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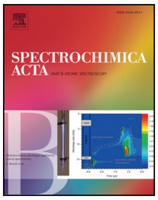

Utilizing the ratio and the summation of two spectral lines for estimation of optical depth: Focus on thick plasmas

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ABSTRACT

In this paper, a study is performed on the spectral lines of plasma radiations created from focusing of the Nd:YAG laser on Al standard alloys at atmospheric air pressure. A new theoretical method is presented to investigate the evolution of the optical depth of the plasma based on the radiative transfer equation, in LTE condition. This work relies on the Boltzmann distribution, lines broadening equations, and as well as the self-absorption relation. Then, an experimental set-up is devised to extract some of plasma parameters such as temperature from modified line ratio analysis, electron density from Stark broadening mechanism, line intensities of two spectral lines in the same order of ionization from similar species, and the plasma length from the shadowgraphy section. In this method, the summation and the ratio of two spectral lines are considered for evaluation of the temporal variations of the plasma parameters in a LIBS homogeneous plasma. The main advantage of this method is that it comprises the both of thin and thick laser induced plasmas without straight calculation of self-absorption coefficient. Moreover, the presented model can also be utilized for evaluation the transition of plasma from the thin condition to the thick one. The results illustrated that by measuring the line intensities of two spectral lines at different evolution times, the plasma cooling and the growth of the optical depth can be followed.

1. Introduction

The basic characteristics of different laboratory and cosmic plasmas are represented in term of the elements number densities n, and the plasma temperature T. The other plasma parameters such as Debye length λ_D, electron plasma frequency ω_{pe}, and so on … can be evaluated by knowing these main parameters [1]. In laser-induced plasmas (LIPs), the variations of plasma temperature and species number densities influence considerably on spectral emissions and their line broadening. Generally, the plasmas are studied in two categories of thin and thick cases according to the magnitude of optical depth which can be diagnosed by utilizing the different optical spectroscopic methods. For instance, in thin plasmas, in LTE condition, the methods of Boltzmann plot (or modified Boltzmann and Saha-Boltzmann methods), line-to-continuum intensity ratio or two lines ratio analysis can estimate the plasma temperature. Moreover, Stark broadening, Saha equations and rate equations are used for evaluation of the number densities of electrons and different species in thin LIBS plasmas. In thick plasma conditions, in LIBS technique and in equilibrium condition, several models such as curve of growth, duplicating mirror [2] and numerical models [3–7] are introduced for evaluation of plasma parameters. Furthermore, it should be mentioned that in non-equilibrium plasmas, the various reactions of ionization, recombination, excitation and detachment must be considered together for extraction of plasma parameters [8–11].

Different research groups [7,12–19] have analyzed the LIBS plasma dynamics by utilizing appropriate experimental set-up and proposing various useful models in LTE condition. For instance, Aragon and Aguilera [20–25] have introduced the curve of growth (COG) and CSigma graphs for estimation of LIBS plasma parameters. They have fitted the theoretical and experimental curves and they have extracted plasma parameters. In CSigma plots, the line cross section σ_l of each experimental data have been estimated. Then, by fitting the experimental $C\sigma$ graphs to the calculated curves, they have characterized the LIBS system by a set of four parameters of βA (the instrumental factor of the system multiplied by transverse area of the plasma), Nl (columnar density), T (plasma temperature), and N_e (electron density). Bredice et al. [26] have investigated the plasma dynamic in single and double pulse scheme by utilizing line ratios in different cases of weak, moderate and strong self-absorption. They have evaluated the temporal evolution of self-absorption coefficient and the plasma parameters by applying the analytical equations and experimental methods. It should be mentioned that some research groups have paid attention to optically thick plasma parameters with introducing new models [27–29]. For example, Gornunshkin et al. [27] have studied an optically thick inhomogeneous laser produced plasma by using a simplified theoretical approach. The input parameters of this model have been the atomic

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ratio of silicon to nitrogen and the total number densities of plasma species. Furthermore, they have proposed some functions for describing the size and temperature variations of the LIBS plasma. The model inputs have been easily measured from the experiment. The model has predicted the spatial and temporal evolutions of the atom, ion and electron number densities, and as well as the distribution of the atomic line profile, optical thickness, and the final absolute intensity of the plasma radiation close to a strong non-resonance atomic transition. In previous work of our group [30], three lines method has been proposed in a thick plasma instead of using traditional two lines ratio technique in thin plasmas for estimation of the plasma parameters. In the present work, the plasma parameters are extracted from the summation and the ratio of two spectral lines by applying new theoretical equations and devising an experimental set-up. Here, at first, electron density is extracted from a weak spectral line width and plasma temperature is obtained from the modified line ratio method. Then, species number densities and optical depth can be calculated according to proposed theoretical relations.

In principle, the illustrated approach in this paper has two major advantages: a) the diagnostic tools for discrimination between thin and thick lines are not needed for estimation of number densities and optical depth. Since, it predicts the plasma dynamic in the both thin and thick conditions. b) It is very accurate and simple against other traditional techniques described in thick LIBS plasmas.

