 1991; Besner 1990; Dobreva et al. 1990). However, in some cases, the OH spectra are too weak. For that, another possibility is to determine \(T_g\) from Doppler or Van der Waals broadenings of the spectral lines emitted by the plasma. The expression that connects the Doppler width \((\Delta \lambda_D)\) with \(T_g\) is given by:

\[
\Delta \lambda_D = 7.16 \times 10^{-7} \lambda \sqrt{\frac{T_g}{M}} \tag{3}
\]

where \(T_g\) is in K, \(M\) is the mass of the radiating atom in atomic mass units, and \(\lambda\) is the wavelength in nm. In the case of van der Waals broadening \((\Delta \lambda_W)\), the expression is (Ali \\& Griem 1966; Konjević \\& Konjević 1997):

\[
\Delta \lambda_W = 8.18 \times 10^{-5} \lambda^2 \left(\alpha \langle R^2 \rangle \right)^{2/5} \left(\frac{T_g}{\mu} \right) N \tag{4}
\]

with \(N\) in \(\text{cm}^{-3}\), \(T_g\) in K and \(\lambda\) in cm, \(\mu\) is the reduced emitter-perturber mass, \(\alpha\) the polarizability in \(\text{cm}^3\) and \(\langle R^2 \rangle\) the mean square radius of the emitting atoms in the upper and lower levels of the transition.

For a value of \(T_g = 1500\) K, the Doppler broadening varies from 0.0024 nm at 522.1 nm to 0.0033 nm at 737.2 nm. Since \(\Delta \lambda_D\) is an order of magnitude lower than \(\Delta \lambda_I\) \((10^{-3}\) nm), we can assume that, under experimental conditions, the instrumental broadening dominates the Gaussian component of the recorded profile. For that, it is not possible to measure the gas temperature from the Doppler broadening of the atomic lines. Figure 2 shows that the Van der Waals broadening of the 603.2 nm argon line yields an axial variation of the gas temperature with a similar trend to that of the gas temperature inferred from the OH radical. Moreover, the values of \(T_g\) determined from both methods are nearly the same.
4.2. Electron temperature

The energy of the electrons (electron temperature, $T_e$) is a measurement of a part of the available energy in the discharge, this energy being used in the ionization and excitation processes that take place in the plasma. The electron temperature is one of the plasma parameters more difficult to measure.

The well-known Thomson scattering (i.e. scattering of light by free plasma electrons) can be used for measuring it (Kempkens & Uhlenbush 2000). But, this technique is quite difficult to implement especially in small dimension plasmas. In addition, it requires access to a powerful laser system which makes the method costly. Another possibility is to use methods of passive spectroscopy such as the Boltzmann-plot and the line-continuum ratio methods.

The use of the Boltzmann-plot method requires assuming that the distribution of population of the top levels obeys the Saha-Boltzmann’s distribution, what is to say that the plasma is, at least, in Partial Local Thermodynamic Equilibrium (PLTE). This procedure utilizes the (assumed) linear dependence of $\log(I/\lambda g_p A_p)$, among the atomic levels of the plasma atoms, as a function of the energy $(E_{exc})$ of the upper level of the transitions. Here, $I$ is the intensity from the total area of spectral line, $\lambda$ the wavelength, $g_p$ the statistical weight of upper level and $A_p$ the probability of spontaneous emission. This dependence leads to $T_e$ from the slope of the straight line ($-0.625/T_e$). Table 1 lists the lines and their characteristic parameters used in the Boltzmann-plot.

But the Boltzmann-plot method cannot be used in plasmas created with gases such as He or Ne because they are very far from the pLTE. In this case, it is necessary to use other methods. An alternative is the line-continuum ratio method that utilises the intensity $I$ emitted and the adjacent continuum $\varepsilon_c$, $I/\varepsilon_c$ being a function of $T_e$. For an argon plasma the used line is 430.01 nm and the expression of the $I/\varepsilon_c$ is (Sola et al. 1995):

$$\frac{I}{\varepsilon_c} = \frac{A \exp\left(\frac{B}{T_e}\right)}{T_c}$$
Table 2. Comparison between the \( T_e(\pm15\%) \) values obtained from the Boltzmann-plot and the line-continuum ratio method

<table>
<thead>
<tr>
<th>Methods</th>
<th>( z ) position (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann-plot</td>
<td>2 4 6 8 10 12</td>
</tr>
<tr>
<td>Line-continuum</td>
<td>4300 4800 5500 5800 6300 6800</td>
</tr>
</tbody>
</table>

\[
\times \exp \left( -\frac{C}{T_{exc}} \right) \left[ 1.8 - 0.7 \exp \left( -\frac{D}{T_e} \right) \right] ^{(5)}
\]

with \( A = 255.2 \) in nmK, and \( B = 182839.7 \), \( C = 168320.4 \) and \( D = 33450.1 \) in K. In Table 2 the \( T_e \) values obtained by both methods, Boltzmann-plot and line-continuum ratio are presented. One observes that the electron temperature increases with \( z \), and this behavior is different to the gas temperature, whose value remains constant along the plasma column. Also the values provided by both methods are very similar and they can be considered equals.

