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A novel approach to elemental analysis by Laser Induced Breakdown Spectroscopy based on direct correlation between the electron impact excitation cross section and the optical emission intensity

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ABSTRACT

In Laser Induced Plasma Spectroscopy (LIPS) or Laser Induced Breakdown Spectroscopy (LIBS) the relation between recombining electrons and optical emission intensity has been studied in hydrogen and different metals targets. The role played by the electron impact excitation cross section on the temporal trend of emission lines has addressed and a methodology for the evaluation of the excitation cross sections by optical emission spectroscopy has been tested on several species including H I, Fe I, Ni I, Co I and Ti II. In connection with the theory drawn in this paper, the results show a good agreement with respect to theoretical ones. These results allow the direct linking of the emission intensity to the electronic excitation binary collision. The latter does not depend on experimental conditions and can be applied for elemental analysis. The use of estimated cross sections forms the basis for a different calibration free approach. LIBS elemental analysis on iron meteorites (to be considered as ternary alloys) and on a set of copper based alloys demonstrates the promising use of this analytical approach.

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1. Introduction

Laser Induced Plasma Spectroscopy (LIPS) or Laser Induced Breakdown Spectroscopy (LIBS) refers the optical emission of plasma generated by laser-matter interaction, when laser pulses with irradiance around 1 GW cm^{-2} are employed [1]. Emission Spectroscopy is indeed one of the most powerful diagnostic techniques for the investigation of high density ideal plasmas ($N>10^{17}$ cm^{-3}), which is the case of Laser Induced Plasma (LIP) and it allows determining the excitation temperature by using the Boltzmann plot technique [2], the composition [3] and electron number density by Stark broadening [4]. The main assumption for studying plasma parameters is Local Thermal Equilibrium (LTE) [5]. Different criteria can be adopted to justify this assumption in the plasma [6]: when this condition is established, it implies that all the elementary processes involving material particles (electron and heavy particles, i.e. atoms and ions) are balanced while radiative processes, such as spontaneous emission, are not in equilibrium with their backward reactions [7]. On the other hand, in LTE, this deviation in the plasma energy balance is so minor that it does not affect the collisional processes so that all the material particles are characterized by equilibrium distributions in all their degrees of freedom.

In the last decades a strong effort has been directed toward a better clarification of the LTE validity and the development of suitable analytical methods for the investigation of LIP and for the use of LIBS as analytical tool [8–10]. In spite of fast LIBS instrumental development and the increasing interest in studying LIP for various applications in material science, most experimental methodologies have been built in the direction of statistical thermodynamics and macroscopic physical quantities. This paper discusses a novel approach to the interpretation of emission intensity in the plasma based on the use of electron impact excitation cross sections and of the number of electrons subtracted to the plasma by recombination. In this context, the emission is treated as a non-equilibrium phenomenon, as indeed it is, and is interpreted as the decay route of those excitation collisional processes not counterbalanced by superelastic collision. This slight unbalance between the excitation/de-excitation collisional processes is ascribed to the fact that the recombining electrons are characterized by low kinetic energy and so they are mainly involved in the electron impact de-excitation. In this hypothesis the cross section value of excitation electron impact can be estimated by the temporal evolution of LIBS spectra.

The idea of connecting the emission intensity temporal trend and the cross section acquires a fundamental relevance when we realize that the former quantity is strongly dependent on experimental conditions, while the cross section depends only on the species involved in the electron impact excitation binary collision. The prospective of establishing the dependence of emission intensity features in LIP on

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an absolute quantity, such as the excitation cross section, suggests the possibility of adopting a universal database for fast diagnostics of this kind of plasmas as well as the development of a different approach to calibration-free methodology, as discussed in the last section of the present paper. Last but not least, the estimation of cross sections, as a general topic, is a crucial issue in plasma fundamental research, and the possibility of having at one's disposal an easy tool for its evaluation should indeed be useful to the plasma scientific community.

With the aim of exploring these issues, several previously published experimental data are revisited in this paper and analyzed again with a different approach. In this context, it is essential to stress that, since the laser induced plasma is also strongly inhomogeneous in space, we assume that the different optical systems utilized do not influence the resolved emission data.

2. Experimental set-up

The experimental set-up is a typical LIBS system [8], consisting of Nd:YAG laser sources operating at 10 Hz, 7 ns nominal pulse duration at 1064, 532, 355 nm, a mono-chromator (TRIAX 550 Jobin Yvon with 1800 gr/mm grating) connected to an (ICCD i3000 Jobin Yvon) and a pulse generator (Stanford inc. DG 535) for selecting the delay time and the gate width of the detector. The plasma emission light is imaged by a 7.5 cm focal length biconvex lens directly on the monochromator slit or on the aperture of a fused silica optical fiber. For most of the experiments investigated here, the experimental details have been previously published and the reader is referred to the pertinent references [11–14]. Nevertheless the main experimental features, such as the laser wavelength and fluence, are reported in the present text in order to facilitate its readability.

