COMPARATIVE STUDY OF LASER INDUCED PLASMA IN ARGON USING OPTICAL EMISSION SPECTROSCOPY AND THOMSON SCATTERING

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ABSTRACT

We investigate the laser generated plasma in argon using Thomson scattering (TS) and optical emission spectroscopy (OES) techniques. The experiment is performed with two nanosecond Nd:YAG lasers. One generates the plasma while the second one probes the formed spark. The main objective of this work is to validate results of plasma diagnostics carried out with these two methods. Moreover, the existence of local thermodynamic equilibrium is studied by comparing the rates of the collisional to radiative processes (the McWhirter criterion), as well as relaxation times and diffusion lengths of argon neutrals and ions. Our results show satisfactory agreement between electron densities obtained with these two methods while we find very big discrepancy between electron temperature determined from the TS spectra and the excitation temperature from OES data.

1. *INTRODUCTION*

Laser induced plasma (LIP) which was first reported in 1963 by Maker *et al*., has achieved a great interest as a source of spectroscopic data. LIP has also many applications like X-ray sources for lithography, plasma igniters, pulsed laser deposition or it has become very popular analytical technique. The latter is mainly due to its applicability to different kinds of samples, no sample preparation or in-situ and remote sensing capability. However, despite many theoretical and experimental works and significant advances in instrumentation over the last decade, the performance of the LIBS method is not considerably better. The sensitivity still remains modest (at most few ppm), the quantitative results are subject to large uncertainties and the matrix strongly affects the signal. The quantitative elemental analysis by LIBS requires a thorough knowledge of atom, ion and electron number densities and their temperatures. These parameters are commonly deduced in indirect way from the optical emission spectra assuming plasma in local thermodynamic equilibrium (LTE).

The electron number density N_e^{OES} is usually determined from the Stark width of some reference emission lines while electron temperature T_{ex}^{OES} is obtained from emission data applying either Boltzmann or Saha-Boltzmann equations. The use of Stark widths is difficult because of the limited number of lines with Stark data of satisfactory accuracy with respect to both their N_e and T_e dependencies. Also the use of Boltzmann and Saha-Boltzmann equations is only possible if plasma is at least in the partial local thermodynamic equilibrium. Moreover, the intensity recorded using OES is laterally integrated and Abel inversion must be performed to get the local values of emission coefficients. Therefore, TS was applied in order to validate OES measurements. This method presents the advantage over OES yielding the local plasma parameters (N_e^{TS}, T_e^{TS}) without any assumption on the LTE.

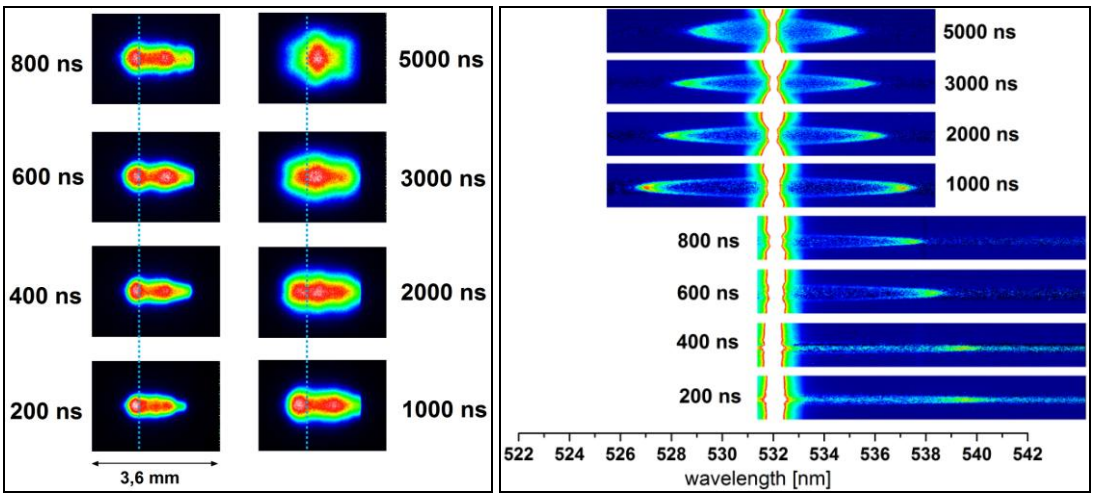

Fig. 1 Plasma imaging at the left and TS spectra at the right. Dash blue line corresponds to the position of the probe beam

2. EXPERIMENTAL SET UP

The experiment was carried out in a vacuum chamber, purged and filled with argon and equipped with six optical view ports. Two frequency-doubled Q-switched Nd:YAG lasers operating at 10 Hz repetition rates were used to generate the plasma and to probe the plasma plume in TS experiments. The durations of laser pulses were 4.5 ns and 6 ns, respectively. The laser beams were arranged orthogonally and were focused using anti-reflection coated plano-convex lenses with focal lengths of 100 mm for generating laser and 500 mm for the probe one. The emission and the TS spectra were recorded using a gated two dimensional intensified charge-coupled device (ICCD) camera mounted on a spectrometer.

