DIAGNOSTICS OF PLASMA PRODUCED BY LASER ABLATION OF CARBON-BASED POLYMER MATERIAL

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INTRODUCTION

Applications of LIBS for quantitative analysis of liquid solutions are still challenging and suffer from low sensitivity and poor repeatability of measurements. One of the available methods for improvement of analytical performance is to convert liquid to a solid matrix, for example by depositing micro-drops of analyte solutions on a substrate and drying. Commonly, inert material is chosen as a substrate in order to reduce a portion of the laser energy that is spent on substrate vaporization, i.e. to ensure that the induced plasma mainly involves the deposited material. Carbon-based polymer materials such as Teflon are often used for this purpose: see De Giacomo et al. 2016. Teflon molecules contain only carbon and fluorine and because of the low excitation efficiency of fluorine, the spectral contribution from the substrate is practically limited to carbon. In case the LIBS analysis is carried out in the ambience air, along with carbon atomic and ionic lines molecular bands of diatomic species such as CN and C_2 could be registered in the plasma. In this work, emission from the laser-induced Teflon plasma was utilized for diagnostics of plasma, i.e. estimation of plasma temperature and electron number density.

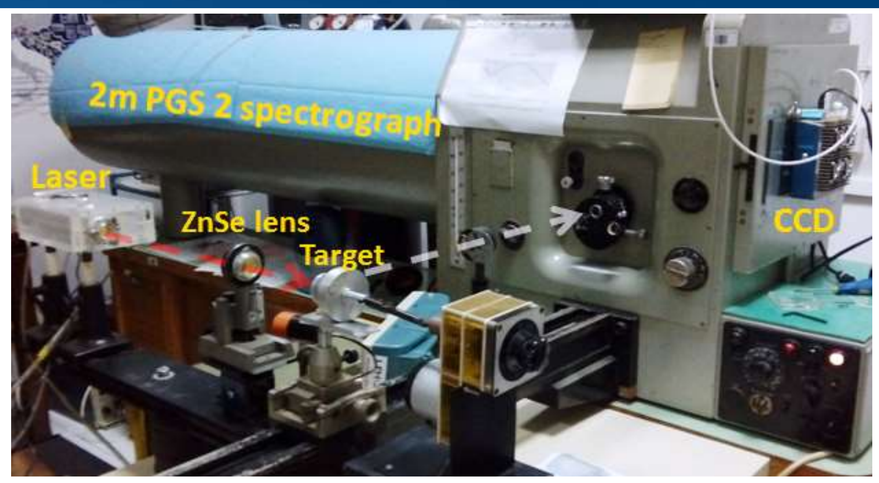

Figure 1. Experimental setup

Estimated plasma parameters may be used for correction of the measured intensities of analyte lines whose variations are caused by fluctuations of signal intensities.

RESULTS AND DISCUSSION

When the TEA CO_2 laser beam was focused on the Teflon target surface reproducible plasma could not be obtained even with the highest attainable laser pulse energy of 170 mJ. On the contrary, spectrochemically usable plasma was obtained by focusing the laser beam 5 mm in front of the target. In that case the threshold energy for plasma creation on the Teflon was 130 mJ. Teflon plasma emits strong atomic and ionic carbon lines and C_2 and CN molecular bands, suitable for plasma diagnostics.

The electron number density was determined from Stark width of carbon ionic C II 283.67 nm line. Figure 2a shows the profiles of C II spectral lines obtained using laser pulse energy of 150 mJ focused 5 mm in front of the Teflon target, emitted from a part of the plasma 1 mm from the target surface. The estimated electron number density was in the range $1.9 \cdot 10^{17}$ to $9.4 \cdot 10^{17}$ cm^{-3}, depending on the plasma observation zone (1 to 3 mm from the target). The carbon lines, C II 250.91 nm and C I 247.86 nm (Figure 2b) were used for determination of the ionization temperature using the ion-to-atom spectral line integral intensities ratios. The estimated plasma temperature was in the range of 16500 K (0.9 mm) to 20500 K (0.3 mm).