3. Theoretical considerations

In plasmas with high electron number density ($Ne>10^{16}\ cm^{-3}$), electrons are expected to thermalize via elastic collisions, with an instantaneous establishment of a Maxwell-like electron energy distribution function (eedf). Nevertheless, this condition is not sufficient to underpin the equilibrium assumption in the plasma. To clarify this point, the effect of the recombination character of the plasma on the eedf can be considered in two opposite cases. The first applies when strong deviations from equilibrium occur because the characteristic times associated with the elastic electron impacts and ion-electron recombination are comparable. In this case, a departure of eedf from the Maxwell distribution is observed for low energy electrons, which in turn results in a considerable overpopulation of high excited levels of heavy particles involved in the recombination processes [9,15] with consequent enhancement of emission intensity from these levels. This scenario generally belongs to weakly ionized, low-density plasmas. In the second case, if the recombination processes proceed slower than elastic electron impacts, the eedf is still Maxwell-like. This means that, whereas slow electrons are lost because of ion-electron recombination, the excess of energy delivered to the heavy particles, involved in the recombination process, is distributed among all the energy levels. This second scenario is that occurring in plasmas with high electron number density in near LTE condition, and it is the one discussed in this paper.

In general, the temporal evolution of the population, N_u, in the upper level u of a species in the plasma is given by:

$$\frac{dN_u}{dt} = N_e N_l k_{lu} - N_e N_u k_{ul} - A_{ul} N_u \tag{1}$$

where N_e is the electron number density, N_l is the population of the species in the lower level l, k_{lu}, k_{ul} and A_{ul} are the rate coefficients of electron impact excitation, de-excitation and spontaneous emission coefficient respectively.

In the Eq. (1) the contribution of the subsequent excitations as well as of the corresponding de-excitation processes linked to the level u have been neglected because the plasma is close to LTE so that those processes are mostly balanced [9]. Note that the effect of metastable levels has been neglected too because of the high density of colliding electrons in the plasma. Here it is assumed that level u can only be populated via collisional process. e.g., the absorption of the continuum emitted by the plasma as well as the contribution to the population of high-excited levels due to the recombination processes, requiring additional terms in Eq. (1), are considered unimportant [9]. This approximation is justified because the contribution of both continuum absorption and recombination to the level population is important only in the early stage of the plasma expansion [16].

In quasi-stationary condition $\frac{dN_u}{dt} = 0$ and so the population N_u is given by the following ratio:

$$N_u = \frac{N_e N_l k_{lu}}{N_e k_{ul} + A_{ul}} \tag{2}$$

Eq. (2) clearly shows that for high electron number density values the collisional term in the denominator prevails over the spontaneous emission coefficient leading to the well-known Mc Whirter criterion for the estimation of LTE condition [6,10].

Eq. (2) can be rearranged as follows:

$$A_{ul} N_u = N_e N_l k_{lu} - N_e N_u k_{ul} \tag{3}$$

Eq. (3) suggests that when the electron impact forward and backward processes are completely balanced, their reaction rates are equal and the emission decay is negligible. More precisely, if excitation/de-excitation rate by electron impact are equal, the only way of depopulation of level *u* is by spontaneous emission which also means that $\frac{dN_u}{dt} \neq 0$, since the radiative processes are not balanced. However, the quasi-stationary-condition still holds since the radiative rates are much less than collisional rates and therefore the emission decay of level *u* is negligible.

Based on Eqs. (2) and (3) it can be stated that the emission contribution strongly depends on the electron number density, N_e, and lower or negligible contribution may be expected for high N_e values.

In the LIP temporal evolution of emission lines, an exponential decay of the intensity is observed because of the decrease of the emitters number density and, to a lesser extent, of the excitation temperature during the expansion [11]. On the other hand, the temporal trend of electron number density is similar to that of the emission lines, with a fast decrease at the beginning of the temporal evolution, as a result of recombination and expansion [5,6,11]. As an example, Fig. 1 reports the temporal evolution of the second Balmer line at 486 nm and the corresponding electron number density (calculated by the same spectral line broadening) in a 150 Torr hydrogen LIP. While the effect of the expansion is the same for all the particles in the plasma (electrons and heavy particles), recombination processes involve only slow electrons [9,17,18]. In Fig. 2 it is shown the cross section energy function of three-body [17] and radiative recombination [18] in the case of hydrogen. By the inspection of Fig. 2 it can be noted that these processes are due almost entirely to electrons with energy below 5000 cm^{-1} (0.62 eV) and, in the energy range 0–5000 cm^{-1}, the cross sections decrease more than two orders of magnitude. That means that these recombining electrons do not affect markedly the excitation processes as their energy is below the energy threshold of the excitation transitions involving the most populated levels in any atomic system. On the contrary slow electrons are extremely important for what concerns super-elastic (quenching) collisions. It is reasonable to suppose that the exit of slow electrons from the system as a consequence of recombination processes, prevents electron impact de-excitation to completely balance the excitation processes induced by the fast electrons. To clarify this concept a qualitative scheme is reported in Fig. 3.

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