Spectrochimica Acta Part B 88 (2013) 98–103

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

On the determination of plasma electron number density from Stark broadened hydrogen Balmer series lines in Laser-Induced Breakdown Spectroscopy experiments

L. Pardini [a,*], S. Legnaioli [a], G. Lorenzetti [a], V. Palleschi [a], R. Gaudiuso [b], A. De Giacomo [b], D.M. Diaz Pace [c], F. Anabitarte Garcia [d], G. de Holanda Cavalcanti [e], C. Parigger [f]

[a] *Istituto di Chimica dei Composti Organometallici del CNR, Area della Ricerca del CNR di Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy*
[b] *Dipartimento di Chimica, Università di Bari, Via Orabona 4, 70126 Bari, Italy*
[c] *Instituto de Física 'Arroyo Seco', Facultad de Ciencias Exactas, Paraje Arroyo Seco, B7000GHG Tandil, Argentina*
[d] *Photonic Engineering Group, Universidad de Cantabria, Edificio I+D+iTelecomunicación, Dpto. TEISA, 39005 Santander, Spain*
[e] *Institute of Physics, Universidade Federal Fluminense, UFF, Campus da Praia Vermelha, Av. Gal Milton Tavares de Souza, Gragoatá, 24310 240 Niterói, RJ, Brazil*
[f] *University of Tennessee Space Institute, 411 B. H. Goethert Parkway, Tullahoma, TN 37388-9700, USA*

ARTICLE INFO

Article history:
Received 5 November 2012
Accepted 23 May 2013
Available online 10 June 2013

Keywords:
LIBS
Plasma
Hydrogen
Balmer series
Electron density

ABSTRACT

In this work, different theories for the determination of the electron density in Laser-Induced Breakdown Spectroscopy (LIBS) utilizing the emission lines belonging to the hydrogen Balmer series have been investigated. The plasmas were generated by a Nd:Yag laser (1064 nm) pulsed irradiation of pure hydrogen gas at a pressure of $2 \cdot 10^4$ Pa. H_α, H_β, H_γ, H_δ, and H_ε Balmer lines were recorded at different delay times after the laser pulse. The plasma electron density was evaluated through the measurement of the Stark broadenings and the experimental results were compared with the predictions of three theories (the Standard Theory as developed by Kepple and Griem, the Advanced Generalized Theory by Oks et al., and the method discussed by Gigosos et al.) that are commonly employed for plasma diagnostics and that describe LIBS plasmas at different levels of approximations. A simple formula for pure hydrogen plasma in thermal equilibrium was also proposed to infer plasma electron density using the H_α line. The results obtained showed that at high hydrogen concentration, the H_α line is affected by considerable self-absorption. In this case, it is preferable to use the H_β line for a reliable calculation of the electron density.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) has received recent interest in both basic and applied research, mainly due to its inherent advantages of rapid multi-elemental measurements in solid, liquid, and gaseous samples requiring a minimum preparation [1]. LIBS is based on the spectral analysis of the radiation emitted by a laser-induced plasma (LIP), which can be characterized through determination of its physical parameters, such as temperature, electron density, and atom and ion densities. The most widely used methods for determining the plasma parameters are based on measurement of temperature using the Saha–Boltzmann plot, together with determination of electron density from measurement of Stark broadened spectral lines, utilizing available results for corresponding Stark broadening parameters [2]. Diagnostics of LIPs is of paramount importance in order to get valuable insight about plasma dynamics, with results beneficial for improvement of the LIBS technique in view of analytical applications as well as determination of spectroscopic parameters such as Stark broadening coefficients and transition probabilities [3–15].

Several studies have been devoted to investigate post-breakdown plasma radiation, aimed at matching predictions of theory with experiments [13]. The theory is largely based on the assumption of existence of Local Thermal Equilibrium (LTE) in the measurement time interval (together with the stoichiometry of the ablation process) [1]. A criterion proposed by McWhirter [16], based on the existence of a critical electron density for which the collisions with electrons dominate over the radiative processes, is commonly reported in the literature as a necessary requirement. Thus, a reliable determination of the electron density is critical for evaluation of necessary conditions for establishment of LTE [17].