5. Measurement of the electron density

The electron density \( (n_e) \) is one of the most important parameter to measure in laboratory plasmas because the electrons control the processes of ionization and excitation that take place in them.

The Stark broadening of the spectral lines is often used as a technique for the diagnosis of the electron density, with applications not only in the laboratory plasmas, but also in the astrophysics. The procedure is based on this broadening, but it depends on the density of charged particles in the surrounding of the emitter, according to the Stark effect.

The hydrogen Balmer lines such as H\(_\alpha\), H\(_\beta\) and H\(_\gamma\) are classically utilized by this purpose. However, under certain experimental conditions, these lines are not intense enough, and it is necessary to introduce small quantities of hydrogen into the plasma as water vapour. This introduction, even very slight (~1%), produces changes in the internal kinetics of the discharge. A straightforward solution to this problem is to determine \( n_e \) from the Stark broadening of spectral lines emitted by the discharge gas itself.

5.1. Stark broadening of the Balmer series

Stark broadening of the Balmer lines is the most popular approach to the determination of \( n_e \), since the broadening of hydrogen lines is the strongest: these lines are thus the most sensitive to electron density variations. The classical expression connecting the Stark width with \( n_e \) has been derived by Kepple & Griem (1968) theory \((KG\ theory)\), who did not take into account the influence of the ion dynamics on the spectral profiles of the Balmer lines. This expression is written as:

\[
\Delta \lambda_S = 2.50 \times 10^{-10} a_{\nu'\nu}(n_e T_e) n_e^{2/3}
\]

where \( \Delta \lambda_S \) is in nm. The electron density is expressed in cm\(^{-3}\) and the parameter \( a_{\nu'\nu}(n_e T_e) \) is tabulated for each element, each transition \( \nu'\nu \) and different values of \( T_e \) and \( n_e \) (Griem 1974).

According with this theory, the theoretical profiles of the Balmer lines of the hydrogen have a different structure respect to the ones of the experimental profiles. In this way, the discrepancy between the theoretical and experimental profiles is normally ascribed to the ion dynamics effect, which must not be neglected if we have a plasma with a low electron density.

To introduce an important effect such as the ion dynamics on the line profiles several mod-
The electron density values obtained from the hydrogen Balmer lines and using the KG theory (without ion dynamics) and the GC model (with ion dynamics) are shown in Table 3.

<table>
<thead>
<tr>
<th>Lines</th>
<th>$n_e \times 10^{14} \text{cm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KG theory</td>
<td>GC model</td>
</tr>
<tr>
<td>H$_\alpha$</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>H$_\beta$</td>
<td>3.3 ± 0.7</td>
</tr>
<tr>
<td>H$_\gamma$</td>
<td>4.9 ± 0.3</td>
</tr>
</tbody>
</table>

Gigosos & Cardeñoso (1996) have developed a computational model (GC model) to describe the line profiles including this effect on them. From their computational model, they have obtained a series of tables that provide the Stark broadening ($\Delta \lambda_S$) of the line profile depending on the electron density, electron temperature and the reduced mass ($\mu$) of the pair emitter-ion. The use of this model provides the same electron density value from the different Balmer lines.

Table 3 shows the electron density values obtained from H$_\alpha$, H$_\beta$ and H$_\gamma$ lines using the KG theory (without ion dynamics) and the GC model (with ion dynamics). This shows that the profile of H$_\alpha$ line is much more greatly influenced by the ion dynamics than the H$_\beta$ line. So, from Eq. (6) the electron density is overestimated by a factor of 10 in the case of H$_\alpha$ with respect to the value obtained when the GC model is used. The H$_\beta$ line is almost insensitive to the effect of the ion dynamics, as can be observed when comparing both procedures and this has allowed to use it, until now, as an effective tool for the diagnostics of the electron density.

Our results for H$_\alpha$ and H$_\beta$ lines have been compared to the ones obtained experimentally by Ehrich & Kelleher (1980) and Weber et al. (1983) (Figs. 3a and 3b). In these figures, the continuous line corresponds to the theoretical values obtained from Eq. (6), and the discontinuous line to extrapolated values of this expression for densities in the interval $10^{13} - 10^{15} \text{cm}^{-3}$.

In Fig. 3a (line H$_\beta$) one can see that our values follow Eq. (6) and shows the same tendency as other author values. Besides this, the deviation of the obtained values of $n_e$ taking into account, or not, the effect of ion dynamics on the profiles is very small. Only in the interval $10^{13} - 10^{14} \text{cm}^{-3}$ there is a slight difference which can be mainly attributed to the effect of ion dynamics at these densities.

