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Review

A simple and accurate analytical model of the Stark profile and its application to plasma characterization

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ABSTRACT

Optical Emission Spectroscopy techniques are among the most employed to perform the characterization of laboratory plasmas. The analysis of the obtained data is based on the convolution of three different types of profiles: Lorentzians, Gaussians and Starks. While analytic expressions are available for the first two types, the Stark profile has been traditionally obtained through theoretical calculations using different models. In this paper, we propose is a simple and accurate analytical function that can be employed as approximation of a Stark profile. The application of this new model may simplify the analysis of plasmas.

1. Introduction

During past decades, plasmas have found application in a wide range of fields such as gas detoxification, materials processing, catalysis, elemental analysis, treatment of liquids (water), sterilization... [1–6]. This increasing interest in plasmas has led to the need of a good understanding of its internal mechanisms and governing parameters, since the optimization for its different applications depends on it. The knowledge of the electron density is crucial because it plays an important role in the ability of plasmas to induce reactions.

Optical Emission Spectroscopy (OES) is a passive spectroscopy technique widely used in the study of plasma parameters, being a non-perturbing method that does not alter the internal kinetics of the discharges during the measurement process [7–10]. This technique is based on the collection of the radiation coming from the plasma and its subsequent molecular and atomic emission spectra. Experimental atomic spectral lines have a distribution of intensity around their central wavelength (line profile). The profile shape and its characteristic parameters such as its width (full width at half maximum, FWHM) and intensity (area under this profile) are of great importance since they depend on the internal processes taking place in the discharge. More specifically, these processes contribute to the total width of a spectral line in an independent manner [11,12]. Among them, Hydrogen Balmer series lines (and more concretely the H_β line) are usually used for determining the electron density in laboratory plasma since the electron density is related to their width [7].

The most relevant processes to be taken into account are the collisions of the emitter hydrogen atom with the charged particles in its surroundings (Stark broadening) [13–16], 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 line shape described by a Lorentzian function [17], the movement of emitter atoms (Doppler broadening) [18] and the error induced by the device used for the plasma radiation registration (Instrumental broadening) which both generate a Gaussian function [7]. All these effects produce a deformation in the measured spectral profiles from the plasma, which allow us to determine the values of its characteristic parameters: electron density, electron temperature and gas temperature [12].

There are two different kinds of methods to analyze this Hydrogen Balmer series lines. First, the methods assuming a Lorentzian function for the Stark profile like as, commonly used for commercial software which discriminates, by means a Levenberg–Marquardt non-linear fitting algorithm for minimum squares, the Lorentzian and Gaussian contributions of the profile shape. The main advantage of these techniques lies in their readiness and quickness of calculus. However, the assumption of Lorentzian shape for Stark profile is valid only when broadening by the collisions with ions is negligible or for temperatures high enough that the impact approximation is valid not only for electrons but also for ions. If ions are quasistatic, their contribution results in asymmetry of line shape [10]. Also ion dynamics effects modify lineshapes which is the consequence of the kinetics of the emitter and perturber [16]. Additionally, if at high densities the no-

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quenching approximation is violated, the coupling of levels with different principal quantum numbers contributes to the asymmetry of spectral line [18,19]. The error introduced by non-Lorentzian ion broadening has been studied by Konjević et al. [20] and this error is most significant in an electron density range below the "low n_e limit", when the separation between Fine Structure Components becomes larger than the Stark broadened line width. As an example, this occurs in argon plasmas generated at pressures higher than 100 Torr, where the electron density is of the order of 10^{14} cm^{-3}.

The second method is based on the models and theories which describe Stark broadening taking into account ion dynamics and other effects producing asymmetry of the line profile and departure from the Lorentzian shape [13–16]. This method consists of comparison between the experimental profile shape and the profile calculated through the convolution of different functions corresponding to the different phenomena provoking its broadening. In this sense, there are several works using this method for the H_β line: Ranson and Chapelle [21] and Thomsen and Helbig [22] applied it to a plasma with electron densities around 10^{15} cm^{-3}, Acon et al. [23] applied this method to calculate the electron density values in an Ar Inductively Coupled Plasma (ICP) (10^{15} cm^{-3}), a He ICP (10^{13} cm^{-3}), a glow discharge (10^{13} cm^{-3}) and a High Voltage (HV) spark ($>10^{15}$ cm^{-3}) and Žikić et al. in [24] used plasmas with electron density within the range between 10^{15} and 10^{17} cm^{-3}. Among them, the most used model explaining the Stark broadening of hydrogen is the one developed by Gigosos et al. (CS model) [16] 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). However, this model does not offer an analytical function which can be employed to generate a Stark profile.

