Journal of Materials Science & Nanotechnology
Volume 10 | Issue 1
ISSN: 2348-9812

Research Article Open Access

Optical Depth Measurement of Self-Reversed Line Emitted from In-Homogenous Plasma in Laser Induced Breakdown Spectroscopy

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Citation: Trabelsi J, Terzi N (2022) Optical Depth Measurement of Self-Reversed Line Emitted from In-Homogenous Plasma in Laser Induced Breakdown Spectroscopy. J Mater Sci Nanotechnol 10(1): 101

Abstract

In this work, an original method is proposed and used for measurement of the optical depth of a self-reversed spectral line. A theoretical approach is utilized in an in homogenous laser induced plasma at local thermodynamic to simulate self-reversed line and then to get the main line profile without self-absorption. In this research, the spatial and temporal evolution of optical depth of two spectral lines of Ca II at 393.4 nm and 396,9 nm is studied. Furthermore, the variation of optical depth versus the concentration of species emitter inside of plasma plume is investigated. In addition, the validity of this method is affirmed during comparison with results obtained by other techniques.

Keywords: Optical Depth, Self-Reversed Line, Laser Induced Breakdown Spectroscopy

Introduction

The focus of pulsed laser beam to different samples produces plasma including various parameters varying with time and space [1-4]. During the first femtosecond after laser pulse irradiation, some electrons are created during simultaneous absorption of sufficient number of laser's photon. These electrons attain sufficient energy by absorbing the constituent photons of laser pulse, and ignite the cascade ionization. Then, the plasma expands during the laser pulse irradiation [5-6]. A few nanoseconds after the laser beam emission, the generated plasma can be characterized by high ionization containing atoms and ions species and free electrons, in which these species are in interacting together. Between consecutive laser pulses, the relaxation phase of plasma will be happened. In general, the relaxation process are characterized by energy loss in the form of emission light during the expansion of kinetics particles in the surrounding medium [7-11] and also by electron-ion recombination process. In this phase, the neutral atoms and then molecules will be formed.

It can be stressed that the spectral line intensities depend on the temperature and the line-width broadening are a function of ionized particle density. In LIBS spectroscopy, Stark broadening is the dominant mechanism in line width. Determination of the lines shape is based on the spectroscopic methods which can present the information about the middle region of the plasma [12-14]. Generally, the relation between plasma characteristics and spectral line properties can be altered due to the self-absorption phenomenon [15-20]. Most of spectral lines affected by self-absorption are ones in ground state or located in lower level of transition. Different research group have studied on self-absorption correction in LIBS spectroscopy. For instance, Rezaei et al. [21] used the peak intensity of self-absorbed spectral lines to study the temporal evolution of their optical depth. Tang et al. [22] evaluate the self-absorption using a method based on the fitting of the calibration curve for a given line.

In practical analytical spectroscopy, the usage of self-absorbed line is avoided or it is needed to be corrected before exploitation. This work tries to correct the self-absorption phenomena for exact quantitative analysis. In previous work of the author, a theoretical model has presented to understand the kinetics of plasma radiation process [5,13,14]. It should be mentioned that this research is continuation of our previous work [20] where a computer code was built to simulate a self-reversed spectral line, but in this study, the code is developed so that it can correct the emission line from auto-absorption and also can measure the optical depth. This research permits the space exploration of optical depth using a spatial integration of the line intensity. Then, the obtained results are compared with those extracted from the technique based on the ratio of line intensity presented in Ref. [23]. It must be noted that the main aim of this work is understanding and investigation of the local absorption of light which can permit to control the application of photodynamic therapy [24-26]. Moreover, the development and the sophistication of organic and inorganic photovoltaic cells is based on the amelioration the absorption of light for increasing the desired efficiency [27].

Theoretical Background

In our experimental condition, the plasma is supposed to be in local thermodynamic equilibrium for time delay t<5μs after the laser pulse14. For complete local thermodynamic equilibrium, the collisional excitation rate must be much larger than the radiative excitation or deexcitation rate for the first excited state. This condition leads to assume that the resonance lines are self-absorbed [28], the minimum of electron density N_c which assure this condition is given by Griem [29]: $N_e \geq 10^{17}\left(\frac{E_2-E_1}{E_H}\right)\left(\frac{KT}{E_H}\right)^{\frac{1}{2}}$

Where: E_1 is the ground state, E_2 is the upper level of resonance line and E_H is the ionization energy of the hydrogen atom. In our case $N_e \geq 5.3 \times 10^{16}\ cm^{-3}$. This requirement is satisfied and the resonance lines are self-absorbed.

