Spectroscopy methods applied to the research in plasmas at atmospheric pressure

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Abstract. Plasmas operated at atmospheric pressure are being the object of an increased attention due to their potential and current use in various fields of science and technology (excitation source for elemental analysis, purification of noble gases, hydrogen production and sterilization of medical instruments). In order to ensure that the industrial and technological applications of plasmas are being carried out with a maximum of efficiency it is necessary to know and control the processes that take place in the plasmas during their applications. These processes depend on the densities of different plasma species such as electron density and both atoms and molecules at excited levels together with the energy available in the discharge. This energy is fundamentally in form of the kinetic energy of electrons, that is, electron temperature and heavy particles like atoms and ions, called gas temperature. Passive spectroscopy techniques can be used to measure the densities and temperatures in plasma. Classical and new methods can be used for this purpose. An example of the use of the spectroscopy to know the processes that take place in plasmas corresponds to the study of the capacity of a surface wave discharge to dissociate the alcohols molecules for obtaining hydrogen.

1. Introduction
Plasmas operated at atmospheric pressure are being the object of an increased attention due to their potential and current use in various applications such as excitation source for elemental analysis [1], purification of noble gases [2] and more recently hydrogen production [3] and sterilization of medical instruments [4].

In order to ensure that the technological applications of plasmas are carried out with a maximum of efficiency it is necessary to know the ability of the discharge to induce the desired microscopic processes. This ability depends on the densities of different plasma species such as electron density and both atoms and molecules at excited levels together with the energy available in the discharge. This energy is fundamentally in form of the kinetic energy of electrons (electron temperature) and heavy particles like atoms and ions (gas temperature).

Passive spectroscopy techniques can be used to measure the temperatures and densities in plasma. These techniques are based on the analysis of the radiation emitted by the own plasma. So, the use of passive spectroscopy does not perturb the internal kinetics of the discharge when the observation and control of plasma application are being carried out. Therefore, an important part of the effort in experimental and theoretical research in plasmas is devoted for devising, developing and proving spectroscopy methods for the purpose mentioned above. New methods have been recently developed in order to measure the electron density of plasmas at atmospheric pressure which can be considered as a complement to the classical methods.

Moreover, these techniques also allow us to know and control the processes that take place in the plasmas during their applications in specific fields. In this way, an example it is the study of the ability...
of a surface wave discharge (special type of microwave discharge) to dissociate the alcohols molecules for obtaining molecular hydrogen. This hydrogen could be used to generate electricity by fuel cells.

2. Spectroscopic methods applied at atmospheric pressure: temperatures and densities

Methods of passive spectroscopy are used for measuring temperatures and densities in plasmas generated at atmospheric pressure because the wide range and intensity of the spectral lines emitted by the atoms and ions into the discharge. These methods are based on the profile analysis of these spectral lines. So, starting from intensities and broadenings of them, we can obtain information about the values of the plasma parameters (temperatures and densities).

The shape and width of a spectral line emitted by the plasma are a consequence of the processes that happen in the discharge. Moreover, the optical device used in the laboratory to register the radiation introduces additional broadening on its profile. The line width is considered as the full width at half maximum (FWHM) and it is represented by $\Delta \lambda$ in the case where the profile of the line is given as a function of the wavelength.

At atmospheric pressure the spectral line profile can be approached to a Voigt function (Voigt profile). This function is the result of the deconvolution of a Gaussian function with a Lorentzian function, their broadenings being $\Delta \lambda_G$ and $\Delta \lambda_L$, respectively. The Gaussian part of the profile is due to the Doppler ($\Delta \lambda_D$) and the instrumental broadenings ($\Delta \lambda_I$); the Lorentzian part to the Stark ($\Delta \lambda_S$) and the van der Waals ($\Delta \lambda_W$) ones. To unfold the Voigt profile into its Lorentzian and Gaussian components it should be used adequate software. The other broadenings that contribute to the total profile width can be considered negligible for different reasons: a) natural broadening because it is very small compared to the rest of the broadenings, for instance, it is approximately equal to $10^{-4}$ nm for argon atomic lines, b) resonant broadening because the transitions used in the different methods that are going to describe do not involve the ground state and c) broadening from self-absorption when a proper choice of spectral lines is made.

2.1 Gas temperature

This temperature ($T_g$) is a measurement of the energy acquired by the heavy particles (atoms and ions) of the discharge, fundamentally, from the collisions with the plasma electrons.

It is habitual to determine the gas temperature from the ro-vibrational spectra emitted by molecular species like N$_2^+$, C$_2$, CN and OH, which are present in the plasma at trace level and assuming that these molecules are in equilibrium with the plasma atoms. The OH radical is the most common for this purpose; then, the rotational temperature obtained from the slope of the plot $\log(I/\lambda)$ as a function of the transition of the upper state energy can be assumed to be equal to the gas temperature. In this expression $I$ is the maximum value of the line intensity and $A$ the corresponding transition probability. For surface wave plasma, the corresponding axial distribution of the gas obtained from the OH radical is almost constant along the plasma column with values approximately equal to 1400-1500 K, 1600 K and 2200 K for Ar [5], Ne [6] and He [7], respectively.

