Simple and analytical function for the Stark profile of the H_α line and its application to plasma characterization

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Abstract

The increasing application of plasma based technologies over a wide range of fields has led to the necessity of an optimal determination of the characteristic parameters of the plasma systems. Optical Emission Spectroscopy techniques have been proved as an excellent tool to that end. These techniques are based on the collection and analysis of the radiation coming from the plasma, being classified between molecular and atomic emission. Among atomic emission lines, Hydrogen Balmer series lines are the most measured. The H_β line is usually the most employed one for plasma diagnosis but under some conditions, the H_β line is not always detectable and only the H_α line can be detected. For these lines, it is well known that their shapes are the result of the convolution of three profile types: Lorentzians, Gaussians and Starks. But while the first two types present analytical functions, models explaining the Stark profile do not offer these. So, in this paper we propose an accurate analytical function for the Stark profile of the H_α line allowing improving the determination of characteristic parameters of plasma with respect to the methods traditionally used.

Keyword: Plasma, Spectroscopy, Simulated Profiles, Stark Effect

1. Introduction

In recent years, plasmas have gained a lot of interest among researchers [1-6], so the development of new techniques for characterizing them has become an important topic.

Every plasma source emits light in a given range of wavelengths, establishing a classification between molecular and atomic emission and its collection gives rise to the technique named Optical Emission Spectroscopy (OES). The atomic emission is associated to the atomic components of plasmas; however, hydrogen atoms are presented in most laboratory plasmas since they are formed from the dissociation of water impurities in the carrier gas. This fact is the reason why hydrogen atomic lines are so useful for spectroscopic diagnosis.

The line shape of these Hydrogen Balmer lines is characterized by its width (full width at half maximum, FWHM) and intensity (area under this atomic line), which are related to the internal processes taking place in the discharge. These internal processes contribute to the total width of a spectral line in an independent manner [7, 8]. The most relevant processes to be taken into account are: the dipole moment induced by neutral atom perturbers in the instantaneous oscillating electric field of the excited emitter atom (van der Waals broadening), which generates the shape described by a Lorentzian function [9], the movement of emitter atoms (Doppler broadening) [10] and the error induced by the device used for the plasma radiation registration (Instrumental broadening), which both generate a Gaussian function [11], and finally the collisions of the emitter hydrogen atom with the charged particles in its surroundings (Stark broadening) [12-15], which cannot be assumed by a Lorentzian function in general [16-19]. The use of one Lorentzian is only valid when ion collision broadening is negligible, or for temperatures high enough that the impact approximation is valid not only for electrons but also for ions. The error introduced by non-Lorentzian ion broadening has been studied by Konjević *et al.* [19].

There are several models and theories which describe the Stark broadening taking into account ion dynamics and other effects producing asymmetry in the line profile and departure from the Lorentzian shape [12-15]. Among them, one of the most used model explaining the Stark broadening of hydrogen is the Computer Simulation model (CS model), developed by Gigosos *et al.* [15], based on the inclusion of the non-equilibrium conditions existing in two-temperature plasmas (plasma with electron temperature, T_e, higher than the gas temperature, T_g). One important advantage of this model is that it provides data files of theoretical profiles simulated for different values of μ_r, T_e and n_e. However, this model does not offer an analytical function which can be employed to generate a Stark profile.

An analytical function for the Stark profile is interesting because such function can be convoluted with the other analytical functions in order to obtain the theoretical profile which can be compared with the experimental one. This allows us to determine the characteristic parameters of the plasma [20-23] (being the electron density (n_e) one of the most relevant), together with the Gaussian and the Lorentzian widths (ω_G and ω_L respectively).

Among Hydrogen Balmer lines, the H_β line is usually the most employed one for plasma diagnosis because its Stark contribution is practically independent of the electron temperature and the ion dynamics effect [24]. In previous work [25], an accurate and analytical function has been proposed as an approximation to the CS profile in order to convolute this function with the ones corresponding to other different phenomena in plasmas. Under some conditions, the H_β line is not always detectable; especially in plasmas generated at atmospheric pressure where the entrance of air from the surroundings is significant, which causes the quenching of atomic hydrogen levels, being this effect more significant for the less intense H_β line [26]. Under those circumstances only the H_α line can be detected.

In this work, we extend for the H_α line, the analytical fit proposed in [25] for the H_β one. The structure of the article is as follows: in Section 2 we explain previous models employed to describe Stark profiles; in Section 3 we present a simple analytical expression tailored to reproduce the profiles for the case of the H_α line. The coefficients are obtained by means of statistical procedures; in Section 4 this functional form is applied to the characterization of two real plasmas in order to validate with experimental values; and, finally, the last section is devoted to present the conclusions obtained in this work.