The variation of spectral line intensity, taking into account of the spontaneous emission, stimulated emission and absorption, can be calculated as:

$$\frac{dI_\omega(r)}{dr} = \varepsilon_\omega - K_\omega \ I_\omega(r) \qquad (1)$$

here, r is the position of plasma plume, $I_\omega(r)$ is the intensity at position r and the emission coefficient is $\varepsilon_\omega = \frac{\hbar\omega}{4\pi} A_{ki} N_k$ where A_{ki} is the transition probability, N_k is the population of the level *k*, and K_ω is the absorption coefficient which is defined as:

$$K_\omega = \frac{\hbar\omega}{4\pi} B_{ik} N_i \left(1 - \frac{g_i N_k}{g_k N_i}\right) P(\omega) \quad (2)$$

here, $P(\omega)$ is the corresponding emission line profile, g_i and g_k are the statistical weights, and B_{ik} is the Einstein coefficient.

The optical depth of the plasma is defined as $\tau_\omega(l) = K_w l$ where, *l* is the plasma dimension.

The intensity of light emitted from the plasma taking into account the auto-absorption phenomenon is given by[20]:

$$I = \frac{I_\omega^\varepsilon}{\tau_\omega(l)} (1 - \exp(-\tau_\omega(l))) \quad (3)$$

In above equation $I_\omega^\varepsilon = \epsilon_\omega l$. In current study, the plasma is assumed to be constructed from a number of uniform regions. Each region is characterized by different plasma parameters including electron density, electron temperature and the optical depth τ_i. The expression of a self-reversed line emitted from an in homogenous laser induced plasma is given by[20]:

$$I = \sum_i \left(\frac{I_i}{\tau_i}(1 - \exp(-\tau_i)) \exp\left(\sum_{j>i} (-\tau_j)\right)\right) \quad (4)$$

here, *i* and *j* indicate the number of regions.

The magnitude of the self-reversal of the spectral line is computed by a simple method program. The program adjusts the values of the intensity I_i and the optical depth τ_i in order to obtain the best fit of experimental spectra line profile. The optical depth of the line is given by: $\tau = \sum_i \tau_i$. To correct the self-reversed spectral line from auto-absorption, we affect zero to the different values of τ_i obtained by adjustment.

The optical depth τ of the selected line can be measured using the ratios R of thick line to thin line as [23]:

$$R = \frac{I_1(thick)}{I_2(thin)}$$

where, $I_{thick} = \frac{h\nu_{ul}}{4\pi} A_{ul} N_u L \left\{\frac{1-\exp(-\tau)}{\tau}\right\}$ and $I_{thin} = \frac{h\nu_{u'l'}}{4\pi} A_{u'l'} N_{u'} L$

In this equation, N_u, L, A_{ul} and ν_{ul} are the population of level *u*, the plasma dimension, probability of transition, and the frequency, respectively.

$$R = \frac{I_1(thick)}{I_2(thin)} = F(T) \times \frac{1 - \exp(-\tau)}{\tau}$$

It should be mentioned that $F(T)$ is a term dependent on the temperature T which can be extracted experimentally.

Experimental Set Up

In this paper, the laser beam is irradiated on the sample with utilizing of a Nd: YAG laser at wavelength of 532 nm, pulse energy of 75 mg., pulse duration of 10 ns and repetition rate of 2 Hz. A plasma is generated during laser irradiation which is collected by a lens and is guided into the slit of monochromator. The observed plasma region is a slice with the width depending on the width of the entrance slit and the total height of the plasma. In this work, the spatial integration of the plasma region is about 100 μm width and approximately 2 mm height. The observed region is selected by the imaging lens position as shown in figure 1. In addition, here, laser induced plasma is characterized by the fast temporal evolution of their parameters such as optical depth. In present work, the fulfilment of time resolution has been carried out using photomultiplier tubes by observation of the signal in an oscilloscope.