3. RESULTS AND DISCUSSIONS

3.1. Evolution of electron density and temperature with OES and TS

Images of plasma and TS spectra as registered by the ICCD camera are shown in figure 1. For the emission, only spectral ranges with lines of interest are recorded. T_e^{TS} and N_e^{TS} are obtained by fitting Salpeter function [1] to the experimental spectra. Parameters are highly precise and independent of the equilibrium hypothesis.

On the other hand, T_{ex}^{OES} and N_{ex}^{OES} are determined from OES measurements. In this case experimental spectra are compared to the spectral radiance of plasma in LTE. The plasma parameters, e.g. N_{ex}^{OES} and T_{ex}^{OES}, are deduced from the best agreement between measured and computed spectra, using iterative procedure as presented in [2]. Calculations take into account the self-absorption of emission lines by dividing the plasma in two zones. That is the hot and dense core and cooler boundary responsible for self-absorption of spectral lines emitted from the core. The temporal evolution of temperature and electron density on the plasma axis and in the focal plane of the breakdown pulse is presented in figures 2 and 3.

N_{ex}^{OES} Decreases from 1, 1×10^{18} cm^{-3} at 200 ns to 4.2×10^{16} cm^{-3} at 5 µs after the breakdown pulse. At the same time T_{ex}^{OES} drops from 22300 K to 6700 K, N_e^{TS} decreases from 5.4×10^{17} cm^{-3} at 200 ns to 6×10^{16} cm^{-3} at 5 µs, while T_e^{TS} drops from 68500 K to 16200 K. The decays of temperatures and densities with time were fitted with power laws. We found N_e^{TS} and T_e^{TS} to fall off respectively as $t^{-0.91}$ and $t^{-0.52}$, whereas N_{ex}^{OES} and T_{ex}^{OES} evolve respectively as $t^{-0.95}$ and $t^{-0,38}$. As shown in figure 2 the concordance between N_{ex}^{OES} and N_e^{TS} seems to be reasonably good and differences remain in the uncertainty limits. Concerning temperatures (figure 3), T_e^{TS} is much higher than T_{ex}^{OES} at each time. The discrepancy is sometimes bigger than a factor of 2. Parameters from TS are comparable to the results of Mendys et al [3]. In fact, the temperature varies from 50700 K to 16000 K and electron density from 4.3 to 0.7×10^{17} cm^{-3}, respectively 400 ns and 5 µs.

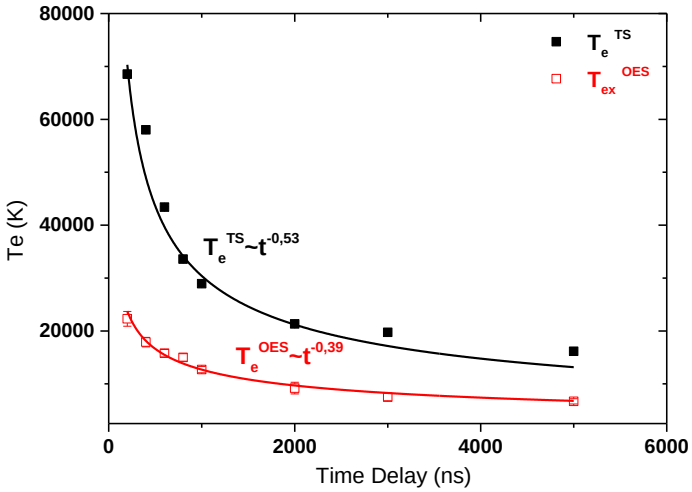

Fig. 2 Evolution of temperature in time

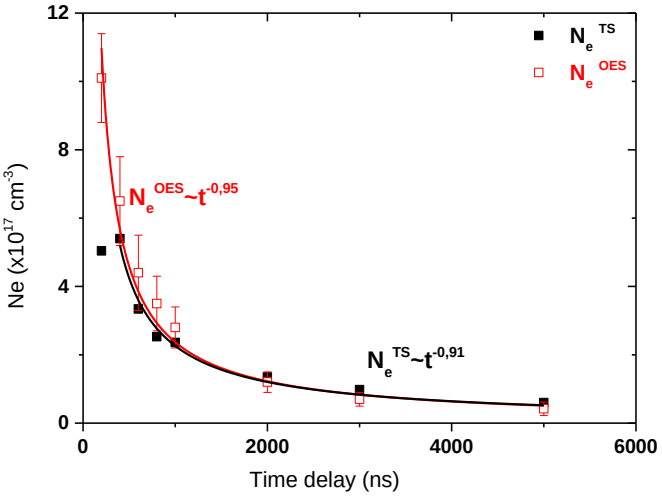

Fig. 3 Evolution of electron number density in time

As mentioned previously in this paper T_e^{TS} varies from 68000 K to 16100 K and N_e^{TS} from 5.4 to 0.6×10^{17} cm^{-3}. In order to have complete characterization of the plasma state the spatial evolution of its parameters was also determined. We emphasize a quasi-uniform spatial profile for temperatures while electron densities reveal much stronger gradients.