2. Theory

As mentioned above, different theories and models exist for explaining the Stark profile, being the most relevant the CS model [15]. This model is the starting point of our previous analysis for the H_β line.

This CS model considers a weakly coupled, globally neutral, homogeneous and isotropic plasma, where the particles (ions and free electrons) are independent classical particles that move along rectilinear paths with constant velocity. Velocities are given by the Maxwell-Boltzmann distribution. In addition, this model takes into account the non-equilibrium conditions existing in two-temperature plasmas ($T_e > T_g$). This is controlled by means of the parameter $\mu_r = \mu\, T_e/T_g$, which is a fictitious reduced mass used in order to adjust the perturbing ion mobility to that of the emitter (μ is the reduced mass of the pair emitter-ion). As a result, this model provides Stark theoretical profiles simulated with different values of μ_r, T_e and n_e [15].

In order to find an analytical expression which fits these simulated profiles from the CS model, we consider the same situation that the one considered in our previous work [25]. The electric fields, influencing the emitter, are slowly varying in comparison with the time of the atom emission; in this case, the electric fields produce a splitting of the energy levels of the emitter and they give rise to "a typical Stark" [27] profile which can be described as a superposition of Stark components, each with homogeneous broadening (Lorentzian curves). Consequently the profile can be considered as a superposition of individually shifted spectral lines similarly to Doppler broadening, which is the result of superposition of Doppler shifted lines. Under this assumption, a sum of an odd number of Lorentzian profiles has been used for fitting the Stark profile for the H_α line given by the CS model. Namely, the Stark profile (P_S) may be decomposed in a centered Lorentzian profile (P_L), with amplitude (A_C) and width (ω_{LC}) and a sum of pair of symmetrical Lorentzian profiles (P_L) with amplitude (A_i), width (ω_{Li}) and central wavelength (λ_{oi}).

$$P_S \backsim P_L^C(A_C, \omega_{LC}) + \sum_{i=1}^{N}[P_L(A_i, \lambda_{oi}, \omega_{Li}) + P_L(A_i, -\lambda_{oi}, \omega_{Li})] \quad (1)$$

Where,

$$P_L^C(A_C, \omega_{LC}) = \frac{2A_C}{\pi}\frac{\omega_{LC}}{4(\lambda)^2 + \omega_{LC}^2} \quad (2)$$

and

$$P_L(A_i, \pm\lambda_{oi}, \omega_{Li}) = \frac{2A_i}{\pi}\frac{\omega_{Li}}{4(\lambda \mp \lambda_{oi})^2 + \omega_{Li}^2} \quad (3)$$

Equation 1 shows the proposed analytical Stark profile expression, while equations 2 and 3 present generic Lorentzian profiles. As can be seen, each Lorentzian function depends on the amplitude (A_C, A_i), central wavelength (λ_{oi}) and width (ω_{LC}, ω_{Li}). Once the fitting of the profiles is carried out, it is possible to obtain these parameters in terms of electron density, electron temperature and fictitious reduced mass.

In equation 1 the first term is the central Lorentzian profile, while the rest of Lorentzians are added in symmetrical pairs; as the number of pairs increase, a higher precision is expected to be achieved but with a correspondent increment of computational cost. Unlike in the case of H_β lines, the Stark profiles associated to the H_α lines must be obtained as a sum of an odd number of Lorentzian profiles. This is the consequence of the fact that the central part of these Stark profiles has a pointed shape and it is not depressed as in the H_β lines. Figure 1 shows a comparison between the theoretical Stark profiles in the H_α and H_β cases, and these two different functional forms are clearly seen.