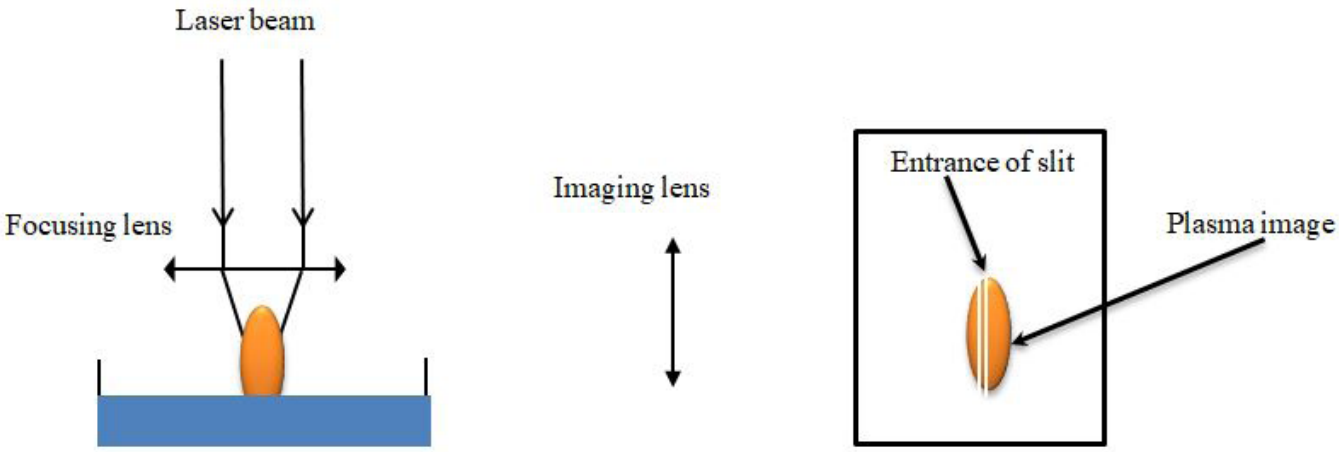

Figure 1: A schematic of plasma formation during laser irradiation after passing the slit entrance of monochromator

Results And Discussions

Correction Of Spectra Line from Self-Absorption

The plasma is produced on the surface of a 0.2, 0.4 and 0.8 mol/L $CaCl_2$ solution. These concentrations are chosen to estimate the self-absorption phenomena. The plasma emission at range wavelength from 392 nm to 398 nm are studied. In these wavelength intervals, the two resonances lines are observed clearly.

Figures 2a, Figures 3a and Figures 4a illustrate the experimental and the simulation of the spectral lines at 393.4 nm and 396,9 nm related to Ca II at 1500 ns, 2500 ns and 3000 ns delays after laser pulse irradiation, respectively. The observed reversal in the spectral lines are attributed primarily to the electron density gradient along the plasma volume. The Stark broadening of line width is encountered to a redshift for the line center wavelength leading to an asymmetrical self-absorbed profile. Experimental spectrum are simulated using formula (4) and by adjusting the values of the line intensity I_i and the optical depth τ_i. *i* indicates the region *i* of plasma. To obtain the spectra line corrected from self-absorption, we affect zero to different τ_i. Figures 2b, Figures 3b and Figures 4b show the self-absorbed and the corrected spectrum at different delay times.