The experimental values of $n_e$ obtained from H$_\alpha$ line (Fig. 3b) are very different to those obtained with KG theory, even at densities of $10^{15} \text{cm}^{-3}$, which proves that ion dynamics strongly affect the profile of this line. These results show that the use of the GC model improves the overestimation of the density that results when Eq. (6) is used, principally in the case of the H$_\alpha$ line.
5.2. Stark broadening of neutral atom lines

For the atomic lines, the quadratic Stark effect results in a FWHM which can be expressed by the following classical relationship (Griem 1974; Pellerin et al. 1996):

$$\Delta \lambda_s = 2w[1 + 1.75\alpha(1 - 0.75r)],$$

(7)

where $w$ is the half width at half-maximum due to the collisions with the electrons, $\alpha$ represents the broadening due to the ions and $r$ is the ratio of the mean distance between ions to the Debye length. There are certain restrictions applying to Eq. (7), namely $\alpha \leq 0.5$ and $r \leq 0.8$.

Recently, we have made a study of the lorentzian broadening of the ArI spectral lines in order to use their Stark broadening to measure the electron density and not this broadening for Balmer lines. Figure 4 shows the axial variation of the lorentzian component ($\Delta \lambda_L$) of the profile for argon lines belonging to the nd-4p transitions ($4 \leq n \leq 7$). We observe that the total Lorentzian width, resulting from Stark and Van der Waals broadenings, increases with the excitation energy of the upper level of the transition, which corresponds to an increase of the effective quantum number ($n^*$).

In a surface-wave plasma of Ar, the electron density shows an axial distribution which decreases towards the end of the plasma column. For spectral lines corresponding to $n^*$ higher than 5 (522.1 and 549.6 nm), the Lorentzian width varies significantly along the plasma column as shown in Fig. 4. This increase corresponds to an increase in the electron density along the axis since the gas temperature being axially almost constant requires the Van der Waals broadening to be constant. The observed substantial increase in the line broadening reflects the sensitivity of these lines to electron density variation.

Figure 5 shows the axial distribution of $n_e$ determined from both the broadening of the 549.6 nm argon line and H$_\beta$ line for comparison. We observe that the variation of electron density, from both lines, with $z$ is similar. However, the actual values stemming from the Ar line is approximately 1.5 or 1.8 times higher than those obtained from the H$_\beta$ line. The observed difference could be due to the uncertainties of the semi-empirical values of $w$ and $\alpha$ given by Eq. (7) for the 549.6 nm line.

6. Populations of metastable atoms

Absorption methods have been used to measure the population of the metastable and resonant levels in discharges (Mitchell & Zemansky 1971; Moussounda et al. 1985; Jolly & Tozeau 1975). These methods are based on the interaction between the radiation and the absorbing atoms, described by
(Mitchell & Zemansky, 1971). In this way, a fraction of the radiation emitted by an external source of light is mainly absorbed by the metastable and resonant atoms and this absorbed radiation is related to their densities. However, an external source is not needed when the self-absorption techniques are used with this purpose. These techniques employ the discharge as source of radiation and an absorbing medium (Jolly & Tozeau, 1975). Then, the light emitted from the discharge has to travel through the interior of the plasma before coming out to outside. During this passage, part of the radiation is being absorbed by the atoms or molecules of the same kind that causes the emission (Sola et al., 1995). This absorption phenomenon in the light source itself is called self-absorption.

In the self-absorption method, the ratio of the total intensities of two partially self-absorbed lines emitted by the discharge is used. Both lines end in the same level whose population is aimed to determine: line (1), with the highest oscillator strength, will be more strongly absorbed than line (2). If we measure the total intensities emitted by these lines in the absence of absorption, $I_{01}$ and $I_{02}$, and the total self-absorbed intensities, $I_{1}$ and $I_{2}$, the ratio of these amounts, which depends on the population of the absorbing level, will be written as follows:

$$r = \frac{I_{1}}{I_{2}} = \frac{I_{01}I_{02}}{I_{01}I_{02}} = r \left( \frac{k_{01}}{k_{02}}, a_{1}, a_{2} \right), \quad (8)$$

where $k_{0}$ has the expression:

$$k_{0} = \frac{2e^{2}}{mc} \sqrt{\pi \ln 2} \frac{N}{\Delta V_{D}}, \quad (9)$$

$f$ being the oscillator strength of the spectral line and $N$ the absorbing atoms concentrations (metastables or resonants) and the $a$-parameter is the ratio of the Lorentzian and Doppler widths at half-height of the line and it can be expressed in wavelength units as $a = \Delta \lambda_{L}/\Delta \lambda_{D}$.

