Spectroscopic estimation of plasma parameters, in the 100–400 ns stage, of a laser-induced plasma in vacuum

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ABSTRACT

This work is focused on the interpretation of the emission spectra in laser-induced plasma observed in the phase at 100–400 ns from after the laser pulse, when the discrete emission lines prevail on the continuum emission, can be important to retrieve the initial stage of expansion. A Q-switched neodymium-doped yttrium aluminum garnet laser has been used for the ablation of a lead sample in vacuum. The observed line profiles, corresponding to different species of lead, were analyzed in terms of delay time. Measurements of parameters of the produced plasmas are performed. The results obtained corroborate the importance of considering nonequilibrium effects in the initial stage of plasma expansion. Also, Stark width for two spectral lines of triply ionized lead is given.

Introduction

The optical emission spectroscopy (OES) of laser-induced plasma (LIP) has become a powerful tool for the fundamental studies of laser-material interaction, resulting to be of paramount importance to investigate laser-produced plasmas, providing to information about the plasma state generated, and also in view of its usefulness in many practical applications both in material science as in analytical spectroscopy. LIP industrial applications require a parallel investigation of the formed plasma from a fundamental point of view; see for example a work recent by this author^[1] method applied to the treated material in Laser Shock Processing (LSP) processes. While the generation of LIP requires an easy experimental set-up, the LIP phenomena need a lot of theoretical and experimental work to be understood, especially in the initial stage.^[2–4] Also, a great effort has been made to be understood the LIP at delays after the laser pulse of the microsecond order, where atomic and ionic lines can be detected unambiguously, a choice that is essentially due to compliance with local thermodynamic equilibrium (LTE), an essential condition for interpreting the results. LIP is generated by irradiating samples with irradiance high enough to exceed the breakdown threshold of the examined material. By the interaction of high power laser with matter, the vaporization of surface layers leads to the formation of an expanding atomic plasma. In LIP, all the energy is delivered during the laser pulse and the plasma generated evolves for a few microseconds. The dynamics may be very different, under different experimental conditions, observing on succession of prevailing species from ions to atoms and from atoms to molecules. LIP changes its

parameters of plasma fast during its evolution, decreases, the temperature decreases inducing recombination and decreasing the number of charged particles in the plasma.^[2,3] The dynamics of the LIP strongly depends on the characteristics of the external environment in which the LIP is expanding.^[4] To generalize the characteristics of the LIP, it is necessary to specify the experimental conditions.^[2–4] From the experimental point of view, LIP has proved to be a valuable and versatile source of spectroscopic data on neutral and ionized species as has been shown, recently, by this author in.^[5–8]

In this work, time-resolved optical emission spectroscopy has been successfully employed to investigate the evolution of LIP generated, in vacuum, on a lead target by irradiation with the Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) fundamental emission (pulse width 7 ns). In the review of the spectra obtained in the initial stage, the continuum emission very high is observed, masking a greater degree of atomization and excitation. Therefore, given the difficulty of studying the plasma when the spectrum is dominated by continuum radiation, this work focuses on the understanding of the spectral peculiarities observed the 100–400 ns after the laser pulse, when the discrete emission lines prevail on the continuum radiation in LIP emission spectra and thus obtain information on the appearance and the disappearance of different species of lead, is important to understand the composition and the temporal evolution of the species in the plasma. From 100 ns after the laser pulse, up to three successive ionic stages appear, that is, spectral lines of the lead neutral Pb I, and the first Pb II, second Pb III, and third Pb IV ionized

appear, being very interesting from the spectroscopic point of view.

The evolution and the character of the spectral lines of Pb I, Pb II, Pb III, and Pb IV were analyzed in terms of delay time, through the analysis of spectra obtained experimentally, as well as the lead plasma temperature and electron density. It is well known that the optical emission of LIP allows the estimation of plasma parameters such as electron temperature, T_e , electron number density, N_e , plasma expansion rate, and plasma composition. We do not forget that LIP, being an expanding plasma, changes its parameters fast during its evolution. Also due to developments in the physical and chemical processes occurring in the LIP, issuing this varies primarily with time, the temporal evolution of plasma is characterized by the transition through different stages and can be related to the changes of plasma number density (decreasing during the life of the plasma). To verify all the mentioned is as well part of the motivation of the present work.