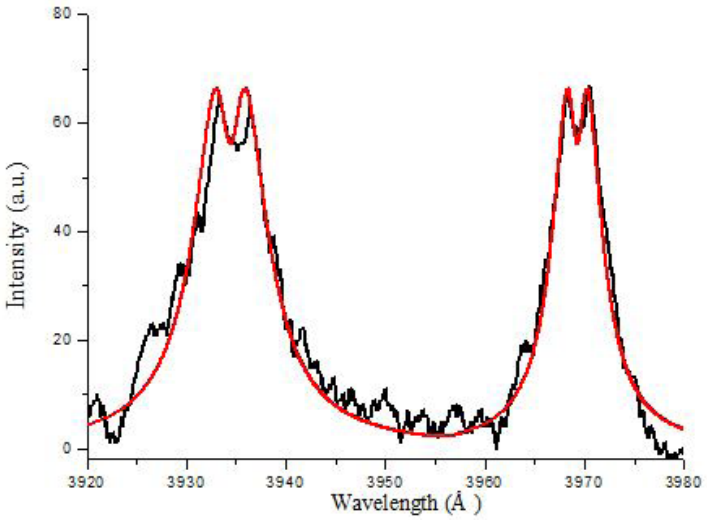

Figure 2a: Experimental and calculated spectrum at t=1500ns

The plasmas is induced on the surface of a 0.8 mol/L CaCl2 solution

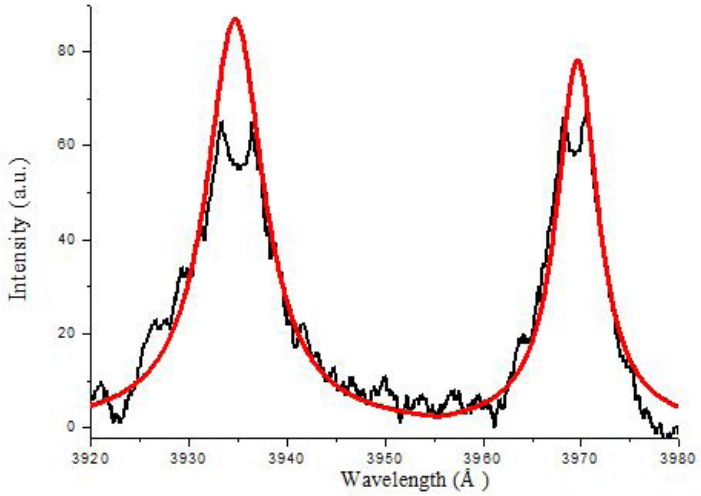

Figure 2b: Experimental and corrected spectrum at t=1500ns,

The plasmas is induced on the surface of a 0.8 mol/L CaCl2 solution

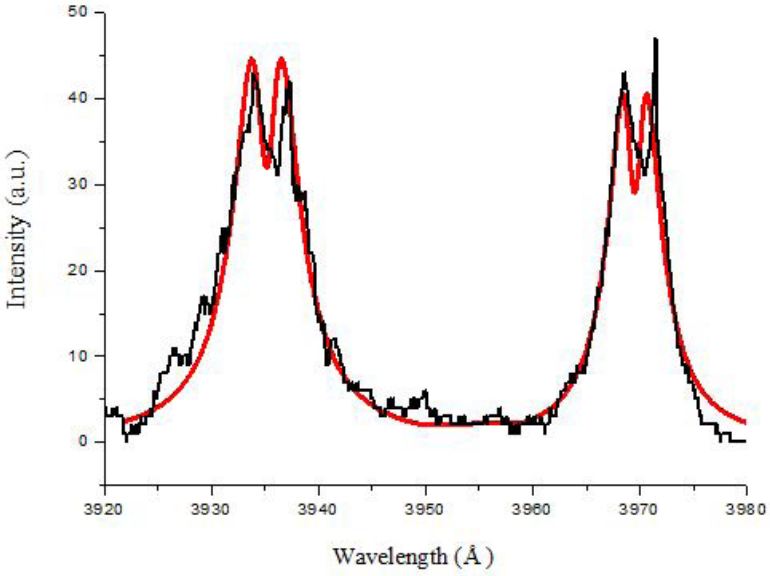

Figure 3a: Experimental and calculated spectrum at t=2500ns

The plasmas is induced on the surface of a 0.8 mol/L CaCl2 solution

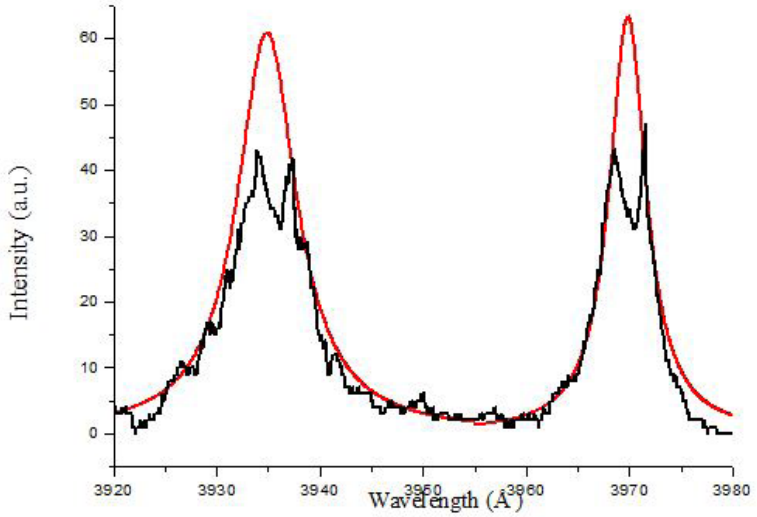

Figure 3b: Experimental and corrected spectrum at t=2500ns
