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Temporal evolution of the spectral lines emission and temperatures in laser induced plasmas through characteristic parameters

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ABSTRACT

In this work, we propose an extended Boltzmann plot method to determine the usefulness of spectral lines for plasma parameter calculations. Based on the assumption that transient plasmas are under ideal conditions during an specific interval of time Δt, (i.e. thin, homogeneous and in local thermodynamic equilibrium (LTE)), the associated Boltzmann plots describe a surface in the space defined by the coordinates $X = Energy$, $Y = Time$ and $Z = ln\,(\lambda_{jl}I_j/g_jA_{jl})$, where I_j is the integrated intensity of the spectral line, g_j is the statistical weight of the level j, λ_{jl} is the wavelength of the considered line and A_{jl} is its transition rate. In order to express the Boltzmann plot surface in terms of a reduced set of constants B_i, and δ_i, we developed as a power series of time, the logarithm of $I_n(t)/I_n(t_0)$, where $I_n(t)$ is the integrated intensity of any spectral line at time t, and $I_n(t_0)$ at initial time. Moreover, the temporal evolution of the intensity of any spectral line and consequently the temperature of the plasma can be also expressed with these constants. The comparison of the temporal evolution of the line intensity calculated using these constants with their experimental values, can be used as a criterion for selecting useful lines in plasma analysis. Furthermore, this method can also be applied to determine self-absorption or enhancement of the spectral lines, to evaluate a possible departure of LTE, and to check or estimate the upper level energy value of any spectral line. An advantage of this method is that the value of these constants does not depend on the spectral response of the detection system, the uncertainty of the transition rates belonging to the analyzed spectral lines or any other time-independent parameters. In order to prove our method, we determined the constants B_i and δ_i and therefore the Boltzmann plot surface from the temporal evolution of carbon lines obtained from a plasma generated by a Nd:YAG laser. The plasma was produced in vacuum and was observed at different distances from the target. A good agreement between the temperature calculated by the traditional Boltzmann plot and by this method was obtained.

1. Introduction

It is well known that laser-induced plasmas (LIPs) have become a powerful tool whose applications to different fields of physics and technology are countless. For example, LIPs are useful for material characterization using the technique known as laser induced-breakdown spectroscopy (LIBS) [1–4], for materials deposition either for thin films or nanostructured materials [5–7], for laser propulsion applications [8,9] and cultural heritage applications [4,10]. Moreover, LIPs have been used to simulate lightnings and to study a double return-stroke lightning flash [11,12]. Through the spectroscopic analysis of these plasmas, it is possible to obtain their relevant parameters and improve the performance of these techniques. In addition to spectroscopic analysis, there are other optical and electrical diagnostic techniques used for the determination of the electron temperature [13–15]. Electrostatic probes have been widely used to characterize plasmas due to their experimental simplicity, however they can affect the plasma during the measurements. The main advantage of optical analyses is that they are non-invasive methods. But, in particular for LIBS an adequate selection of spectral lines is necessary for the measurements of the plasma parameters.

In LIPs, the temporal evolution of the intensity of the spectral lines and their temperature depend, among other factors, on the pulse energy, laser wavelength, the observation point of the plasma and the conditions of confinement of the target. There are several works dealing with the calculation of the electron temperature of LIPs and its evolution in time [13,16–20]. The determination of plasma temperature and electron density through spectroscopic analysis is possible assuming some conditions. For electron number density determination by Stark broadening, the plasma needs to be thin. For the calculation of plasma temperature the assumption of LTE is also necessary [21]. Therefore, it is important to know how the real sources are deviated from the ideality, i.e. thin and LTE. It is also necessary to determine the interval of time

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and the observation region in which these assumptions are valid. Then, an adequate characterization of plasmas is essential to understand the mechanisms of the processes involved in their generation, evolution and extinction. Extensive literature has been published on this subject [21–28].

If thin plasma is in LTE, its temperature can be determined by the Boltzmann plot. In transient plasmas such as LIP, the slope of the Boltzmann plot varies with time (t) depending on the experimental conditions in which the plasma was generated. The variation in time of the Boltzmann plot describes a surface in the space defined by the coordinates $X = Energy$, $Y = Time$ and $Z = \ln(\lambda_{jl} I_j / g_j A_{jl})$, where λ_{jl} is the wavelength of the considered line, I_j is the integrated intensity of the spectral line, g_j is the statistical weight of the level j, and A_{jl} is the transition rate of the considered line. Hereafter we will refer to this surface as “Boltzmann surface”.

The aim of this work is to represent the Boltzmann surface through a reduced number of constants B_i, and δ_i. Consequently, the temporal evolution of the intensity of any spectral line and the temperature of the plasma can be also expressed with these constants. If we know the Boltzmann surface, we can determine the temporal evolution of any spectral line belonging to the ion under study. Also, it is possible to verify if any line presents self-absorption or enhancement and if its upper level energy value was correctly assigned. This procedure is applicable to any transient plasma that satisfies the abovementioned conditions, i.e. thin plasma and LTE.