The main mechanisms responsible for the plasma obtained are the same occurring during ablation in any environment. The nature of ambient gas has a strong influence on the properties of laser-induced ablation plumes. It is important to note that the differences between formation in one environment, or another are related to the plasma confinement. Plasma expansion into vacuum is a subject of great interest for many applications ranging from ultra-cold plasmas,^[9] over laser acceleration,^[10] to short-wavelength light sources,^[11] in obtaining different data on parameter for atomic structure studies.^[7,8,12]

To carry out the characterization of LIPs, T_e and N_e are very important parameters, being necessary requirement for the understanding of processes in the plasma, the problem is how to determine them. One approach to the measurement of both T_e and N_e is the observation of line spectra. T_e and N_e are diagnostic indicators because one can predict from these two parameters the thermodynamic equilibrium existing in this plasma. There are many works in the literature where researchers use commonly use the line broadening method and the Boltzmann plot method to determine the electron number density and the electron temperature, see for example some of the works by this author,^[6-8,13-15] that is, the classical approach based on the existence of LTE conditions and of optically thin plasma. However, this method can be only used in the case of the continuous spectrum is very weak relative to the characteristic lines and the emission spectrum without obvious self-absorption. In the LIP technique, the existence of LTE is the essential requisite for meaningful application of theoretical Boltzmann–Maxwell and Saha–Eggert expressions that relate fundamental plasma parameters and concentration of species. A detailed systematic discussion of plasma characterization was reported in references.^[16-20] For LIPs characterization one of the utmost important factors is to find out emission lines of interest with good signal-to-noise ratio (S/N) having known spectroscopic constant values.

In the present work, temperature and the electron number density of the lead plasma were determined, in the

different delay time, using the different emission lines, by the Saha–Boltzmann plot method and the line broadening method, respectively, as explained later. Also, study possibility of deviations from equilibrium conditions has been taken into account in the different delays. The knowledge of the deviation from LTE is really important to take it into account in practical applications.

Lead is the heaviest element thus far detected in the interstellar medium. O’Toole, in 2004,^[21] identified Pb IV lines in the space telescope ultraviolet spectra of the sdB stars Feige 48 and PG 1219 + 534. The Pb III and Pb IV resonance lines have been detected in the Far Ultraviolet Spectroscopic Explorer spectra of hot subdwarf B (sdB) stars by Chayer et al.^[22] Naslim et al.,^[23] they have reported the discovery that two stars, HE 2359–2844 and HE 1256–2738, show an atmospheric abundance of lead which is nearly 10,000 times from seen in the Sun. This is measured from optical Pb IV absorption lines (at 3962.48 Å, 4049.8 Å, and 4496.1 Å, to our knowledge these lines have not been observed in any other astronomical object), never previously seen in any star. According to Naslim et al.,^[23] the lead abundance is 10–100 times that measured in normal hot-subdwarf atmospheres from ultraviolet spectroscopy.

LIPs have been used with extensively as spectroscopic sources for the measurement of Stark widths. The determination of Stark broadening parameters (widths and shifts) of the spectral lines is a vast field of research on account of its considerable interest in applications to astrophysics and in industrial applications. Bukvić et al.^[24] presented experimental Stark full-width at half of the maximum line intensity, W , for 34 spectral lines from Pb IV spectra emitted by the pulsed helium discharge. Theoretical calculations of the Stark broadening parameters for 58 lines of Pb IV they have been made using a set of wave-functions obtained from Hartree–Fock relativistic calculations including core-polarization effects, Alonso-Medina et al.^[25] Later, Hamdi et al.^[26] calculated Stark-broadening parameters for 114 spectral lines of triply charged lead ion (Pb IV) using semi-classical perturbation approach in the impact approximation. An aim of this paper is to provide new experimental value of Stark width for spectral lines Pb IV at 3962.48 Å and 4049.8 Å, with a good agreement with the few experimental values existing in the literature.