The plasmas is induced on the surface of a 0.8 mol/L CaCl2 solution

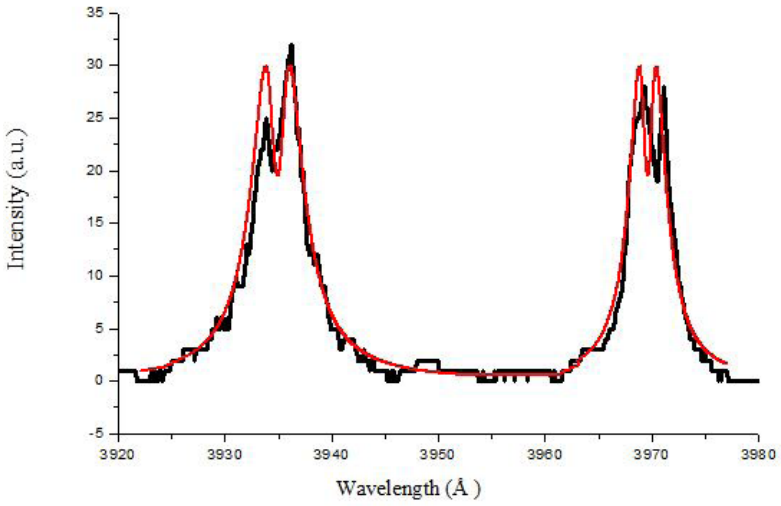

Figure 4a: Experimental and calculated spectrum at t=3000ns
The plasmas is induced on the surface of a 0.8 mol/L CaCl2 solution

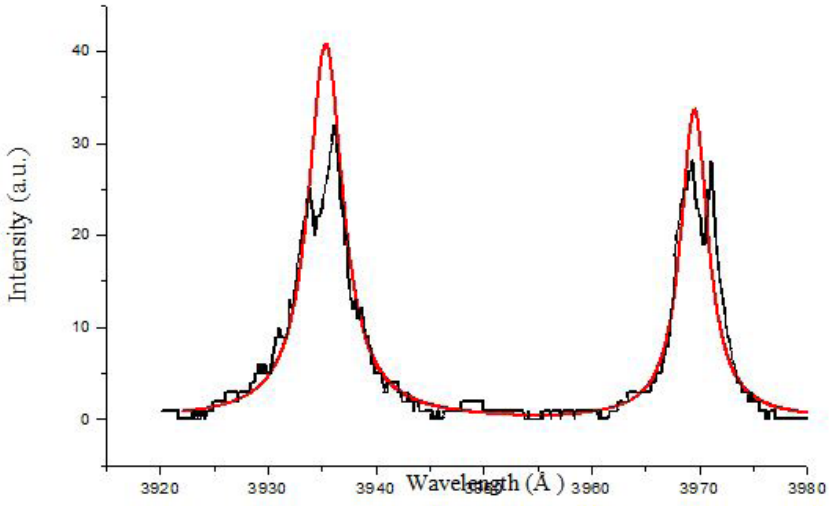

Figure 4b: Experimental and corrected spectrum at t=3000ns
The plasmas is induced on the surface of a 0.8 mol/L CaCl2 solution

To verify the reliability of proposed approximate method for self-absorption correction, we have used the corrected spectrum to deduce electron density and compare the values with those obtained with thin line. It is found that the results are similar.

