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Laser-induced plasma characterization using line profile analysis of chromium neutral atom and ion transitions

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In this paper, line profile analysis of several Cr transitions was carried out for characterization of a laser-induced plasma. The plasma was generated on a metallic alloy (nominal Cr concentration 29.7%) in air at atmospheric pressure by using an infrared Nd:YAG laser. The emission intensities of 24 Cr I lines and 25 Cr II lines were measured spatially integrated along the line-of-sight with good resolution. Their line profiles were analyzed applying a computational fitting algorithm under a framework of a homogeneous plasma in thermodynamic equilibrium. The effects of self-absorption and spatial inhomogeneity were taken into account. The plasma temperature and the parameters *Nl* (the atom/ion concentration times the length of the plasma along the line-of-sight) were accurately determined, and the electron density was estimated. The results were properly interpreted under the employed approach, demonstrating the important influence of the issues investigated on characterizing the physical state of laser-induced plasmas.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an optical technique based on the spectral measurement of the radiation emitted by a laser-induced plasma (LIP) for chemical analysis of the elemental composition of solid, liquid and gaseous targets [1–3]. The LIP can be characterized through determination of the temperature, the electron density, and the atom/ion number densities of the present species [4]. Plasma characterization is of prime importance to achieve a better insight of the physical processes involved in its dynamic behavior and, thus, improving the applications. A recent review by Hahn et al. [5] summarized the current state-of-the-art on this issue and highlighted the necessity of further research to accomplish the full LIBS potential as analytical method.

A reliable characterization of the LIP is essential to LIBS studies devoted to both basic and applied investigations. For instance, two important LIBS approaches relying on accurate plasma characterization are (i) calibration-free (CF-LIBS) methods, which are aimed at obtaining quantitative results without the need for calibration standards [6], and (ii) the use of LIPs as spectroscopic sources for measurement of atomic parameters such as Stark broadenings [7–10] and transition probabilities [11–15]. In the characterization procedure, the plasma temperature has a crucial relevance because it governs the particle–radiation interaction processes in the plasma [16]. The temperature is generally estimated as the first step and, then, subsequently employed in the calculation of the other physical parameters, i.e., electron, atom and ion densities. Therefore, if an inaccurate value of the temperature is obtained, this will cause even larger uncertainties in the subsequent calculus of other plasma parameters and, finally, in the elemental concentrations.

The most frequently used method to determine the temperature is the Boltzmann plot, which is constructed with the line intensities measured from different transitions from one ionization species, i.e., atoms or ions, with available spectroscopic data. The Boltzmann plot provides the excitation temperature from the single species assuming a spatially

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homogeneous optically thin plasma in local thermodynamic equilibrium (LTE). In order to achieve an accurate calculus of the temperature, a large number of different lines having a widespread range of upper level energies should be measured. Even higher accuracy is obtained by including in the same plot, called Saha–Boltzmann plot, lines of both atoms and ions (or any two successive ionization stages) of a given element because the level energy difference results increased by the ionization energy [4]. In this case, the ionization temperature is obtained under the same assumptions as the Boltzmann plot method. For a plasma in LTE, the excitation and ionization temperatures coincide with the electronic temperature corresponding to the Maxwell's distribution of electron velocities [17].

Most LIBS experiments are carried out recording spatially-integrated line intensities from LIPs generated in air atmosphere. This configuration is generally chosen because of its simplicity and versatility, which make feasible many applications [18]. Nevertheless, it is well-known that LIPs are very complex sources of radiation which evolve with time; hence, the description of its physical state based on the measurement of emitted radiation is not straightforward. For a given time of observation, self-absorption of spectral transitions and spatial inhomogeneity of the plume make difficult the characterization of the LIP. They affect the line emission intensities leading to inaccurate results for the plasma parameters. The problem of evaluating and compensating self-absorption of spectral lines has been widely discussed in the literature [19–25]. Models of inhomogeneous plasmas has been also reported [26–31], but these are intrinsically more elaborated and time-consuming, which may reduce their practical applicability.