Experimental set-up and measurement details

Experimental set-up applied in this work is similar to the LIPs system used in previous papers from Alonso-Medina^[5-8,12-15] although the more detailed description is presented in.^[7,12,13] The schematic diagram of the experimental system is shown in Fig. 1 of the mentioned references.^[5,12,15] A Q-switched laser Nd:YAG (Quantel YG585) (with a 10,640 Å wavelength, pulse energy 290 mJ, pulse width 7 ns, and repetition rate 20 Hz) is used to produce the laser plasma. The laser energy is measured by a digital energy meter. The laser light was focused at a right angle onto, a spot about 0.5 mm in diameter, in the sample with a 12-cm focal length lens. In this work, a lead target (99.99%

Figure 1. Emission spectrum of laser-induced lead plasma, using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns in vacuum, at different delay times: 150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively. Observation of the time evolution of plasma in order to investigate the time evolution of excited plasma species showing predominantly the spectral lines of Pb I, Pb II, and Pb III and two molecular bands of N₂ of the spectral region from 3690 to 3790 Å.

purity, impurity Ca) was used. The laser irradiance on the blank was $2 \times 10^{10} \text{ W cm}^{-2}$. The target was located inside a chamber, on top of a device capable of moving it horizontally with respect to the laser beam, focused in such a way that the plasma was formed in each measurement on the smooth surface of the target and not on the crater formed during the previous measurement, this could influence the intensity of the spectral lines and could lead to the destruction of the sample. The chamber was readied to generate the plasma with the target in vacuum ($\approx 6.6 \text{ Pa}$).

A 1-m Czerny–Turner spectrometer, range 1900–7000 Å, is equipped with a 2400 grooves/mm holographic grating, and a 50-μm external slit, equipped with a gated optical multichannel analyzer (OMA III EG&G PARC), which allowed the detection of each spectrum and its digital recording for later numerical analysis. The computer has a card used for communications, through which the communication is made with the central unit OMA. From this, the computer has been programmed the whole process of acquisition of data from the OMA and has been received the spectrum, after the end throughout the measurement process. It has a time resolution, with a minimum duration of the time window of 100–200 ns, and the spectral band detected by the device is about 100 Å. This system allowed

recording of spectral regions at different delays after the laser pulse and during a selected time interval. The Pb I, Pb II, Pb III, and Pb IV spectral lines were recorded and various fragments of molecular bands of N₂ and N₂⁺ also appear, at short delays. The spectral lines have been obtained in the wavelength range from 2000 to 7000 Å.

The chamber features a quartz window that lets through the light that is sent to the spectrometer entrance slit, located 8 cm from the plasma. Therefore, the radiation emitted by the plasma is collected directly by the entrance slit of the spectrometer, that is to say, we have integrated the emission along the line of sight. The measurements consist in the accumulation of 15 laser pulses at a delay time and were obtained, after ablative cleaning the target for two laser pulses in order to remove impurities. The temperature, electron number density, and time evolution of laser-produced plasma can be controlled. The relative spectral response of the experimental system has been determined by using a calibrated deuterium lamp (2000–4000 Å range) and a calibrated quartz-tungsten lamp (3500–7000 Å range) with the same experimental conditions that were used in the measurements (reaching the maximum efficiency of the system in the range 3500–4500 Å, system sensitivity goes from 4%, in 2400 Å, to 60%, in 4400 Å). The estimated error of this

measurement was about 3%. More details about the calibration of the system can also be found in previous work.^[6,12,14]

The measurements were repeated at several delay times (in the range of 100–400 ns, delay from the laser pulse) and at a fixed gate time of 100 ns. The analysis of the spectra was made by fitting the observed line, to numerically generated Voigt profiles and, with them, make de-convolution to obtain the Lorentzian and Gaussian profiles, the instrumental profile is convoluted into the resulting profile. The instrumental profile needed for the numerical analysis of each spectrum was determined from the observation of several narrow spectral lines emitted by a hollow-cathode lamp. This instrumental profile ($\Delta\lambda_{\text{instrumental}}$) has been Voigt profile full width of half maximum (FWHM) = 0.30 Å, (Gaussian FWHM = 0.19 Å, and Lorentzian FWHM = 0.17 Å. for a wavelength of 3900 Å). Each spectrum is the average of five spectra at five different positions on the target little differences were observed between the five collected spectra, so an error of 5%.