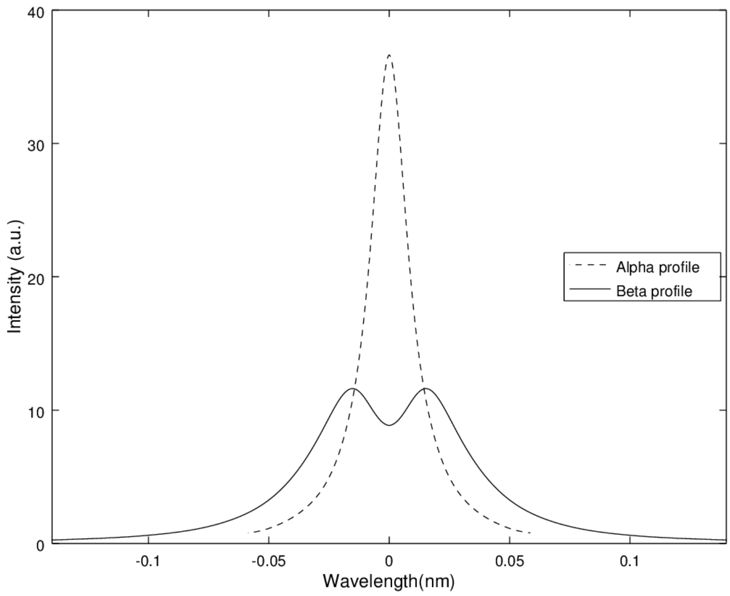

Figure 1. Stark profiles of H_α and H_β lines from CS model for T_e = 7751 K, $n_e = 2.14\cdot10^{14}$ cm^{-3} and $\mu_r = 4.0$

3. The proposed analytical fit

Seven CS model Stark profiles for the H_α line will be used as *theoretical* cases in our comparative process. Ranging from a temperature of 6000 K to 8000 K, an electron density from 1×10^{14} to 1×10^{16} cm^{-3} and a reduced mass of 4.0. Table 1 present the exact parameters of these profiles. These conditions are the same as those used in our previous study of the H_β line [25].

	1	**2**	**3**	**4**	**5**	**6**	**7**
n_e (cm^{-3})	1.00×10^{14}	2.14×10^{14}	4.67×10^{14}	1.00×10^{15}	2.14×10^{15}	4.67×10^{15}	1.00×10^{16}
T_e (K)	6001	7751	6952	6597	6523	6657	6964

Table 1. Plasma conditions of theoretical Stark profiles obtained by means of the CS model for the H_α line.

The fitting process for equation 1 was performed in the cases of one, three, five and seven Lorentzian functions. The Levenberg-Marquardt algorithm for non-linear functions was employed to carry out the fitting. Root Mean Square (RMS) and Pearson coefficient (*r*) were used to establish the goodness of the fittings.

Figures 2 and 3 present the averaged RMS and *r* for the seven theoretical profiles as a function of the number of Lorentzian profiles used in the fitting process.

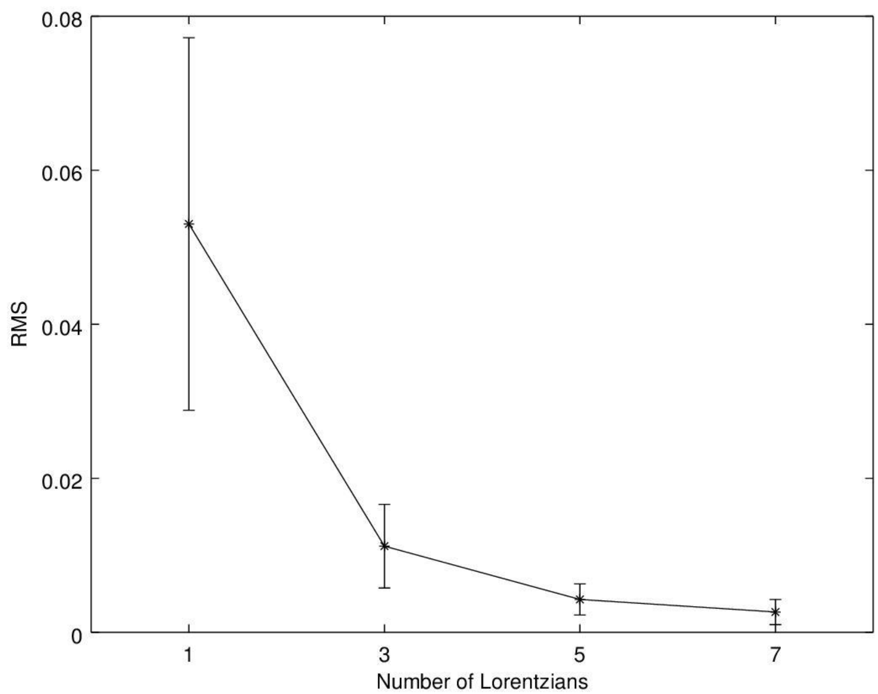

Figure 2. Averaged RMS of the seven theoretical cases for the Stark profile approximation as sum of 1, 3, 5 and 7 Lorentzian profiles. The lines are for guiding the eye.

