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Detection of deuterium retention by LIBS at different background pressures

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Abstract

To develop laser induced breakdown spectroscopy (LIBS) for quantitative diagnostics of fuel retention during the maintenance breaks of ITER, the effect of background gas pressure on the laser-induced plasma characteristics has been studied. It was found that at atmospheric pressures the plasma has a long life-time and confined in a limited volume near the target. Besides, at near-atmospheric pressure and at longer delay times after the laser pulse the temporal changes of the electron temperature are slow. These findings are important from the viewpoint of quantitative characterisation of fuel retention by calibration-free LIBS method. At atmospheric pressure the resolving of hydrogen isotopes H and D becomes possible at delay times > 2000 ns when Stark broadening caused by electron concentration has decreased to small enough value. However, longer delay times lead to the decay of these lines intensities and to a considerable increase of the shot noise.

Keywords: laser induced breakdown spectroscopy, spatial regularities of the laser-induced plasma plume, detection of hydrogen isotopes.

1. Introduction

The ITER safety strategy foresees that the early years of ITER operations will be used to improve the understanding of T retention and reduce uncertainties [1]. Laser Induced Breakdown Spectroscopy (LIBS) is a potential technique for monitoring where the T is locally trapped. In the case of LIBS, the laser radiation evaporates a small amount of the tested material and by analyzing the spectrum of the formed plasma plume, the elemental composition of the studied sample can be determined. LIBS has been proposed to be applied during maintenance breaks, at atmospheric pressure, and the main goal will be the quantification of the amount of tritium (T) on the plasma facing components (PFCs).
To this end, resolving Balmer α-lines of deuterium (D_α) and tritium (T_α) is necessary. The governing factor for resolving different hydrogen isotopes is the Stark broadening of the relevant lines in the laser-induced plasma. Results from a number of measurements in vacuum and at a pressure of a few hundreds of Pascals [2,3,4] have shown that LIBS allows reliable resolving of deuterium and hydrogen lines (spectral gap $\Delta\lambda \approx 0.18$ nm). Furthermore, simulations in, e.g., Ref. [5] have demonstrated that the separation of tritium and deuterium ($\Delta\lambda \approx 0.06$ nm) should be possible even at atmospheric pressures. In addition to the reliable reconstruction of the depth profiles of H, D, and T, obtaining quantitative information of the fuel content on first-wall structures could be got by the calibration-free LIBS (CF LIBS) method [6]. The method assumes the local thermal equilibrium of the laser-produced plasma. Besides, electron temperature T_e and electron density n_e have to be known accurately.

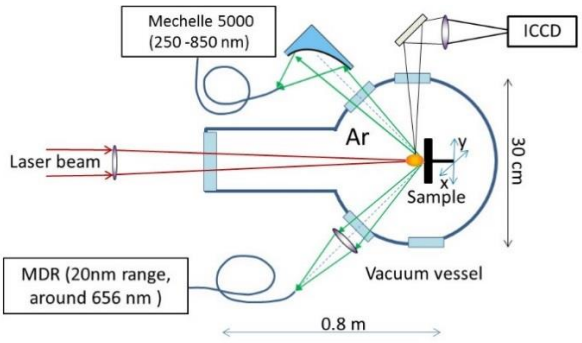

Figure 1. Schematic illustration of the experimental setup.

Both T_e and n_e are found from the measurements of intensities and contours of a number of spectral lines. Their reliable determination requires careful choosing of the recording parameters, most importantly the delay time, t_d, from the laser pulse and the width of the recording window, Δt. At short (~ 100 ns) values for t_d, the intense background continuous emission dominates the spectrum while as t_d increases, the ionic and neutral spectral lines start to appear. In this regime the signal-to-noise (S/N) ratio is governed by shot noise [7]. In addition, independently of t_d, the S/N ratio is influenced by shot-to-shot spatial fluctuations of the plasma plume. Usually, a compromise is selected such that both the S/N is high and the emission has not yet faded away.

Here we study the effect of the background gas pressure on the characteristics of the laser created plasma plume (density, temperature) and determine an optimal delay t_d to resolve D_α and H_α lines. The focus will be on ITER-relevant conditions: near atmospheric pressure and W-Al coated D-doped samples.

2. Experimental

Schematic illustration of the experimental setup is shown in Figure 1. The focussed laser beam was directed onto a movable sample surface. Argon of 5.0 purity was used as the background gas. Two cycles of measurements were carried out.