2. Theoretical analysis

In order to determine the constants B_i, and δ_i, we assume that the plasma is in condition of LTE and thinness, then the integrated intensity of an emitting spectral line from the state j to a lower state l is given by [27]

$$I_j = \frac{hcg_j A_{jl} N}{\lambda_{jl}} \frac{\exp\left(-{}^{E_j}/_{kT}\right)}{U(T)},$$

where h is the Planck constant, c is the speed of light, λ_{jl} is the central wavelength of the transition, A_{jl} is the transition rate from level j to level l, E_j and g_j are the energy and the statistical weight of level j, N is the total density number of emitting atoms, $U(T)$ is the atomic species partition function at temperature T and k is the Boltzmann constant.

Furthermore, the temporal evolution of the intensity of this kind of spectral lines can be described as:

$$I_n(t-t_0) = \frac{C_n \exp\left(-{}^{E_n}/_{kT(t-t_0)}\right)}{U(T(t-t_0))}, \tag{1}$$

where $C_n = \frac{hcg_n A_{nk} N}{\lambda_{nk}}$,and t_0 is the time from which we can consider that the plasma satisfies the LTE condition. Without loss of generality we can take $t_0 = 0$, then

$$I_n(t) = \frac{C_n \exp\left(-{}^{E_n}/_{kT(t)}\right)}{U(T(t))}.$$

For any spectral line, the logarithm of the ratio between its intensity at time t and its intensity at $t = 0$ is given by:

$$\ln\left(\frac{I_n(t)}{I_n(0)}\right) = E_n\left(\frac{1}{kT(0)} - \frac{1}{kT(t)}\right) + \ln\left(\frac{U(0)}{U(t)}\right). \tag{2}$$

Developing both terms of the right side as a power series of time, we obtained:

$$\frac{1}{kT(0)} - \frac{1}{kT(t)} = \sum_{i=1}^{s} B_i t^i \tag{3}$$

and

$$\ln\left(\frac{U(0)}{U(t)}\right) = \sum_{i=1}^{s} \delta_i t^i. \tag{4}$$

Therefore

$$\ln\left(\frac{I_n(t)}{I_n(0)}\right) = \sum_{i=1}^{s} (B_i E_n + \delta_i) t^i. \tag{5}$$

On the other hand, the Eq. (5) can be fitted as

$$\ln\left(\frac{I_n(t)}{I_n(0)}\right) = \sum_{i=1}^{s} b_i^n t^i. \tag{6}$$

The degree s of the polynomial arises from the best fit of the curve. Then, from Eq. (5) and from Eq. (6) it follows that

$$b_i^n = B_i E_n + \delta_i.$$

Thus, for two generic lines “u” and “v”, the constants B_i are given by

$$B_i = \frac{b_i^u - b_i^v}{E_u - E_v}. \tag{7}$$

If the coefficients b_i^u are plotted as a function of $E_u - E_v$ according to Eq. (7) (See Fig. (3)), they must be aligned in a straight line which has a slope B_i, and δ_i is the value corresponding to $E_v = 0$.

From (5), the time dependence of the intensity of any spectral line can be expressed as:

$$I_n(t) = I_n(0) \exp\left(\sum_{i=1}^{s} (B_i E_n + \delta_i) \cdot t^i\right). \tag{8}$$

where B_i and δ_i represent the characteristic constants of the plasma. The calculation of the constants B_i arises from a fit of the coefficients b_i vs. energy, besides, the b_i values result from the fit of the $ln\ (I_n(t)/I_n(t_0))$. This means that the value of each constant B_i results from all spectral lines used in the analysis. From the knowledge of these constants it is possible to obtain all the information about the temporal evolution of any other line if its upper energy level is known. It must be noted that the values of the coefficients b_i and therefore B_i constants are deduced from a quotient of the intensities (Eq. (6)), and thus they do not depend of any time-independent factor, namely the spectral response of the detector and the uncertainty of the transition rate of the considered line. In contrast, if the intensity of a spectral line is affected in time either by self-absorption or enhancement, its coefficients b_i will depart from the straight line of the plot b_i vs. energy. Moreover, according to Saha–Boltzmann equation, the population of ionic and neutral species varies in time, but this fact does not affect the value of coefficients b_i or constants B_i because they are obtained from the ratio of spectral line intensities belonging to the same species.

3. Experimental procedure—B_i calculation

In order to verify our method, we analyzed the evolution of the spectral lines of carbon LIP generated by a Nd:YAG laser. The carbon plasma was produced in a vacuum chamber at a fixed pressure of 10^{-5} Torr using laser pulses of 1064 nm with 10 ns of duration. The laser beam