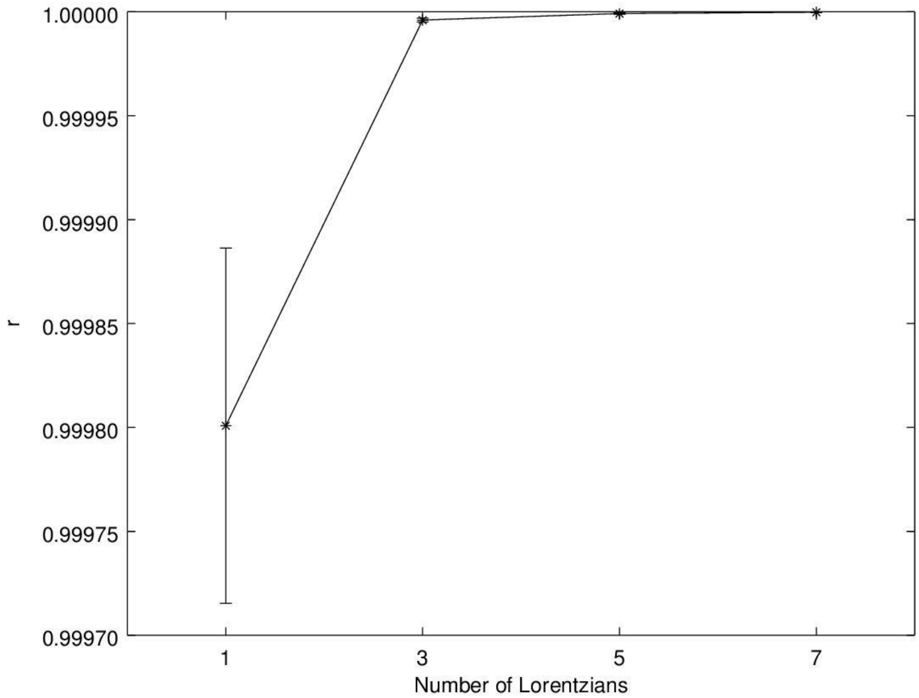

Figure 3. Averaged Pearson coefficient of the seven theoretical cases for the Stark profile approximation as sum of 1, 3, 5 and 7 Lorentzian profiles. The lines are for guiding the eye. (The errors are smaller than symbols for 3, 5 and 7 Lorentzian profiles)

As can be seen in both figures, there is a difference between the case of only one Lorentzian approximation and the rest of the cases, especially in the RMS parameter (Figure 2). Also, the quality of the fitting is poorer for the one Lorentzian case (more error). It can be observed in the averaged Pearson coefficient (Figure 3). Since the increment in computational cost associated to the using more functions is considerable and the precision gained is small, the three Lorentzians approximation is adopted here.

$$P_S(A_C, A_1, \pm\lambda_{o1}, \omega_{LC},\ \omega_{L1}) \backsim \frac{2A_C}{\pi}\frac{\omega_{LC}}{4(\lambda)^2+\omega_{LC}^2} + \frac{2A_1}{\pi}\frac{\omega_{L1}}{4(\lambda-\lambda_{o1})^2+\omega_{L1}^2} + \frac{2A_1}{\pi}\frac{\omega_{L1}}{4(\lambda+\lambda_{o1})^2+\omega L_1^2} \tag{4}$$

Figure 4 shows the comparison between a theoretical CS profile (corresponding to the profile 4 of Table 1) with the correspondent analytical fit obtained from equation (4).