2. Theoretical background

2.1. Basic equations

The spectral emission of the LIBS plasma can be estimated by knowing the plasma parameters (including temperature and number density of emitters), line width and transition parameters [21,22]. Here, a theoretical model for absolute spectral intensity is presented by considering the line profile due to transition between the two levels of u and l in an optically thick plasma. By assumption of holding the local thermal equilibrium (LTE) condition, the local electron temperature T in each point explains the population of the energy levels of the species in the plasma according to the Boltzmann distribution. From the population relation, the spatially integrated spectral radiation emitted by the atoms of a given species in the plasma can be estimated by the equation [30–35]:

$$I_{thick}(\upsilon)=\frac{\left(1-e^{-kl}\right)}{\left(1-e^{\frac{-(E_u-E_l)}{k_BT}}\right)}\frac{C8\pi}{\lambda_0^2}e^{-\frac{(E_u-E_l)}{k_BT}}, \tag{1}$$

where, E_u and E_l are energy of upper and lower levels, respectively. T, k_B, h, λ_0, l and c are plasma temperature (K), Boltzmann constant (J·K^{-1}), Planck's constant (J·s), central wavelength (m), plasma thickness (m) and light velocity (m·s^{-1}), respectively. In this equation, C (J·m^{-1}) is the instrumental function which accounts for the solid angle of the detection system, and as well as its efficiency (in this paper, C is considered as 1.5×10^8 from Ref. [30]). In Eq. (1), k is absorption coefficient which is very important parameter for prediction of the self-absorption magnitude of the various spectral lines, and as well as for optical depth ($\tau = kl$) calculation and can be calculated by knowing the plasma temperature and species densities in the international system of units (SI) as:

$$k(\upsilon,\upsilon_0)=\frac{g_uA_{ul}N_{Al}\lambda_0^2}{8\pi Z}e^{-\frac{E_l}{k_BT}}\left(1-e^{-\frac{(E_u-E_l)}{k_BT}}\right)L(\upsilon,\upsilon_0,\gamma_{ul}). \tag{2}$$

In above equation, g_u is degeneracy of upper level u (dimensionless), A_{ul} is transition probability (s^{-1}), υ_0 is the central frequency (s^{-1}), and N_{Al} is total density of a specific ion or neutral atom (m^{-3}). Here, Z is partition function of emitting species (dimensionless) which is obtained by two and three levels method. The details of this method are explained completely in Ref. [36].

$L(\upsilon,\upsilon_0,\gamma_{ul})$ is the Lorentzian width which is related to the pressure broadening mechanisms. In the experimental condition of this paper, the most dominant factors in pressure broadenings are attributed to the Stark effect. Since Stark broadening is mainly created due to interactions of plasma ions and electrons, while other pressure broadenings are negligible compared to this effect. Generally, Stark broadening can be determined by knowing the electron density (n_e) and Stark broadening width (w) as:

$$L(\upsilon,\upsilon_0,\gamma_{ul})=\frac{\left(\frac{\gamma_{ul}}{4\pi^2}\right)}{(\upsilon-\upsilon_0)^2+\left(\frac{\gamma_{ul}}{4\pi}\right)^2}. \tag{3}$$

γ_{ul} is the decay rate which is proportional to the line width as follows:

$$\gamma_{ul}=2\pi\left(c/\lambda_0^2\right)\Delta\lambda_{stark}. \tag{4}$$

$\Delta\lambda_{stark}$ is full width at half maximum (FWHM) of the spectral line due to Stark broadening which is calculated as below:

$$\Delta\lambda_{stark}=\frac{2wn_e}{n_{ref}}, \tag{5}$$

here, n_e and w are electron number density and electron impact parameter, respectively. n_{ref} is reference electron density (here 10^{16} cm^{-3}) at which w is calculated. In this work, the plasma is assumed to be homogeneous in thick condition.

2.2. Calculation of plasma parameters

Here, by utilizing two spectral line summations and their ratios, and as well as applying appropriate and simple calculations, the plasma parameters are derived. These calculations can be performed for all of the two spectral lines which are related to the same element in similar order of ionization. Hence, two spectral line emissions can be taken into account as the following [30]:

$$I_{thick\_1}(\upsilon)=\frac{\left(1-e^{-k_1l}\right)}{\left(1-e^{-\frac{(E_{u1}-E_{l1})}{k_BT}}\right)}\frac{C8\pi}{\lambda_{01}^2}e^{-\frac{(E_{u1}-E_{l1})}{k_BT}} \tag{6}$$

$$I_{thick\_2}(\upsilon)=\frac{\left(1-e^{-k_2l}\right)}{\left(1-e^{-\frac{(E_{u2}-E_{l2})}{k_BT}}\right)}\frac{C8\pi}{\lambda_{02}^2}e^{-\frac{(E_{u2}-E_{l2})}{k_BT}}. \tag{7}$$

In the above equations, l is the plasma length along the line-of-sight (m). If the terms of $(1-e^{-\frac{hc}{\lambda_{0i}}\frac{1}{k_BT}})$ which are attributed to the stimulated emission contribution are neglected compared to plasma absorption, the calculations will be easier. By definition of:

$$A=\left(1-e^{-k_1l}\right). \tag{8}$$

$$B=\left(1-e^{-k_2l}\right), \tag{9}$$

and by inserting the above equations in Eqs. (6) and (7), the calculations can be simplified as:

$$A=B\times\left[\frac{I_{thick\_1}}{I_{thick\_2}}\times\frac{\lambda_{01}^2}{\lambda_{02}^2}\times\frac{e^{\frac{1}{k_BT}(E_{l2}-E_{u2})}}{e^{\frac{1}{k_BT}(E_{l1}-E_{u1})}}\right]. \tag{10}$$

As mentioned in previous sections, the summation of two spectral lines for the same element in similar ionization state, can be expressed