However, in some cases the ro-vibrational spectra of the molecular species are too weak. Then, another possibility is to determine $T_g$ directly from the Doppler or the van der Waals broadenings of the spectral lines emitted by the plasma because each one of these broadenings is a function of the gas temperature. When the instrumental broadening dominates the Gaussian component of the spectral line, the Doppler broadening can not be used to obtain the gas temperature value; it is the case for an argon plasma in which $\Delta \lambda_D$ gets values at 1400-1500 K of $T_g$ between 0.002 nm for 522.1 nm and 0.003 nm for 737.2 nm lines whereas $\Delta \lambda_I$ is of the $10^{-2}$ nm order [8]; the van der Waals broadening is then considered the most appropriate tool for this purpose [8-9].
As mentioned above, the Lorentzian part of a spectral profile is the sum of the Stark and the van der Waals broadening. In argon plasma created by a surface wave at atmospheric pressure, $\Delta \lambda_L$ of the spectral profiles coming from lower energy levels can be considered equal to $\Delta \lambda_{vp}$ [9] and the gas temperature derived from this broadening has a similar trend to that the one inferred from the OH radical [9].

A recently published method proposes the measurement the gas temperature from lines whose Stark broadening is comparable to their van der Waals one [10]. This method is based on the consideration of a linear dependence on electron density for the Stark broadening of atomic lines. This linear dependence can be assumed when the asymmetry of the spectral line is eliminated, which corresponds to the ion contribution to the Stark broadening of the line. In an argon surface-wave plasma column, the axial profile of gas temperature can be considered constant and thus, the van der Waals too [5,9]. Taking into account these considerations, the origin ordinate of the straight line corresponding to the variation of the Lorentzian width of an Ar atomic line with the electron density is equal to the Lorentzian width for zero electron density value. This ordinate can be considered equal to the van der Waals broadening and used to calculate the plasma gas temperature. In Table 1 the gas temperature obtained by using three Ar atomic lines are shown, which are in agreement with those obtained from the ro-vibrational spectra of OH radical [5].

### Table 1. Values of gas temperature from the origin ordinate of the straight lines for three Ar atomic lines

| Lines   | 522.1 nm | 549.6 nm | 603.2 nm |
|---------|----------|----------|----------|
| $T_{gas}$ (K) | 1260 ± 130 | 1100 ± 60 | 1020 ± 50 |

#### 2.2 Electron temperature

Electron temperature ($T_e$) is one of the plasma parameter more difficult to measure. It corresponds to the energy of the plasma electrons and being use in the ionization and excitation processes that take place in the discharge.

For plasmas in partial Local Thermodynamic Equilibrium (pLTE), the distribution of population of the atomic system top levels obeys the Saha distribution which also implies a Boltzmann balance at equilibrium. Therefore, the excitation temperature ($T_{exc}$) derived from the Boltzmann-plot is considered equal to the electron temperature [5,11]. This procedure utilise the assumed linear dependence of $\lg(I/\lambda gA)$ with the upper level of the considered transitions. Here, $I$ is the intensity of each spectral line, $\lambda$ the wavelength, $g$ the statistical weight of the upper level and $A$ the probability of spontaneous emission. From the slope (- 0.625/$T_{exc}$) of the straight line fitted through these points, $T_{exc}$ is obtained, then, it is considered equal to electron temperature.

However, in plasmas that are far from pLTE, the Boltzmann-plot method can not be used and an alternative is the line-continuum ratio method that utilizes the intensity ($I$) corresponding to an emitted spectral line and the adjacent continuum ($\varepsilon_c$) to this line, $I/\varepsilon_c$ being a function of $T_e$ [12].
2.3 Electron density

The electron density \( n_e \) is one of the most important plasma parameters because the electrons control processes of excitation and ionization that take place in the discharge directly or through processes in various stages in which the electrons also play a fundamental role in the intermediate stages.

The Stark broadening of the spectral lines is the most popular tool to determine plasma electron density. In this way, a deconvolution process is necessary in order to extract the profile Lorentzian part from the total width of the spectral line. In plasmas with electron density value higher that \( 10^{15} \text{ cm}^{-3} \) the contribution of the van der Waals broadening to the Lorentzian width of the spectral profile can be considered negligible; in this case the Lorentzian width is approximately equal to the Stark broadening. However, for plasmas with electron density lower than \( 10^{15} \text{ cm}^{-3} \) it is necessary to calculate the contribution of the van der Waals broadening to the Lorentzian width and eliminate this broadening from that one [10].