An illustrative example is the Calibration-Free (CF) LIBS procedure, developed by Ciucci et al. [18,19]. It allows to carry out quantitative analysis without the necessity of constructing calibration curves, provided that lines from all the elements of interest are measured. In the CF-LIBS algorithm, a Saha–Boltzmann plot is employed to evaluate the plasma temperature. The electron density is independently evaluated by measuring the Stark broadening of a suitable line and using coefficients tabulated by Griem [2]. In the case of plasmas generated from

---

* Corresponding author.
E-mail address: loren.pard@gmail.com (L. Pardini).

0584-8547/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.sab.2013.05.030

solid samples in air, the presence of the hydrogen Balmer α line is utilized in the CF-LIBS method. The usefulness of hydrogen Balmer lines for an accurate measurement of electron densities in LIBS plasmas was also demonstrated by El Sherbini et al. [20].

The Stark broadening, in typical LIBS conditions, is the main broadening mechanism of spectral lines [21]. In addition, at a given electron density of the plasma, Stark broadening of hydrogen lines is larger than the one found in atomic lines from other elements [22]. This feature makes the use of hydrogen lines particularly interesting in LIBS experiments with low spectral resolution. Instrumental broadening introduced by the spectrometer might be comparable, or even larger, than the broadening of the emission lines of elements different from hydrogen. Moreover, the Stark broadening of the emission lines is independent from the fulfillment of the LTE conditions, thus making the electron density measurement from Stark broadened lines a very interesting and powerful tool. In recent years, the use of hydrogen Balmer lines has been employed for measurement of temperature and electron density in plasmas generated in gases including several theoretical approximations [23–30].

The aim of the present work is the experimental investigation of different existing theories relevant to LIBS, i.e.: the Standard Theory (ST) as developed by Kepple and Griem [31], the Advanced Generalized Theory (AGT) by Oks et al. [32], and the method discussed by Gigosos et al. (GT) [33], for determination of electron density using lines from the hydrogen Balmer series. To achieve this goal, we studied the temporal evolution of the electron density of plasmas generated in pure hydrogen gas. The experimental results obtained were subsequently compared with the predictions.

2. Theory

2.1. Broadening of spectral lines

The starting point of the three ST, AGT, and GT approaches mentioned in the above section is the normalized line shape indicating the quantum mechanical expression of the energy per unit time of the total system of emitter and perturbers, i.e., the power induced by the dipole operator x_α between an initial higher level i to a final lower level f,

$$L(\omega)=\sum_{\alpha i f}\delta\left(\omega-\omega_{if}^{s}\right)|<f\,|\,x_\alpha\,|\,i>|^2\rho_i \tag{1}$$

where ρ_i is the probability to find the total system of the perturber and the radiator in the initial state, $\delta(\omega-\omega_{if}^{s})$ is the Dirac Delta distribution, and $L(\omega)$ is the line shape.

In order to find the expression for the line shape, many approximations are needed. This is because the plasma is a very complex system, whose dynamics cannot be exactly described in terms of analytically derived expressions. The usual approach, that is common to all the above-mentioned methods, is to consider only one radiator at a time and to neglect the radiator–radiator interaction. Then, the most demanding task is to model the effect of the surrounding environment, composed of electrons and ions, on the emitting particle. Usually, this effect is separated into two contributions in different frequency regions, since electrons and heavy ions, having different masses, show completely different dynamics. In particular, electrons have a higher mobility, thus resulting in an interaction time with the emitter that is just a fraction of the emitting process; therefore, their influence is treated in the impact approximation [2]. Conversely, ions are treated in the quasi-static approximation [2], since their velocity is low and the effect of the generated electric field is much longer than the duration of the emitting process. This results in Stark-broadening of the lines, i.e., for a given perturber distribution, corrections to ω_{if}^{s} due to the ion microfield are calculated within time-independent perturbation theory.