In addition, from an experimental point of view, there are some issues that should be considered. First, since the plasma properties depend on the experimental parameters, self-absorption and inhomogeneity can be overcome or reduced by a proper choice of measurement conditions and/or selection of adequate emission lines, as shown for instance in Refs. [32,33]. Consequently, after adequate conditions of measurement are matched, those lines showing a plateau (which indicates strong self-absorption) or a self-reversal dip at its top (evidence of a non-uniform distribution of temperature along the direction of observation) are usually discarded. In this way, the characterization is simplified by adopting the approach of an optically thin, homogeneous plasma in LTE. However, depending on the particular experiment and the analyte, optically thin lines could be scarce or hardly detected, i.e. because of a poor signal or spectral interference. On the other hand, recording many emission lines is advisable to achieve an accurate determination of plasma temperature by means of a Boltzmann plot or a Saha–Boltzmann plot. From the reasons mentioned, the measurement of spectral lines affected by some degree of self-absorption as well as inhomogeneity is generally necessary, and almost unavoidable, for an accurate plasma characterization. In this context, it is worth to further investigate how self-absorption and spatial inhomogeneity impact on the determination of the plasma parameters, specially the plasma temperature.

The study of spectral line shapes is of great importance as a diagnostic tool of LIPs because they provide information on physical source conditions [34]. On these steps, the goal of the present work was the analysis of line profiles of several Cr transitions for characterization of a LIP generated on a metallic alloy. In this approach, several lines of Cr I and Cr II with different spectroscopic features were studied applying a simple model of a homogeneous plasma to extract information about plasma features, with special emphasis in a reliable temperature determination. The information of this study will be useful to LIBS experiments in which an accurate plasma characterization is required and also to obtain some insight about the physical processes involved, such as self-absorption and spatial distribution of species in the plume.

2. Theoretical: spectral line emission from a homogeneous plasma in LTE

In this section, the basic equations describing radiation in the case of homogeneous plasma approximation are reminded. The plasma is assumed in LTE and cylinder-symmetrical. The emission and absorption of radiation are described by an emission coefficient ε_λ ($W\,m^{-3}\,sr^{-1}\,nm^{-1}$) and an absorption coefficient $\kappa(\lambda)$ (m^{-1}), respectively. The wavelength-dependent intensity I_λ ($W\,m^{-2}\,sr^{-1}\,nm^{-1}$) of a spectral line emitted along the line-of-sight is given by the solution to the equation of radiation transfer [35]:

$$I_\lambda = CU_\lambda(T)(1-e^{-\tau_\lambda(T)}) \quad (1)$$

where C (a. u.) is a factor that unifies units and depends on the instrumental set-up, U_λ ($W\,m^{-2}\,sr^{-1}\,nm^{-1}$) is the distribution for blackbody radiation, T (K) is the plasma temperature, and τ_λ (dimensionless) is the wavelength-dependant optical thickness of the plasma. For a plasma in LTE, τ_λ can be separated into different contributing factors, similarly to Ref. [36], as

$$\tau_\lambda(T) = \kappa(\lambda)\ \ l = \kappa_e(T)\,N\,l\,P(\lambda) \quad (2)$$

where $\kappa_e(T)$ (m^3) is a coefficient that depends on the atomic parameters of the transition and that can be calculated if the plasma temperature is known. Namely,

$$\kappa_e(T) = \frac{\lambda^4}{8\pi c\,Q(T)} A_{ji}\ g_j\ e^{-E_i/kT}(1-e^{(E_i-E_j)/kT}) \quad (3)$$

where λ (m) is the line wavelength, A_{ji} (s^{-1}) is the transition probability, g_j (dimensionless) is the degeneracy of the upper energy level, and E_i, E_j (eV) are the energy of the levels. N (m^{-3}) is the density of the emitting species in the plasma, l (m) is the length of the plasma along the line-of-sight, $P(\lambda)$ (m^{-1}) is the normalized line profile, in general described by a Voigt profile, and $Q(T)$ (dimensionless) is the atomic partition function.

The optical thickness τ_λ reaches its maximum value τ_0 at the line center λ_0 and decreases toward the line wings. If self-absorption of radiation within the plasma is negligible, $\tau_0 \ll 1$ and the plasma is said to be optically thin. On the other hand, for the stronger lines (generally the resonant) the radiation emitted has a large probability of