3.2. *Discussions on T_e^{TS} and T_{ex}^{OES} discrepancy*

As shown by figure 3 a big discrepancy between T_e^{TS} and T_{ex}^{OES} is observed. A possible explanation is the non presence of LTE in the plasma. As it can be seen later in the paper, criteria for LTE are not fulfilled most of time. This implies that T_{ex}^{OES} cannot be determined precisely. Furthermore, the using of powerful laser as a probe to generate the TS spectra can induce a heating of the plasma. So T_e^{TS} can be overestimated. Dzierzega *et al.* [4] quantified this heating on an argon thermal discharge.

3.3. *Criteria for the validity of LTE using TS parameters*

A system is called to be in LTE when it can be locally described by Saha-Boltzmann and Maxwell equations. According to the spatial and temporal characteristics of investigated plasma, the criteria for assessing LTE are different. Plasmas can be dived into three types: stationary and homogeneous, transient and homogeneous and finally transient and inhomogeneous [5].

In the case of stationary and homogeneous plasma the excitation and de-excitation rates between energy levels have to be dominated by inelastic electron collisions. This requires a minimal electron number density which is well known as the Mc Whirter criterion:

$$Ne > \frac{2.55\times10^{11}}{<g>} T_e(\Delta E_{nm})^3 \ [cm^{-3}] \quad (1)$$

Where g is the gaunt factor and T_e and ΔE_{nm} are respectively the temperature and the largest energy gap between adjacent levels. This usually corresponds to the gap between the ground and the first excited level. For LIP in argon, this criterion is not fulfilled.

For the case of transient and homogeneous plasma the criterion below is required:

$$\left|\frac{N_e(t+\tau)-N_e(t)}{N_e(t)}\right| \ll 1 \quad (2)$$

$$\left|\frac{T_e(t+\tau)-T_e(t)}{T_e(t)}\right| \ll 1 \quad (3)$$

where τ is the relaxation time given by the slowest process leading to re-establishment of LTE once the system is suddenly perturbed from quasi- stationary LTE. The criterion in our case is fulfilled until 1 μs and broken after.

$$\tau\ (s) = \frac{6.3.10^{10}}{N_e f_{12} <g>} \Delta E_{21} (k_B T_e)^{1/2} \exp\left(\frac{\Delta E_{21}}{k_B T_e}\right) \quad (4)$$

Finally, in the case of transient and inhomogeneous plasma, a third and latter criterion must be satisfied. It establishes that the diffusion length λ of atoms and ions during relaxation time is much shorter than variation of plasma parameters.

$$\left|\frac{N_e(r)-N_e(r+\lambda)}{N_e(r)}\right| \ll 1 \quad (5)$$

$$\left|\frac{T_e(r)-T_e(r+\lambda)}{T_e(r)}\right| \ll 1 \quad (6)$$

$$\lambda(m) = 1.4\times10^{16} \frac{(k_B T_e)^{3/2}}{N_e} \left(\frac{\Delta E_{21}}{M_A f_{12} <g>}\right)^{1/2} \exp\left(\frac{\Delta E_{21}}{2k_B T_e}\right) \quad (7)$$

Where M_A and f_{12} are respectively the relative atomic mass of Argon and oscillator's strength of the transition. This last criterion is valid until 2 μs for the temperature and particularly in the center of the plasma plume. For the density the criterion is also fulfilled until 1 μs.

4. SUMMARY AND CONCLUSIONS

In this work Thomson scattering and optical emission spectroscopy were applied to quantify temporally and spatially resolved electron number density and temperature in laser induced spark in argon at atmospheric pressure. We found a fairly good agreement between electron densities calculated by the two methods whereas a large discrepancy is found for temperatures. Spatially T_{ex}^{OES} and T_e^{TS} present approximately the same profile, namely a quasi-uniform distribution. On the other hand, N_{ex}^{OES} and N_e^{TS} have stronger gradients. Under our experimental conditions, the McWhirter criterion is not fulfilled. Inequalities (2), (3), (5) and (6) are valid at least until 1μs.

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