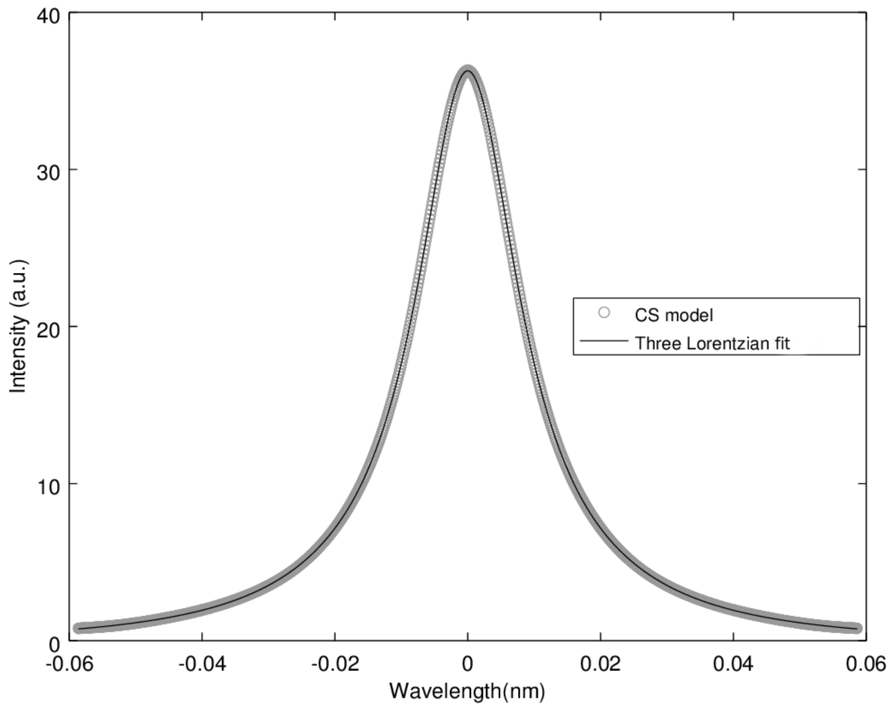

Figure 4. CS model profile compared with our analytical function, sum of three Loretzian profiles from equation (4)

As a second step in our procedure, a relationship between the optimal parameters of the Lorentzian functions (ω_{LC}, ω_{L1}, A_C, A_1 and λ_{o1}) and the physical magnitudes of the plasma (μ_r, T_e and n_e) is found. As can be seen in Table 1, the range of electron temperature is relatively small, so its influence can be assumed to be negligible and the value of the fictitious reduced mass has been fixed to 4.0 in this study. In this sense, the fitting of the ω_{LC}, ω_{L1}, and λ_{o1} in nanometres and A_C, A_1 in arbitrary units has been represented as a function only of the electron density in cm^{-3}. As results, exponential and logarithmic relations have been determined between them.

$$\omega_{LC} = (2.7 \pm 0.9) \cdot 10^{-10} \times (n_e)^{(0.549 \pm 0.009)} \quad (5)$$

$$\omega_{L1} = (1.1 \pm 0.3) \cdot 10^{-12} \times (n_e)^{(0.73 \pm 0.04)} \quad (6)$$

$$A_C = (19.37 \pm 0.15) \cdot (n_e)^{(-0.089 \pm 0.002)} \quad (7)$$

$$A_1 = (0.127 \pm 0.003) \cdot \log(n_e) - (1.77 \pm 0.17) \quad (8)$$

$$\lambda_{o1} = (4.8 \pm 0.8) \cdot 10^{-10} \times (n_e)^{(0.52 \pm 0.05)} \quad (9)$$

To that end, linear regressions were performed and Pearson coefficients above 0.98 were obtained. Therefore, our final expression for the Stark profile results a function with a dependence on electron density, P_S (n_e). It must be recalled that the validity of this approximation is restricted to the mentioned interval of temperatures going from 6000 to 8000 K.

4. Results: Experimental verification and discussion

As a final test for the proposed function, the parameters of two experimental profiles were characterized by means of our analytical function. Two profiles for H_α line from an argon plasma column at atmospheric pressure (z equal to 4 and 12 cm) were measured at the same experimental conditions as the ones measured for the H_β line in the previous work [25, 28]. The radiation emitted by the plasma was picked up across the column by a vertical optical fiber and guided to the entrance slit of the spectrometer. For these conditions an instrumental broadening of (0.021 ± 0.001) nm. On the other hand, because the gas temperature was equal, the electron temperature for the plasma column was equal to ≈ 1450 K and 6000-7000 K respectively, the parameter μ_r used for calculating the Stark profiles from the CS model is approximately 4.0 ($\mu_{\text{Ar-H}}$ = 0.975 a.m.u). And the value of the electron density is of the order of 10^{14} cm^{-3}.

The characterization of the two experimental profiles, H_α would consist on the search for the width of the Lorentzian profile due to Van der Waals and Gaussian profile due to Doppler and Instrumental broadening as well as the electron density for the Stark profile. Once we have the three theoretical profiles, we convolute them to obtain the theoretical profile and compare it with the measured data to test the reliability accuracy of our analytical function. The minimum RMS has been the criteria to choose the optimal fitting profile, being approximately in both cases to 0.11. Figures 5 and 6 show the results in both cases.