During the first cycle a disk of bulk not exposed tungsten, W, was used as a target. The target material was ablated by the second harmonic radiation from a Nd-YAG laser (λ = 532 nm, pulse duration 8 ns). The laser beam energy at the sample surface was 55 mJ and the average value of fluence Φ of the Gaussian beam was 10 J cm^{-2}. Plasma plume image as well as the LIBS spectrum as a function of the delay time t_d, were recorded in the direction parallel to the target surface. ICCD camera (iStar 340T Andor Technology) recorded time-gated images using either a “blue” B filter or a “red” R filter which transmitted light in the 380-480 nm and 600-800 nm regions, respectively. This way, the tungsten radiation (B filter) could be distinguished from that of argon (R filter). For recording of plasma plume spectra in the same lateral direction, the camera was replaced by a Czerny-Turner type spectrometer MDR-23 (focal length 50 cm) coupled with the ICCD camera (not shown in Figure 1). In this case the plasma plume radiation was directed onto the circular end (diameter 0.9 mm) of a fiber bundle consisting of 50 fibers, each of them having a diameter of 125 μm. At the spectrometer entrance the fibers in the bundle were arranged in a linear array. The spectrum could be recorded in a 20 nm range around a selected wavelength. When a grating with 1200 lines/mm was used and the entrance slit of the spectrometer had a width of 20 μm, the half-width of the instrumental contour was 0.055 nm.

During the second cycle of measurements samples with D-doped, 2 μm thick 80%W/20%Al coatings on Mo, prepared by vacuum arc-discharge deposition [8], were used. The coatings simulate possible co-deposits in ITER with Al used as a proxy for Be. The same laser as in the first cycle was used but now

with a fluence of $\Phi \approx 7$ J cm^{-2}. Spectra were recorded simultaneously by two spectrometers (Figure 1). The MDR-23 was now positioned at 45° with respect to the laser beam to record the spectral lines of different hydrogen isotopes around 656 nm, while the other one, a Mechelle 5000 (Andor Technology), recorded spectra in a broad range (250-850 nm) through the another window of the chamber also under the angle 45° such that a multitude of W lines could be recorded for estimating the plasma plume temperature T_e.

3. Results and discussion

The measurements in the first cycle (bulk W samples) were carried out at different pressures and using different values for t_d such that at a fixed pressure, the same spot on the target surface was ablated while scanning the delay time.

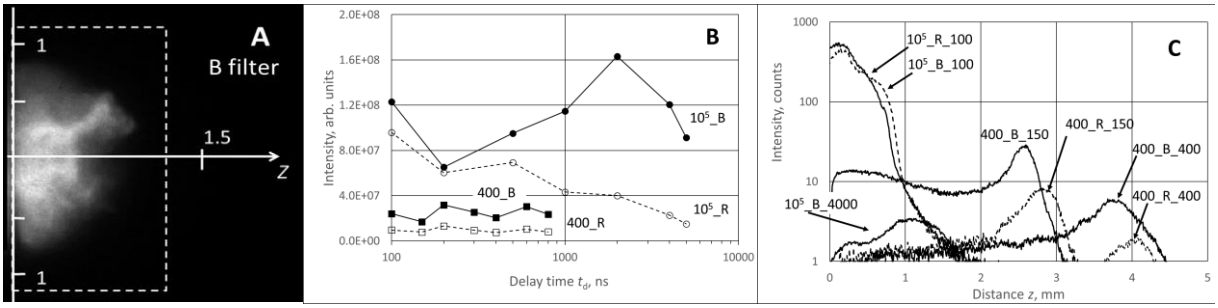

Figure 2. A- image of the plasma plume, distances in mm from the sample centre; the laser beam is moving along the *z* axis from right to left; B filter; pressure – 10^5 Pa; t_d = 200 ns; time-gate - 20 ns, dashed line gives the area from where the "total" emission was found. B – total emission as a function of delay time; labels – pressure in Pa; dashed line - R filter, solid line – B filter. C – spatial emission profiles; labels: pressure in Pa_delay time in ns; dashed line R filter, solid line – B filter. Intensities of R and B filters are not related with each other.