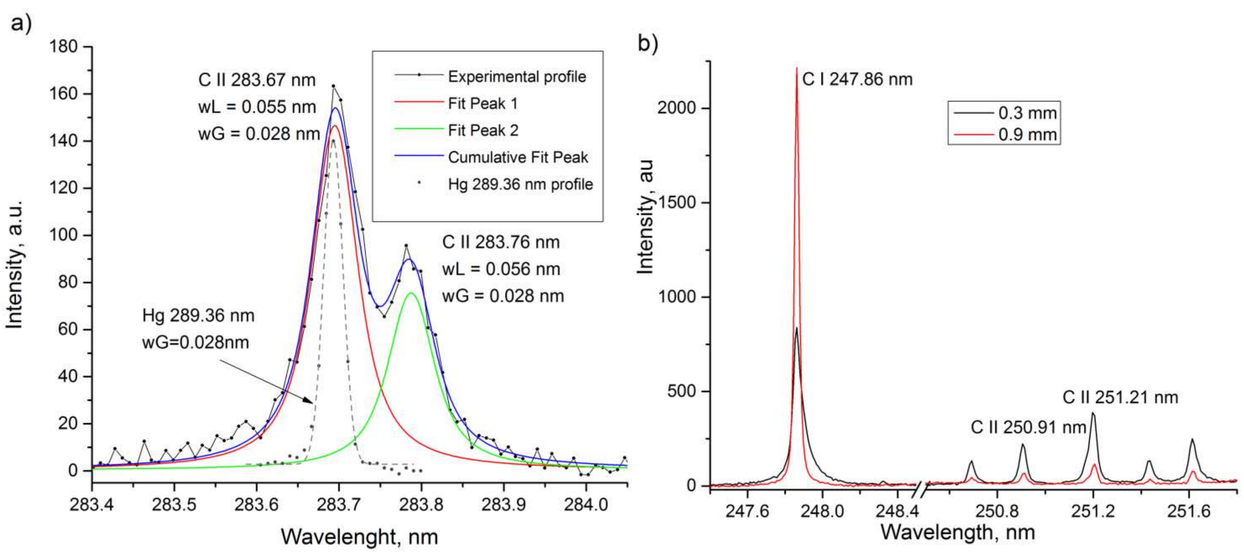

Figure 2. (a) Profile of C II 283.67 nm line used for determination of n_e; (b) Part of LIBS spectra recorded at 0.3 and 0.9 mm from target surface.

The emission spectra of C_2 and CN molecules were used for determination of the rotational (T_{rot}) and vibrational (T_{vib}) temperatures, by comparing the experimentally obtained and synthetic molecular spectra. Because of high dissociation energy of these molecules, relatively low excitation energy of the first excited electronic state, and the favorable value of the transition probabilities their emission intensities are high and suitable for plasma diagnostics: see Kuzmanovic et al. 2019. The emission of the Swan system of C_2 molecules could be obtained only from the plasma region close to the target surface, Figure 4.

On the contrary, the intensive emission of the $\Delta v = 0$ sequence of B-X violet system of CN molecule could be detected at distances up to 2 mm from the target surface, Figure 4. This is understandable as the CN molecule is formed by the reaction of carbon ablated from the target and nitrogen from the air.

From the C_2 spectra, the best matching was obtained for T_{vib} = 3350 K, and the T_{rot} = 5100 K, while from the CN bands, $T_{rot} = T_{vib}$ = 7150 K. The most intense band of the CN violet system showed strong self-absorption and led to overestimated temperature values.