Optical Depth Measurement

This study followed the spatial and temporal evolution of optical depth of self-reversed line emitted from in-homogenous plasma induced on the surface of $CaCl_2$ solution. Figure 5 and 6 show the evolution of optical depth of the Ca^+ spectral lines at 393.4 nm and 396,9 nm wavelengths with space at different delay time, respectively. As it is clearly seen in these figures, a similar behavior is shown for the optical depth. Moreover, it is observed that at a constant delay time, the optical depth decrease with radial position. This behavior can be attributed to reduction of plasma density with radial position. The Ca^+ species are formed by recombination process during relaxation phase so that the density of these spices increases with time[13] which lead to an increase of the optical depth. Admitting that the species is formed by recombination process of electron with ions coming from the solution, we can show that in the evolution with time of the population can be expressed as [30]:

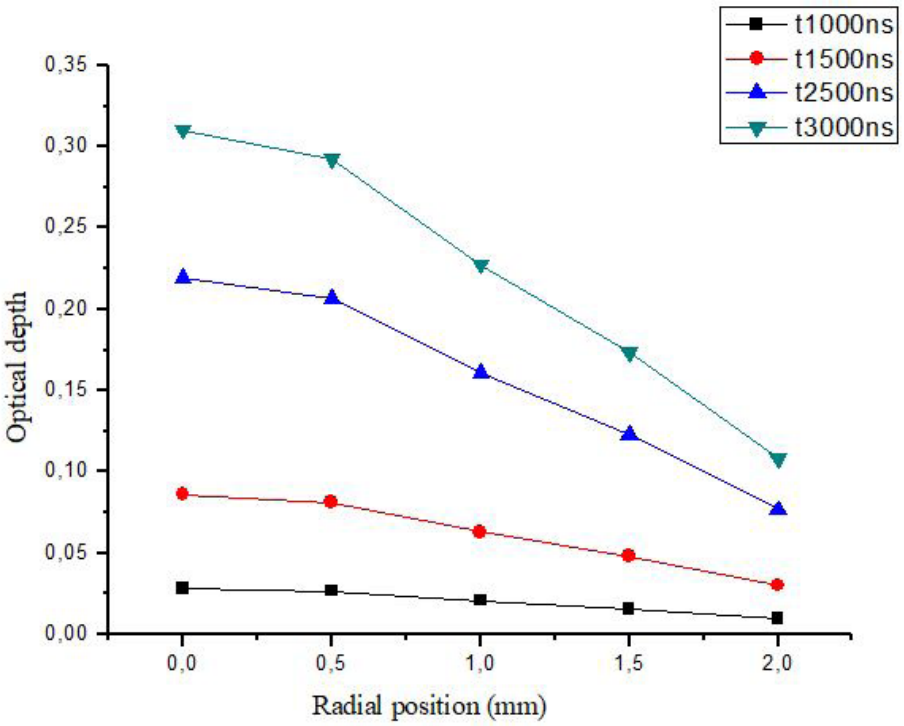

Figure 5: Optical depth variation of emission line at 393,4 nm as a function of radial position at different delay time for 0.8 mol/L CaCl2 solution