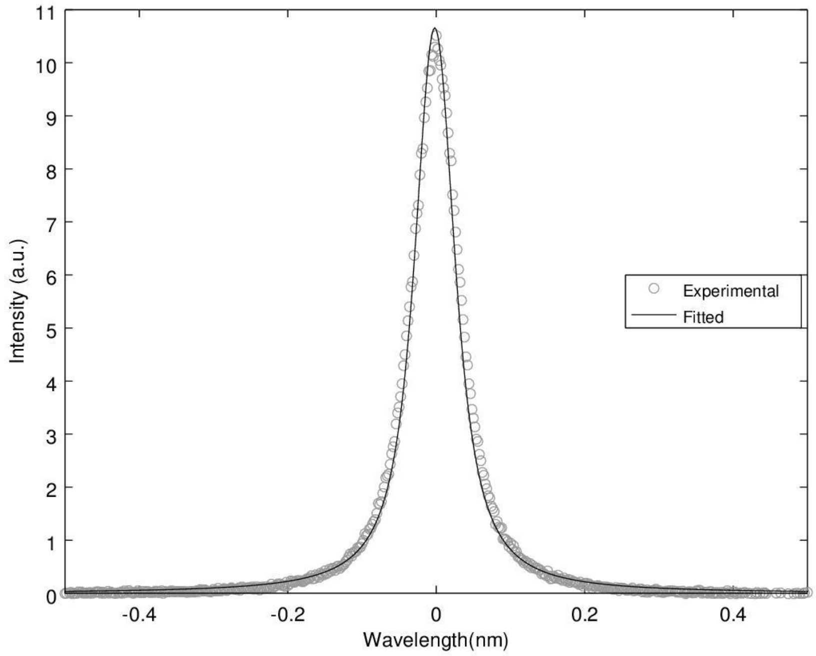

Figure 5. H_α experimental and theoretical profile for a column of plasma of z = 4 cm. The experimental profile has been centered to simplify the calculations.

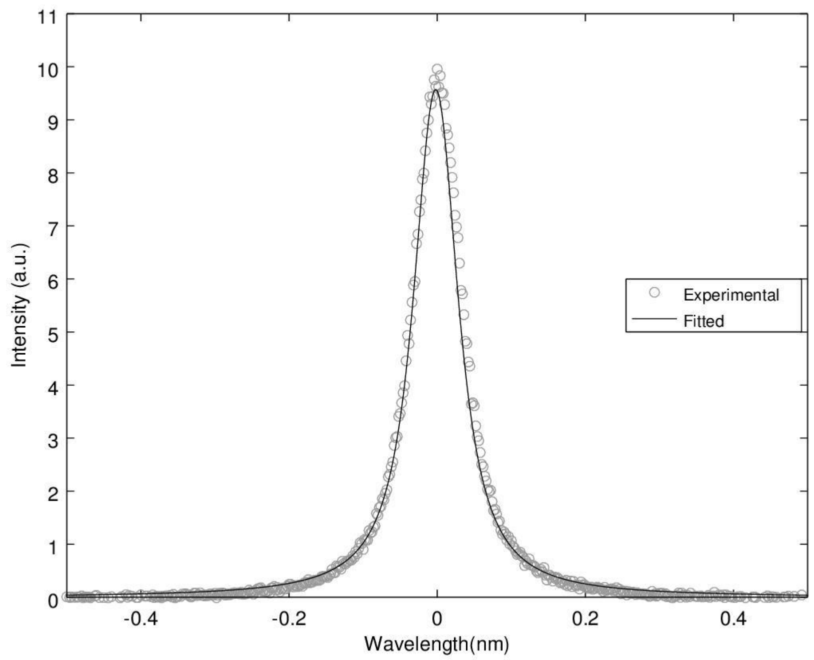

Figure 6. H_α experimental and theoretical profile for a column of plasma of z = 12 cm. The experimental profile has been centered to simplify the calculations.

As can be seen, the experimental data and the theoretical analytical profile obtained from our function show a very good agreement. In Table 2 we compare the theoretical ones obtained from the analysis of the H_β line [25] and those at this work.