Additionally, the no-quenching approximation is used. It means that the effects of the perturbers will not mix the emitter quantum states with different principal quantum numbers. As a consequence, no quadratic or higher order Stark effect can be described by these models, thus limiting their applicability to not-too-high electron densities (i.e., lower than 10^{20} cm^{-3}). Taking into account the above-mentioned approximations, one finds the following formula that is commonly used in ST as well as in AGT:

$$L(\omega)=\frac{1}{\pi}Re\left[Tr\int_0^\infty d\mathrm{F}\mathrm{W}(\mathrm{F})\mathrm{D}\left[i(\omega-\omega(\mathrm{F}))+\Phi(\mathrm{F})\right]^{-1}\right] \tag{2}$$

where F is the ion field, D the dipole–dipole operator, Φ(F) the impact operator and W(F) the ion micro-field distribution function.

The differences between ST and AGT approaches arise after this step: AGT treats one of the components of the electric field **E** generated by electrons in a non-perturbative way (in particular the component which lies along the electric field generated by ions), whereas in ST all the components of **E** are treated perturbatively. However, both theories can describe certain experiments in a satisfactory way, although the contribution of the ion dynamics is not taken into account in both of them.

The method proposed by Gigosos (GT), in turn, takes into account the ion dynamics, so this theory should be, at least in principle, more accurate. In this approach, plasma is considered to be weakly-coupled, globally neutral, homogeneous and isotropic and the perturbing particles are treated as classical particles moving along straight trajectories with constant velocity. The interaction between particles is neglected and it is accounted for ad hoc by adopting a Debye screened potential.

2.2. Spectral line emission from a homogeneous plasma in LTE

The integrated wavelength-dependent spectral intensity of a self-absorbed line $\overline{I_{SA}}$ emitted from a pure hydrogen homogeneous plasma in LTE along the line-of-sight is given by [34]:

$$\overline{I_{SA}}=\overline{I_0}\left(\frac{1-e^{-\tau(\lambda_0)}}{\tau(\lambda_0)}\right)^{0.46}=(SA)^{0.46} \tag{3}$$

where $\tau(\lambda_0)=\tau_0$ (dimensionless) is the wavelength-dependent optical thickness [8]. Optically thin plasma condition is therefore achieved for $\tau(\lambda)$ approaching zero. In Eq. 3, the ratio between H_α and H_β line intensities can be thus written as:

$$\frac{\overline{I_\alpha}}{\overline{I_\beta}}\Big/\frac{\overline{I_{\alpha_0}}}{\overline{I_{\beta_0}}}=(SA)^{0.46}. \tag{4}$$

By comparing the experimental values of the $\frac{\overline{I_\alpha}}{\overline{I_\beta}}$ ratio with the theoretical ones of $\frac{\overline{I_{\alpha_0}}}{\overline{I_{\beta_0}}}$ without self-absorption, τ_0 can be estimated. Considering the data reported in the following sections (see Fig. 6), the ratio in the left-hand side of Eq. 4 is about 0.35, from which we find the estimated value for the optical thickness $\tau_0 \cong 10$.

3. Experimental arrangement

The experimental arrangement as well as the main measured features of the temporal trend of the hydrogen-spectrum has been discussed previously [35]. The experimental arrangement consists of a Nd:YAG laser source operating at 1–20 Hz, 7 ns pulse duration at 1064 nm, a monochromator (TRIAX 550 Jobin Yvon with 150 g/mm grating) connected to an ICCD (i3000 Jobin Yvon) and a pulse generator (Stanford Inc. DG 535) that we used for controlling delay time and detector gate width. The vacuum chamber is a typical Pulsed Laser Deposition (PLD) reactor, equipped with several windows for entrance of the laser radiation, and detection of the emission