To fit the emission line profiles in the analysis and obtain relative intensity and the FWHM, a software tool has been used that is able to numerically generate Voigt profiles, the convolution of the Lorentzian profile from the Stark broadening with the Gaussian profile from Doppler and instrumental broadening, by an analytical function. For the diagnostic of the plasma, the area under each line profile from the aforementioned fitting represents the relative intensity. The line intensities were obtained by subtracting the background intensity. The investigated spectral lines, in this work, were well isolated from other spectral lines emitted by this plasma. We have obtained a good reproducibility ($\approx 3\%$) of the investigated spectral line radiation intensities.

To study the homogeneity of the plasma, the same experimental system was used, but in order to have spatial resolution, the light was focused by means of a lens on a 1 mm light guide being able to select the point of the plasma from which the light emission was observed. The lens and optical fiber connector have been mounted on a telescopic spring that allows one to vary their relative distance to coincide with the focus distance of the image of the plasma. The support was mounted on an optical bench, allowing movement horizontally and vertically in a controlled manner, thereby varying the area of plasma whose image is detected in the optical fiber. The measurement was taken by scanning the plasma emission in two perpendicular directions; through the axis of the plasma with a distance from the blank in the 0.2–2.7 mm range to study the evolution of the plasma in space, and parallel to the surface of the target with a radial distance in the range of 0–1.1 mm, to determine where the different lead atomic species are located in the plasma and to determine the real values of the parameters of the plasma (intensities, widths of spectral lines, temperature and electron number density), more details about this procedure can be found in references.^[6,13,14] It is well known that from the experimental point of view, space resolved characterizations are difficult due to the small size of laser-induced plasmas and their fast expansion dynamics.

Local profiles were obtained after Abel inversion of the integrated intensity.^[18,19]

The high density of particles forming the plasma is not always an advantage because if transitions are studied whose lower level has a high population density, the spectral lines observed may have self-absorption, it is a priority to verify whether in line the self-absorption is present. Estimation of the absorption coefficient of all the lines studied will be shown in a later discussion.

Results and discussion

In this work, all experiments were carried out using a 7-ns laser pulse from an Nd:YAG, already mentioned, which has always been focused on the same lead target (99.99% Pb and 0.01% Ca) in vacuum, and the accumulation of 15 laser pulses in each delay time. Use of pulses multiple and the variables of laser used in this work, as well as the environment (≈ 6.6 Pa vacuum), induce deep modifications in the plasma dynamics and, consequently, in the emission. How is it known, when a laser beam is focused on a solid, the temperature of the locally heated region grows rapidly up to the threshold of vaporization and, if the laser power density exceeds a certain critical value that it depends on the test sample, it triggers a chain of ionization phenomenon, the breakdown, which involves the formation of a plasma. This plasma is formed from excited atoms, ions, electrons, and fragments of molecules, as will see in this work.

LIP is a dynamic system in which all the energy is delivered by the laser pulse and then the system evolves spontaneously before reaching equilibrium with the surrounding environment. Adiabatic expansion of the plasma in three dimensions occurs after termination of the laser pulse this is a conversion of thermal energy into kinetic energy of elements in the plasma. The process is accompanied by a detonation due to the shockwave caused by rapid heating of the ambient surrounding, there being some controversy on the mechanisms leading to excitation and ionization of the ambient during laser plasma generation.^[27] Subsequently, the plasma tends to cool, they are listed the spectra line emission characteristics of transition between bound states, already present in the first instants of the plasma formation, but not observable, by continuous radiation that can be related to the changes of plasma number density.^[27,28] To understand the detailed aspects of laser beam interaction with the target material and recombination processes following the laser ablation, the time-resolved studies of the emission spectra from the plasma offer convenient approach. Spectra emitted by the excited species, neutrals, and ions, and molecules are used to develop quantitative and qualitative analytical information.

It is known that the lifetime of LIP mainly depends on the amount of energy that the laser deposits, as well as the type of the surrounding ambient. The ambient surrounding is a significant factor affecting the ablation process and the properties of plasma; its alteration can change the observed LIPs spectra, and improve such as great, the resolution signal intensity, and overall signal-to-noise ratio (S/N). These

changes are displayed by different spectroscopic peculiarities. For each spectral interval considered and at each instant of the plasma life, the optical emission was detected and analyzed. In order to investigate the time evolution of excited plasma species, we have recorded spectra in the 2000–7000 Å range.