***z* = 4 cm**	**ω_L (nm)**	**ω_G (nm)**	**n_e ($\cdot 10^{14} cm^{-3}$)**
Experimental [28]	0.035 ± 0.004	0.025 ± 0.001	1.42 ± 0.18
Theoretical H_β [25]	0.039 ± 0.006	0.029 ± 0.004	2.0 ± 0.9
Theoretical H_α (this work)	0.035 ± 0.007	0.025 ± 0.001	2.1 ± 0.6
***z* = 12 cm**	**ω_L (nm)**	**ω_G (nm)**	**n_e ($\cdot 10^{14} cm^{-3}$)**
Experimental [28]	0.035 ± 0.004	0.025 ± 0.001	3.7 ± 0.3
Theoretical H_β [25]	0.040 ± 0.005	0.030 ± 0.004	3.5 ± 1.1
Theoretical H_α (this work)	0.033 ± 0.009	0.025 ± 0.011	4 ± 1

Table 2. Experimental [28] and theoretical values for the z = 4 cm and z = 12 cm cases in the same experimental conditions for an argon plasma at atmospheric pressure for the H_β line [25] and theoretical for the H_α line (this work)

The results here obtained are in good agreement with the experimental values of reference [28] and with those obtained by using the H_β line [25], so we can conclude that the proposed analytical function offers an accurate representation of a Stark profile, in the condition studied, for a H_α line. And this function also allows us to identify the characteristic parameters (ω_G, ω_L and n_e) of real plasmas with high precision.

In some plasma, not only the knowledge of the electron density is essential (due to be related to its capacity to induce reactions in technological applications) but also the Lorentzian and Gaussian widths giving useful information about plasma. The so called van der Waals broadening is related to the plasma gas temperature, T_g and it is an important part of the Lorentzian contribution. On the other hand, the Instrumental broadening, introduced by the experimental device, is a part of the Gaussian contribution.

5. Conclusions

An analytical expression for the H_α Stark profile in the Hydrogen Balmer series lines has been proposed. This expression is based on the approximation of the Stark profile as a sum of Lorentzian ones; the symmetry of the original Stark profiles is taken into account by considering an odd number of Lorentzians functions.

In this sense, a set of seven reference Stark profiles (simulated from the CS model) were chosen to act as theoretical cases, and nonlinear fitting processes were performed in order to determine the analytical representation by considering linear combinations of one, three, five and seven Lorentzians respectively. A RMS and Pearson coefficient comparison between the results showed that a sum of the three Lorentzian profiles provides an optimal compromise between quality and computational cost, so the other cases were discarded to continue the study.

Starting from the regression parameters obtained (amplitudes, widths and central wavelength), another fitting process was carried out to find a relation between them and the electron density, the usually desirable magnitude. Exponential and logarithmical dependencies were found, and from them a final analytical function for the Stark profile is obtained.

As a final test, our analytical profile has been applied to determine the characteristic parameters of two real laboratory plasmas. In both cases the agreement between the published experimental parameters and the obtained theoretical results was good, which confirms the accuracy and applicability of this function.

The proposed sum of three Lorentzian profiles can offer an improvement in the quality of the analysis without a significant increment in the computational cost of the simulations. Also by using the functional form of this work, the characteristic parameters (ω_G, ω_L and n_e) of the plasma.

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References

[1] Philip N, Saoudi B, Crevier M, Moisan M, Barbeau J, Pelletier J. The respective roles of UV photons and oxygen atoms in plasma sterilization at reduced gas pressure: the case of N_2–O_2 mixtures. IEEE Trans. Plasma Sci. 2002; 30: 1429–36.

[2] Moisan M, Barbeau J, Crevier MC, Pelletier J, Philip N, Saoudi B. Plasma sterilization. Methods and mechanisms. Pure Appl. Chem. 2003; 74: 349–58.

[3] Moisan M, Barbeau J, Pelletier J. Plasma sterilization - methods and mechanisms, Le vide, Sci. Tech. Appl. 2001; 299: 15–28.

[4] Feugeas J, Gomez B, Craievich A. Ion nitriding of stainless steels. Real time surface characterization by synchrotron X-ray diffraction. Surface & Coatings Technology. 2002; 154 (2-3): 167-75.

[5] Kabouzi Y, Moisan M, Rostaing JC, Trassy C, Guérin C, Kéoroak D, Zakrzewski Z. Abatement of perfluorinated compounds using microwave plasmas at atmospheric pressure. J. Appl. Phys. 2003; 93: 9483–96.

[6] Rostaing JC, Bryselbout F, Moisan M, Parent JC. An efficient method for purifying noble gases using high frequency electric field discharges. C.R. Acad. Sci. Paris Sér. IV Phys. Astrophys. 2000; 1 (1): 99–105.

[7] Zaghloul MR. On the calculation of the Voigt line profile: a single proper integral with a damped sine integrand. Mon. Not. R. Astron. Soc. 2007; 375 (3): 1043-1048.

[8] Griem HR, Spectral Line Broadening by Plasmas, Academia Press, New York; 1974.