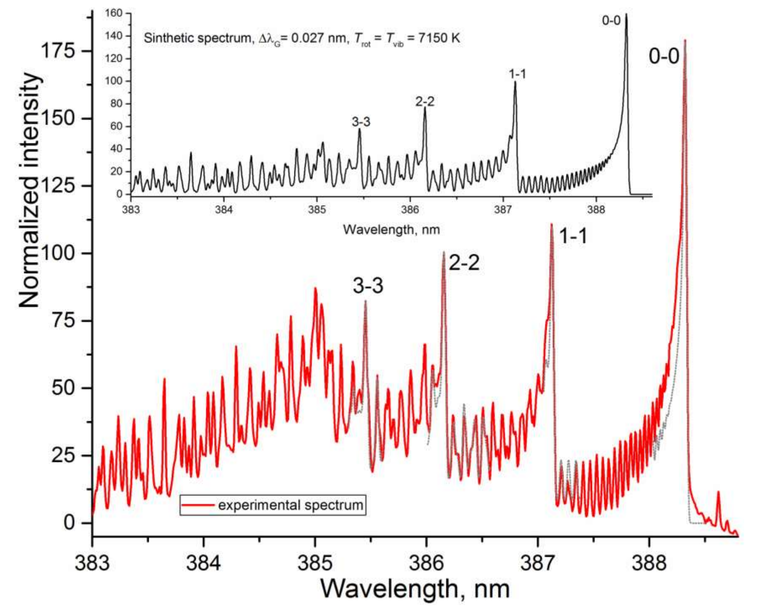

Figure 4. The spectrum of $\Delta v=0$ sequence of CN B-X violet system. Laser pulse energy 150 mJ, laser beam focused 5 mm in front of the target. The spectrum was recorded from a slice of plasma parallel to the target, at a distance of 0.3 mm from the target.

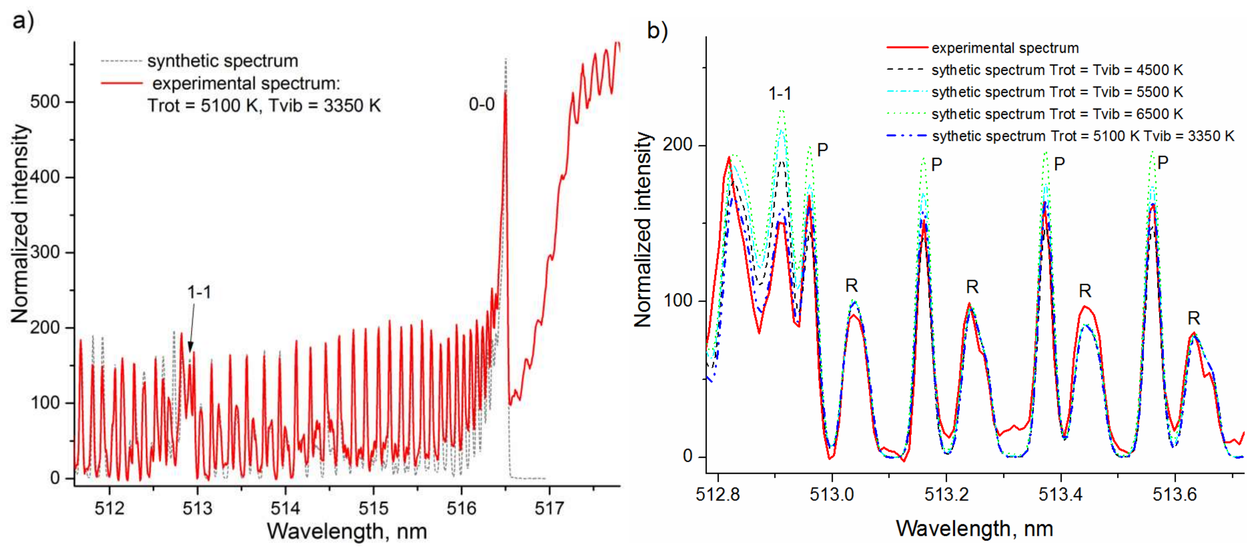

Figure 3. (a) Part of spectrum of sequence $\Delta v=0$ of C_2 Swan system. The spectrum was recorded at a distance of 0.3 mm from the target; (b) the P and R components of the 0-0 band spectrum.

CONCLUSION

Diagnostics of the TEA CO_2 laser induced Teflon plasma was performed using the emission spectroscopy. The plasma parameters, electron density and temperature, were estimated using emission spectra of neutral and singly charged carbon atoms. Depending on the plasma observation zone, the electron number density and temperature were in the range $1.9 \cdot 10^{17}$ to $9.4 \cdot 10^{17}$ cm^{-3}, and 16500 to 20500 K, respectively. Additional information was obtained from the rotational-vibrational structure of C_2 and CN band intensities. The most intense bands of C_2 emission spectra had more distinct band heads and a better resolved rotational structure than bands of CN violet system, thus, they were more convenient for determination of temperature.

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