At fixed values of pressure and delay time, the plasma plume radiation fluctuates from shot to shot and an average of 10 images was used to characterize its spatial distribution at specified general conditions. At pressures $\leq$ 6000 Pa the average light distribution had an axial symmetry, while at higher pressures the light distribution was turbulent (Fig.2A). Compared with the irregular structure of the B filter image characterizing W radiation, the R filter image of radiating Ar is more homogeneous. The "total" emission I_T is obtained as the sum of counts of pixels in a rectangle surrounding (Fig. 2A) of the plasma plume image, separately for the B and R filter cases. Fig. 2B shows that at lower pressures and at t_d < 500 ns the I_T values of the R and B parts of the spectra are almost independent of t_d while at near-atmospheric pressures the measured intensities with R and B filters have a strong dependence on t_d and differ remarkably from each other. Fig. 2C gives the spatial intensity profile of the emission along the Z axis. At a low pressure of 400 Pa the expanding plasma plume exhibits a well-pronounced leading edge. Noticeable is that the R peak (Ar radiation) is somewhat ahead of the front of the tungsten radiation. The average speed of expansion is $\approx 5\times10^5$ cm s^{-1}. At atmospheric pressures (10^5 Pa) the plume expansion takes place only at times less than 100 ns and at least till 6 μs the plasma plume remains confined within ≈ 1 mm distance from the sample. The latter results qualitatively match with the results of earlier studies dealing with the measurements [9] and modelling [10] of the laser ablation in different background gases.

From the viewpoint of CF LIBS the plasma confinement near the target is an advantage of atmospheric pressure gas as it enables to collect the most part of plasma plume radiation to the spectrometer but a drawback is the plasma turbulence due to which a certain part of plume radiation is not recorded. A partial solution to diminish the fluctuations could be the collection of the emission from the entire volume occupied by plasma.

When determining the plasma temperature, for each combination of background gas pressure and delay time the results were extracted from an average of 100 spectra. The average temperature T_e was found from the slope of the Boltzmann plot for selected W lines, see Ref. [7] for details. Choosing analytic W lines in the 400-420 nm spectral range, general considerations described in [11] were kept in mind i.e. only lines with more-or-less negligible self-absorption have been used. The main factor influencing the accuracy of T_e determination was the S/N ratio.

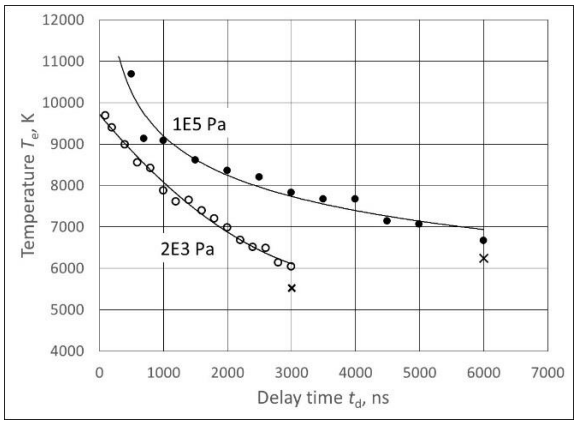

Figure 3. Sample bulk W - T_e as a function of t_d at two background pressures; points – experiment; lines – trendlines. × - 80%W/20%Al coating, temperatures of samples were estimated for t_d values where spectra in Figure 4 were recorded, 3000 ns for 2000 Pa and 6000 ns for 10^5 Pa.

According to Figure 3, at near-atmospheric pressure the plasma temperature at the same t_d is always higher than that at lower pressures and starting from t_d = 3000 ns T_e is approaching to an asymptotic value. This result confirms that at higher pressures it is easier to reach the thermal equilibrium [7].

In the second cycle of measurements (D-doped 80%W/20%Al coatings), spectra were measured as a function of the number of laser shot. The main mechanism of broadening of hydrogenic spectral lines is Stark broadening. A reliable resolving of D_α and H_α becomes possible only at longer delays when the electron concentration has dropped to small enough values.