2.3.1 Stark broadening of the Balmer lines: \( H_\alpha \), \( H_\beta \) and \( H_\gamma \)

The hydrogen Balmer lines such as \( H_\alpha \), \( H_\beta \) and \( H_\gamma \) are classically used to measure the electron density, since the Stark broadening of these lines is the strongest and very sensitive to electron density variations.

The expression that connects this broadening with electron density is derived from the Kepple-Griem theory [13-14] without to take into account the influence of ion dynamics on the spectral profiles of the Balmer lines. So, the theoretical profiles for these lines have a different structure respect to the ones of the experimental profiles and, consequently, the electron density values are different depending of the utilized Balmer lines. In order to resolve this discrepancy, computational models have been or are being developed taking into account the ion dynamics effect on Balmer line profiles. Among them, we find the Gigosos-Cardeñoso model [15] which provides a series of tables that give the relation between the Stark broadening of the line profile and the electron density. The use of these tables permits to obtain the same electron density value independent of the utilized line [16].

2.3.2. Stark broadening of the atomic lines

When hydrogen Balmer lines are not intense enough, the use of the Stark broadening of non-hydrogenic spectral line emitted by the discharge itself is another possibility to measure the electron density [17]. Studies carried out in a surface wave discharge at atmospheric pressure have shown that the line whose Lorentzian broadening present a variation with the electron density can be used for this purpose. For an argon plasma, these lines belong to the upper levels of the atomic system [9]. The values stemmed from the Ar lines are approximately 1.5 or 1.8 times higher than the obtained from the \( H_\beta \) line. The observed differences could be due to the uncertainties of the parameters that appears in the equation given by [14] and for each one of the atomic lines.

2.4 Metastable atom populations

It is habitual to use absorption methods to measure the population of the metastable atoms for plasmas. These methods are based on the interaction between the radiation emitted by an external radiation source (for instance a lamp) and the absorbing medium.

However, an alternative is the self-absorption method; the discharge being radiation source and absorbing medium, at the same time. In the application of this method, the population of a specific level is determined from the ratio of the two partially self-absorbed lines, which both end at the same level whose population wants to be measured. One of the two lines is much less self-absorbed than the other one and is used as reference line. The ratio of the intensities is a function of the absorption coefficient of the line more self-absorbed; this coefficient depends of the population of the metastable levels [18-19].
Self-absorption method was utilized to measure the metastable populations for an argon surface wave discharge generated at atmospheric pressure obtaining values in agreement to those appearing in the literature by using absorption methods [19].

3. Other spectroscopic methods for measuring electron density and gas temperature
In addition to the methods described in the above section, other methods have recently been developed and applied in order to measure such parameters as electron density and gas temperature for plasmas at atmospheric pressure, and these are also based on the analysis of spectral lines.

3.1 Hα and Hβ calibration method
For plasmas generated under certain experimental conditions, only Hα line is detected and its use requires the influence of ion dynamics on the profile of the spectral line to be taken into account. In order to avoid the use of the Hα line, a method called the Hα-Hβ calibration method can be used [20].

In this method, the representation of the Stark broadenings of the Hα and Hβ lines at the introduction of a small amount of hydrogen into the discharge gives a calibration curve. In this way, once the Stark broadening of Hα line is measured, the corresponding one for Hβ can be found from this curve and then the electron density can be calculated. This method was applied to an argon plasma torch open to the air for which Hβ was not detectable, offering a simplified way to estimate electron density when the Hβ line is not detected [20].

3.2 Intersection method
Yubero et al. [21] have studied the possibility for measuring ne and Te simultaneously from Stark broadenings of the Balmer lines Hα, Hβ and Hγ lines. The method is based on the dependence of Stark broadening of the hydrogen Balmer lines on ne and Te. In this way, for a fixed value of Stark broadening for each one of the three Balmer lines, a plot for ne dependence on Te can be depicted. Taking into account the error bars for the Stark broadenings three zones can be depicted and their crossing gives a region where the electron density and temperature values are common for the three lines.

This method was applied to an argon plasma column generated by a surface wave [21], obtaining values for electron density in agreement with those obtained for this discharge in other works [5, 9, 16] but of 30-40% higher than in the case of Te [22]. Thus, this method could be useful for electron density measurement but not for electron temperature.