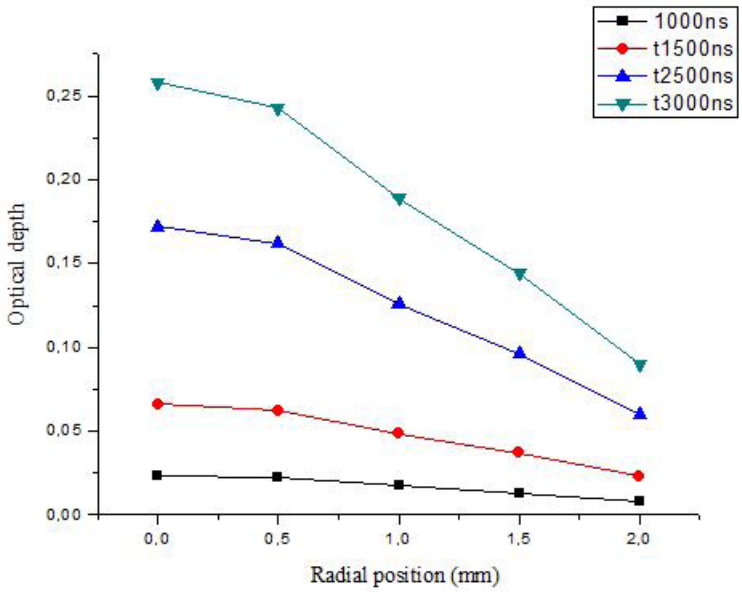

Figure 6: Optical depth evolution for spectral line of 396,9 nm as a function of radial position, at different time for 0.8 mol/L $CaCl_2$ solution

$$[Ca^{+}(t)] = N_0\left(1 - \exp\left(\frac{-t}{\tau_0}\right)\right)$$

Where τ_0 is the plasma life time and N_0 is population formed by recombination process.

Effect of the $CaCl_2$ Concentration on the Optical Depth

In this section, the spatial integrated optical depth $\tau = \sum_i \tau_i$ is measured: as function of $CaCl_2$ concentration which is shown in figure 7 and 8. The optical depth increases significantly with concentration, since the absorption and the emission are proportional to emitter density. It should be noted that the results represented by this method are similar to those obtained by using ratios R of thick line to thin line in ref [23]. Furthermore, figure 9 shows the evolution of the optical depth of the line 393.4 nm emitted from a plasma generated on the surface of solution of $CaCl_2$ ([$CaCl_2$] =0.8 Mol/l). As it is seen in this figure, the optical depth increases as time passes which is due to increase in the concentration of absorbing species.

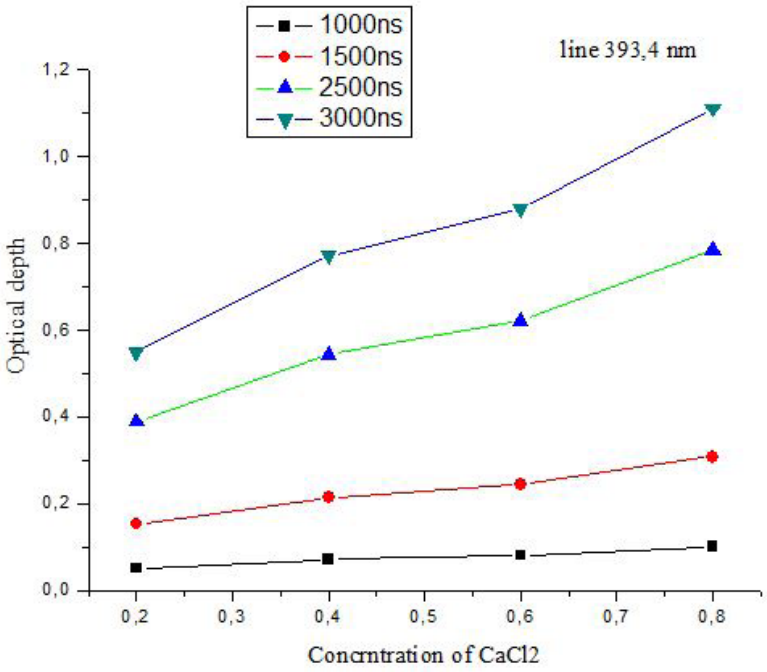

Figure 7: Optical depth variation for emission line of 393,4 nm versus $CaCl_2$ concentration at different time