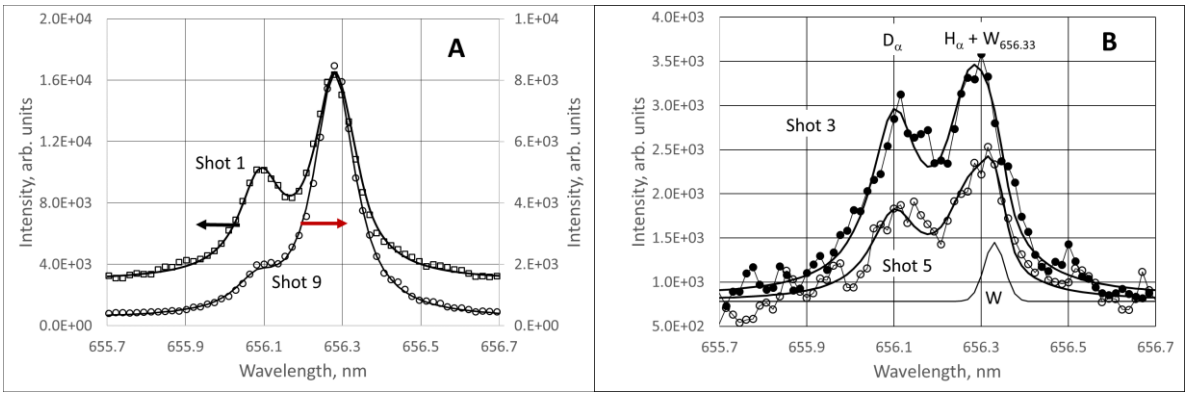

Figure 4. Spectra near 656 nm; symbols - experiment; solid lines –fitting by Voigt contours. A - 2000 Pa pressure, t_d = 3000 ns, $T_e \approx$ 5500 K. B - 10^5 Pa pressure, t_d = 6000 ns, $T_e \approx$ 6300 K; W line belongs to shot 5.

The data in Figure 4 (results around 656 nm) are the averages of spectra extracted from 5 different spots on the sample surface. In both spectra a two-humped structure, corresponding to H_α and D_α, is traceable but at 10^5 Pa pressure the depth of the dip between the humps is already at the noise level. Moreover, at atmospheric pressures the peak near 656.3 nm seems to be slightly shifted towards longer wavelengths. Inspection of spectra shows that at 10^5 Pa intensities of W lines around 656 nm become comparable with those of hydrogen isotopes. The W line at λ = 656.33 nm and H_α lines overlapping causes the shift of recorded peak, and at longer delay times forming a shoulder at the longer wavelength side of H_α line. T_e was found similarly to the case of bulk W samples. However, because now the laser fluence was lower than in the experiments of the first cycle, the line intensity was lower and the uncertainty in T_e determination higher compared to the analyses above. Considering the instrumental width and calculated Doppler widths, the Gaussian half-widths for D_α, H_α and W lines were evaluated. The procedure described in [12] was applied to find the Lorentzian width of lines.
At the 2000 Pa pressure the fitting with Voigt contours gave almost perfect match with the experiment. In spite of a high noise level at the 10^5 Pa pressure, a satisfactory fit was also obtained which allows to build the dependence of the intensities of the different hydrogen isotopes as a function of the number of laser shots. These results allowed to make some estimates related to the separation of D_α and T_α lines. In the case of the used spectrometer and the ICCD camera the gap between the D_α and T_α peaks would be around 6 pixels of ICCD which in principal allows the separation of these lines by the curve-fitting techniques. However, keeping in mind the level of the shot noise a more reliable results could be obtained by using a spectrometer of 2-times higher linear dispersion. The main factor hindering to resolve these lines is the Stark broadening of due to the high charge concentration in the laser created plasma plume. Using the relationship between the Lorentzian width and electron concentration n_e the values 3×10^{21} m^{-3} and 2×10^{21} m^{-3} for 2000 Pa and 10^5 Pa pressure were estimated.

The relative intensity of deuterium $I_D^R = I_D/(I_H + I_D)$ as a function of laser shot number was compared with the substrate Mo (λ = 661.9 nm) profile. In case of both pressures used in experiments, I_D^R had within the limits of the coating almost the same ($\approx$ 0.35) value and it diminished to $\approx$ 0.1 when the substrate was reached.

Conclusions

- At higher pressures the laser-produced plasma plume is turbulent and because of its irregular and fluctuating structure only the average values of T_e and n_e over the plasma plume extent could be estimated.
- At atmospheric pressure the plasma is confined to a small volume where its life-time exceeds that of at a few hundred Pa pressure by an order magnitude. These results indicate that conditions for local thermal equilibrium are better fulfilled at higher pressures.
- Spectral lines belonging to low-lying energy states are influenced by self-absorption and for a reliable determination of T_e these lines should be avoided.
- Using longer delay times allows to resolve H_α and D_α lines also at atmospheric pressure, but for quantitative estimations the presence of a W line near H_α should be considered. The S/N ratio is controlled by shot noise and its increase could be achieved by averaging spectra recorded from a

number of different spots at the sample surface. From our LIBS experiments followed that it is possible to separate deuterium and tritium even at atmospheric pressure.

Acknowledgments

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