3.3 Gas temperature from plasma atomic lines
Under operative condition of atmospheric pressure, the Lorentzian width of a spectral line can be written as the sum of the Stark and the van der Waals broadenings. In an argon surface wave plasma column, the axial profile of gas temperature can be considered constant and thus, the van der Waals broadening can be too [5, 9]. Moreover, Stark broadening has a negligible dependence on electron temperature for this plasma type. Taking into account these considerations, a linear dependence between Lorentzian width and electron density is established. The origin ordinate of the straight line corresponds to the Lorentzian width for zero electron density and it can be considered approximately equal to the van der Waals broadening and used to calculate the plasma gas temperature. The 522.1, 549.6 nm and 603.2 nm spectral lines of ArI were used for this purpose observing a significant discrepancy in the case of 522.1 nm [10]. Analyzing the shape of this line, a significant asymmetry was observed. If the contribution of the asymmetry is eliminated from the total width of the line, a new representation is made for Lorentzian width versus electron density and a new value of the origin ordinate is obtained. In this case, the gas temperature derived from this origin ordinate was in agreement with those obtained from the other considered atomic lines and the gas temperature measured from the ro-vibrational spectra of OH radical [5].
4. Control of processes by emission spectroscopy of: molecular hydrogen production

In this section, an example of the use of the emission spectroscopy to control the processes during the decomposition of alcohol molecules by the plasma is shown.

The discharge was created inside a quartz tube open at one end (1.5 and 4 mm inner and outer diameters, respectively) and plasma flame being the configuration chosen due to its ruggedness withstanding the introduction of alcohol [3].

Alcohols (methanol, ethanol, propanol and butanol) were introduced into the plasma by the method called bubbling at room temperature in order not to involve additional energy in the process. The total Ar gas flow was divided into two parts: one of them was used as carried gas bubbling into the recipient containing the alcohol to drag its molecules, giving place to a mixture of gas and alcohol. This mixture was joined to the rest of argon flow and introduced into the quartz tube, in which the plasma was generated.

The plasma capability to break down the bonds of alcohol molecules was analyzed through the radiation emitted by the discharge. This radiation was collected by an optical fiber and coupled to the entrance slit of a Jobin-Yvon Horiba monochromator, type Czerny-Turner, with a focal distance of 1 m and holographic grating of 2400 lines/mm. A computer-controlled CCD camera was used to register the spectra.

Figures (1a) and (1b) show the characteristic spectra emitted by an Ar plasma without introducing alcohol and when it is introduced into it. For the pure Ar plasma, atomic lines of argon, hydrogen lines and molecular bands of OH and NH radicals were observed; the hydrogen lines and molecular bands are due to the impurities present in the plasma gas. However, when alcohols are introduced new species are detected in the discharge, such as CH, CN and C₂ together with an increase in the intensity of the H α line. Besides, a black solid substance appeared deposited on the discharge tube. All these radicals and increase of hydrogen line come from the dissociation of alcohol molecules. This result shows the good capability of the surface wave plasma to break down the alcohol molecules introduced into it [3].

![Figure 1(a)-1(b). Spectrum emitted by the plasma (a) without alcohol and (b) when alcohols have been introduced into the plasma. From Ref. [3]](image_url)
The kinetics of the decomposition of alcohols can be studied from the observation of the hydrogen lines and the molecular bands that appear in the spectra. Studying the emission of the hydrogen line (H\(_{\alpha}\)), (Figure 2) one shows the variation of the H\(_{\alpha}\) line when different alcohols are introduced into the plasma. One observes that the highest intensity for this line corresponds to the methanol. It is due to H/C ratio and vapour pressure are also highest for a given temperature. As the experiments were carried out under the same temperature and pressure conditions for the four alcohols, the amount of the inlet methanol was the highest one.

![Figure 2](image_url)

**Figure 2.** The H\(_{\alpha}\) line emitted by a plasma of pure argon and when the four alcohols were introduced into it. From Ref. [3]

For comparison, a more detailed study of molecular bands appearing in the spectra corresponding to cases of methanol and ethanol can help to understand the kinetics in the plasma during the decomposition process of alcohols. In Figure (3a), the intensities of C\(_2\) bands are significant for ethanol, which explains the great amount of black deposit in the discharge tube when this alcohol is introduced. Also, the result for CN bands is in agreement with the higher number of carbon atoms in the ethanol molecules (Figure (3b)). However, in case of OH radical, the result appearing in Figure 4 shows a greater decomposition of the methanol molecules which is according to the higher intensity of H\(_{\alpha}\) line shown in Figure 2. The CH, CN and C\(_2\) bands in the spectra indicates the existence of dissociation reactions of the alcohol molecules and, at the same time, recombination reactions which leads to the formation of these new species.

![Figure 3(a)-3(b)](image_url)

**Figure 3(a)-3(b).** (a) The C\(_2\) band and (b) the CN band emitted by the plasma when methanol and ethanol were introduced into it. From Rfe. [3]
5. Conclusions

Classical and new methods to measure the plasma parameters (densities and temperatures) have been described and results from the application of them in surface wave discharges at atmospheric pressure. Besides, the decomposition of alcohol molecules by this discharge type has been shown as an example on the use of emission spectroscopy to control the processes that take place in the plasma.

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