The line-set used in the measurement of metastable and resonant atom populations is shown in Table 4 as well as both their characteristic parameters and the $a$-parameter values.

For the $a$-parameter, we used the expression in function of wavelength; in this way $\Delta \lambda_{L}$ has been determined through the deconvolution of the experimental lines, by using a computational program, and $\Delta \lambda_{D}$ from the discharge gas temperature value.

In Fig. 6, one shows the variation of $r$ as a function of $k_{01}l$, for different values of $k_{01}/k_{02}$, $a_{1}$ and $a_{2}$ corresponding to each line pair used in $3P_{2}$ metastable level population measurement. These curves have been designed using the tables given by Jansson & Korb (1968), who resolved the Voigt integral using the Romberg’s algorithm. Similar curves can be obtained for the lines ending on the $3P_{0}$, $1P_{1}$ and $3P_{1}$ levels.

Figure 7 shows the population of the metastable and resonant argon levels obtained from the intensity ratio of the different line pairs, using the $a$-parameter values experimentally found for them and the $r$ vs. $k_{01}l$ curves previously described by Santiago et al. (2004). The results obtained are between $10^{10}$ and $10^{13}$ cm$^{-3}$ in agreement with the ones reported in the literature (Moussounda et al., 1985), the $3P_{2}$ metastable level being the most populated one. The differences observed among the population values obtained for a same level by using different line pairs are in the error range of the method (20%). This error can be mainly ascribed to the uncertainly in the measurement of the gas temperature, which determined the Doppler broadening that appears in
Table 4. Parameters of the pair lines corresponding to transitions $4p \rightarrow 4s$ used to measure the metastable and resonant atom populations

<table>
<thead>
<tr>
<th>$\lambda$(nm)</th>
<th>Transition</th>
<th>$E_{ex}$(eV)</th>
<th>$f$</th>
<th>$a$</th>
<th>$g_p$</th>
<th>$A_p$(10$^7$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>811.5</td>
<td>$4p^3D_1-4s^3P_2$</td>
<td>13.0719</td>
<td>0.51</td>
<td>0.54</td>
<td>7</td>
<td>3.66</td>
</tr>
<tr>
<td>801.5</td>
<td>$4p^3D_2-4s^3P_2$</td>
<td>13.0910</td>
<td>0.092</td>
<td>0.51</td>
<td>5</td>
<td>0.96</td>
</tr>
<tr>
<td>763.5</td>
<td>$4p^3D_2-4s^3P_2$</td>
<td>13.1680</td>
<td>0.239</td>
<td>0.56</td>
<td>5</td>
<td>2.74</td>
</tr>
<tr>
<td>714.7</td>
<td>$4p^3P_2-4s^3P_2$</td>
<td>13.2788</td>
<td>0.00299</td>
<td>0.00</td>
<td>3</td>
<td>0.065</td>
</tr>
<tr>
<td>706.7</td>
<td>$4p^3P_0-4s^3P_2$</td>
<td>13.2984</td>
<td>0.0296</td>
<td>0.97</td>
<td>5</td>
<td>0.395</td>
</tr>
<tr>
<td>696.5</td>
<td>$4p^3P_1-4s^3P_2$</td>
<td>13.3239</td>
<td>0.0292</td>
<td>0.20</td>
<td>3</td>
<td>0.67</td>
</tr>
<tr>
<td>842.5</td>
<td>$4p^3D_2-4s^3P_1$</td>
<td>13.0910</td>
<td>0.413</td>
<td>1.21</td>
<td>5</td>
<td>2.33</td>
</tr>
<tr>
<td>810.4</td>
<td>$4p^3D_1-4s^3P_1$</td>
<td>13.1493</td>
<td>0.273</td>
<td>0.74</td>
<td>3</td>
<td>2.77</td>
</tr>
<tr>
<td>800.6</td>
<td>$4p^3D_2-4s^3P_1$</td>
<td>13.1680</td>
<td>0.075</td>
<td>0.91</td>
<td>5</td>
<td>0.468</td>
</tr>
<tr>
<td>751.5</td>
<td>$4p^3P_1-4s^3P_1$</td>
<td>13.6910</td>
<td>0.121</td>
<td>1.04</td>
<td>1</td>
<td>4.3</td>
</tr>
<tr>
<td>866.8</td>
<td>$4p^3D_2-4s^3P_1$</td>
<td>13.1493</td>
<td>0.095</td>
<td>1.44</td>
<td>3</td>
<td>0.28</td>
</tr>
<tr>
<td>794.8</td>
<td>$4p^3P_2-4s^3P_1$</td>
<td>13.2788</td>
<td>0.56</td>
<td>0.36</td>
<td>3</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Fig. 7. Metastable and resonant argon populations measured by using different pairs of spectral lines

the expression of $a$-parameter and in the expression used in the calculation of the absorbing atoms (Eq. (9)).

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