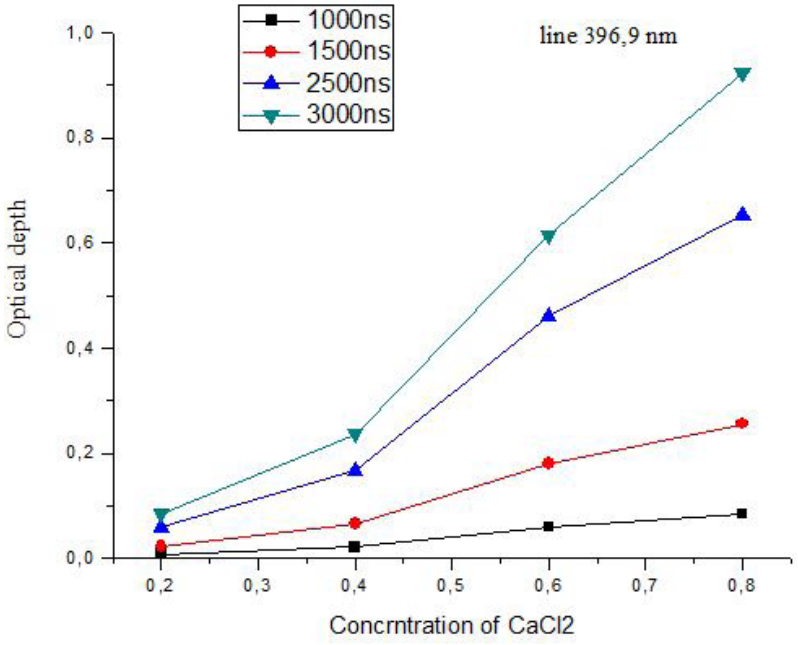

Figure 8: Variation of optical depth of the spectral line of Ca^+ at 396,9 nm wavelength with $CaCl_2$ concentration at different delay time

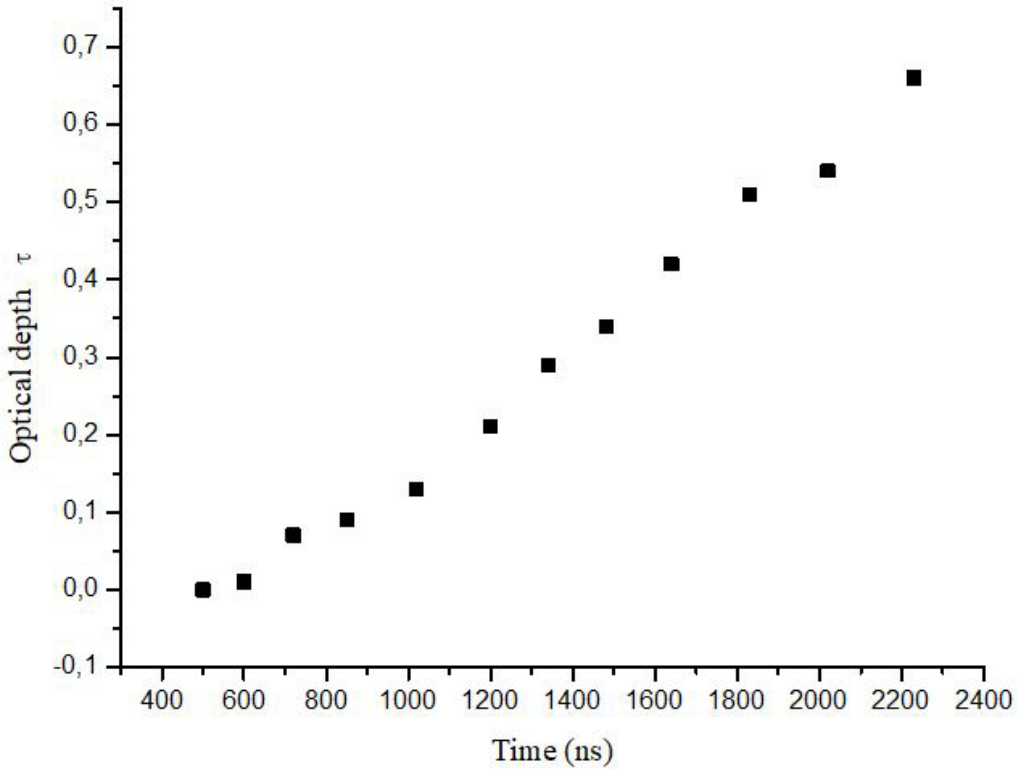

Figure 9: Temporal evolution of optical depth of Ca^+ spectral line at 393.4 nm wavelength [23]

Conclusion

In this work, an original method is presented for simulation of self-reversal line emitted from laser induced plasma on an aqueous surface. In proposed method, the plasma was approximated as comprising different layers characterized by a unique optical depth. After simulation, the line is corrected from self-absorption phenomena. The adjustment of the values of the optical depth during the simulation permits the spatial retirement of this parameter.

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