[9] Findeisen M, Grycuk T, Brielski A and Szudy J. On the role of Maxwellian averaging in the interpretation of pressure broadening and shift of spectral line. J. Phys. B: At. Mol. Phys. 1978; 20: 5997-6003.

[10] Lee RW, Oks E. Breakdown of the line-space concept in Stark broadening of spectral lines by plasmas. Phys. Rev. E 1998; 58: 2441-2445.

[11] Yubero C, Calzada MD, and Garcia MC. Using the Stark Broadening of the H_α, H_β and H_γ Lines for the Measurement of Electron Density and Temperature in a Plasma at Atmospheric Pressure. J. Phys. Soc. Jpn. 2004; 74: 2249 – 54.

[12] Kepple P and Griem HR. Improved Stark Profile Calculations for the Hydrogen Lines Hα, H_β, Hγ, and H_δ. Phys. Rev. 1968; 173: 317-325.

[13] Vidal CR, Cooper J and Smith EW. Hydrogen Stark-broadening of the argon-1. Astrophys. J Suppl.1973; 25: 37-136.

[14] Gigosos MA and Cardeñoso V. New plasma diagnosis tables of hydrogen Stark broadening including ion dynamics. J. Phys. B: At. Mol. Opt. Phys. 1996; 29**:** 4795-828.

[15] Gigosos MA, González MA and Cardeñoso V. Computer simulated Balmer-alpha, -beta and –gamma Stark line profiles for non-equilibrium plasmas diagnostics. Spectrochim. Acta Part B 2003; 58: 1489-1504.

[16] Yubero C, Dimitrijević MS, García MC and Calzada MD. Using the van der Waals broadening of the spectral atomic lines to measure the gas temperature of an argon microwave plasma at atmospheric pressure. Spectrochim. Acta B. 2007; 62: 169-176.

[17] Lee RW, Oks E. Breakdown of the line-space concept in Stark broadening of spectral lines by plasmas. Phys. Rev. E 1998; 58: 2441-2445.

[18] Olchawa WJ. Computer simulations of hydrogen spectral line shapes in dense plasmas. J. Quant. Spectrosc. Radiat. Transfer 2002; 74: 417-429.

[19] Konjević N, Ivković M, Sakan N. Hydrogen Balmer lines for low electron number density plasma diagnostics. Spectrochimic. Acta Part B 2012; 76: 16-26.

[20] Ranson P and Chapelle J. Etude spectroscopique d'un jet de plasma d'argon hors d'equilibre thermodynamique local. J. Quant. Spectrosc. Radiat. Transfer. 1973; 14: 1-18.

[21] Thomsen C and Helbig V. Determination of the electron-density from the Stark-broadening of balmer beta-comparison between experiment and theory. Spectrochim. Acta Part B. 1991; 46: 1215- 25.

[22] Acon BW, Sthelé C, Zhang H and Montaser A. Stark-broadened hydrogen line profiles predicted by the model microfield method for calculating electron number densities. Spectrochim. Acta Part B 2001; 56: 527-39.

[23] Žikić R, Gigosos MA, Ivković M, González MA and Konjević N. A Program for the Evaluation of Electron Number Density from Experimental Hydrogen Balmer Beta Line Profiles. Spectrochim. Acta Part B 2002; 57: 987-98.

[24] Yubero C, Calzada MD, and García MC. Using the Stark Broadening of the H_α, H_β and H_γ Lines for the Measurement of Electron Density and Temperature in a Plasma at Atmospheric Pressure, J. Phys. Soc. Jpn 2004; 74: 2249 – 2254.

[25] Díaz-Soriano A, Alcaraz-Pelegrina JM, Sarsa A. Dimitrijevic MS, Yubero C. A simple and accurate analytical model of the Stark profile and its application to plasma characterization. J. Quant. Spectrosc. Radiat. Transfer.2018; 207: 89-94.

[26] García MC, Yubero C, Calzada MD and Martinez-Jimenez MP. Spectroscopic characterization of two different microwave (2.45 GHz) induced argon plasmas at atmospheric pressure. Appl. Spectrosc. 2005; 59: 519-528.

[27] Gigosos MA. Stark broadening models for plasma diagnostics. J.Phys. D: Appl. Phys. 2014; 47 343001 (33pp)

[28] Yubero C, García MC, Dimitrijevic MS, Sola A, Gamero A. Measuring the electron density in non-thermal plasmas from the difference of Lorentzian widths of two Balmer series hydrogen lines. Spectrochim. Acta. Part B 2015; 107: 164-169.