In this paper we propose an approximate method for the Stark profile which approximates the CS profile when it is convoluted with the profiles due to other broadening mechanisms. If there are no more sophisticated calculations, or a quick check during experiment is needed, this method may be useful. So, the structure of the paper is as follows: in Section 2, we explain the previous models used to describe Stark profiles and our new model is proposed together with the corresponding coefficients deduced by means of statistical procedures; in Section 3, this new model is applied to the characterization of two real plasmas in order to validate it; and finally are presented the conclusions obtained in this work.

2. Theory

2.1. Modeling the Stark profile

As mentioned in the introduction, experimental profiles (P_{exp}) obtained from plasma measurements may be described as the combination of various individual profiles that take into account the impact of each process acting into the system. All these contributions can be basically reduced to the convolution of a Lorentzian (van der Waals broadening), a Gaussian (Instrumental and Doppler broadenings) and a Stark profile (Stark broadening) [16]:

$$P_{exp}(\omega_L, \omega_G, \omega_S) = P_L(\omega_L) \otimes P_G(\omega_G) \otimes P_S(\omega_S) \tag{1}$$

where ω_L and ω_G are the width of the Lorentzian and Gaussian profiles respectively, providing information about the gas temperature [17], while ω_S is the Stark width that contains information about the electron density and temperature [13–16].

While there are analytical expressions for the Lorentzian and Gaussian profiles, there is not such formula for the Stark one if effects like the influence of ion dynamics, quasistatic ions or breakdown of no-quenching approximation have a non negligible influence on the lineshape. The best efforts directed in the past to that end have led us to some more or less sophisticated models that can approximate the Stark profile with high accuracy, but at an expensive computational cost.

In this work we use as starting point the CS model [16], which consider 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 order to take into account the emitter kinetics, a relative movement between emitter-ion pairs introducing the reduced mass of the pair, μ (corresponding to plasmas in thermodynamic equilibrium) is used in the previous model (μ-ion model [15]) and later, Gigosos et al. [16], by means of the Computer Simulation CS model, reinterpreted the μ-ion model in order to include 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. This model provides Stark theoretical profile simulated with different values of μ_r, T_e and n_e [16].

In order to find an analytical expression which fits these simulated profiles from the CS model, we took into account that when electric fields, influencing the emitter, is varying slowly in comparison with the time of the atom emission, they produce "a typical Stark shift of the spectral line" [25]. 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. So, a sum of the symmetrical Lorentzian profiles has been employed for fitting the Stark profile given by the CS model. Each pair of symmetrical Lorentzian profiles has amplitude (A_i), width (ω_{Li}) and central wavelength (λ_{oi}).

$$P_s \sim \sum_{i=1}^{N} [P_L(A_i, \lambda_{oi}, \omega_{Li}) + P_L(A_i, -\lambda_{oi}, \omega_{Li})] \tag{2}$$

where,

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

The minus sign in the second Lorentzian in Eq. (2) is due to the symmetrical character of the paired profiles from the central wavelength of the original Stark profile. As the number of couples increases, a higher precision is expected to be achieved but with the corresponding increment of computational cost.

2.2. New proposed model

The starting point of our work is the CS model. This model has proven its validity in many studies, so we have chosen seven Stark profiles given by this model to be used as *theoretical* cases in our comparative process. As can be seen in Table 1, we have selected these profiles over an interval of temperatures going from 6000 to 8000 K, and a range of densities from 1×10^{14} to 1×10^{16} cm^{-3}, and a reduced mass of 4.

The next step was to apply this fitting to approximate these Stark profiles as a sum of Lorentzian ones. In order to find the optimal number of pairs, we carried out a fitting process of every theoretical case as sum of 2, 4, 6 and 8 Lorentzians respectively. The Levenberg–Marquardt nonlinear regression has been used, calculating the Root Mean Square (RMS) and Pearson coefficient r to establish the goodness of the fittings.

Figs. 1 and 2 show the obtained average values of RMS and Pearson coefficient for the different sums of Lorentzians; the lower the RMS and the nearer to 1 the Pearson coefficient, the better approximation would be. As could be seen, there is a qualitative leap between the two Lorentzian approximations and the rest of