Plasma emission and spectral line analysis

By the analysis of the spectrum, we can see that at the early stages of plasma evolution (first nanoseconds after the laser pulse, $\ll 100$ ns), the amount of energy radiated in form of the continuous spectrum is far greater than the energy radiated by the line spectrum, that is to say, the continuum emission, that dominates over lines emission, is high due to mechanisms involving free electrons, inverse Bremsstrahlung, radiative recombination, and photoionization. In general continuum radiative is due to two processes: Bremsstrahlung and radiative recombination, for the most of the time the continuum emission is detectable, it is the result radiative recombination. The plasma is mainly constituted of ions, atoms, and electrons. The Bremsstrahlung process in plasmas is due to the deceleration of electrons as they pass close to ions. The electron kinetic energy is mainly given by the absorption of laser photons through the inverse Bremsstrahlung mechanism. Adiabatic expansion of the plasma plume occurs after termination of the laser pulse, this is a conversion of thermal energy into kinetic energy of elements the in plasma plume. In general, continuum radiative is due to two processes: Bremsstrahlung and radiative recombination, and that for the most of the time in that the continuum emission is detectable, it is the result radiative recombination, see the detailed study in de Giacomo and Hermann^[2] and de Giacomo et al.^[29]

So, we cannot obtain accurate information about atoms, ions, and fragments of molecules because of the overwhelming continuum emission for short delay times (≈ 100 – 150 ns). The presence of molecular species in the plasma critically depends on the dissociation energy that is the minimum energy to be delivered to separate both atoms from the ground state of the molecule.^[2] At these early times, the electron density is very high and spectral lines of the different species (in this work, atom, and ions of lead) are broadened by the Stark effect due to the electron collisions. The density of the plasma is close to that of the irradiated target. At longer times of the plasma expansion, the spectral lines become narrower, indicating a decrease of the electron density. Discrete emission lines are detectable only after a certain delay time from the laser pulse. The temperature decreases rapidly with plasma expansion, inducing recombination and decreasing the number of heavy particles (atoms, ions, and molecules). The peak widths and profiles in lines spectra are primarily dictated by the temperature and electron density of plasma. It is well known that one approach to the measurement of both electron density and electron temperature is the observation of line and continuum emission intensity, the line to continuum ratio method. In this method, the ratio of the emission intensity

of an atomic line to the emission intensity of the spectrally adjacent continuum, is indicative of electron temperature, while the absolute intensity of the continuum is indicative of the electron density. Although it is also well known that one of the problems encountered with continuum emission measurements of plasmas is that the spectral observation region should not contain any atomic, ionic, or molecular emission, see for more detail in Bastiaans and Mangold.^[30]

Under the conditions considered in this work, the emission spectrum of the lead plasma, in vacuum, consist mainly emission lines of Pb I, Pb II, Pb III, Pb IV, and also fragments of molecules the N_2 (second positive system, $C^3\Pi_u^+$ and $B^3\Pi_g^+$ electronic states at 11.1 eV and 7.39 eV, respectively) and N_2^+ (first negative system, $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ electronic states at 18.7 eV and 15.6 eV, respectively) systems, corresponds to radiative transitions between covering the spectral range of 2000–7000 Å, ambient nitrogen molecules. Also, some spectral lines of Ca II appear since the calcium is an impurity in the sample. Have been observed at different delay times (100–9000 ns), after the laser pulse, and are displayed for several spectral ranges in Figures 1–5 (where is appreciated in detail how the plasma evolution). From the observation of the figures, it is possible to check that in at early delay times there is continuum radiation high, then appear more ionic lines (they have higher ionization energy than atomic ones), and also some atomic lines appear, that subsequently to at longer delay times also become more evident. As we have already mentioned above, in order to extract useful spectroscopic information from plasma, one needs to understand how the shapes of spectral lines evolve with time. In this work, when LTE conditions can be applied, the population of the linked states follow a Boltzmann–Maxwell distribution can be used as a first approximation to determine the temperature and electron number density of the plasma in the different delay times.^[16–20]

Figures 1–4 gives an overview of the plasma evolution. In Figure 1, the emission spectrum of lead plasma are displayed for the spectral range of 3690–3790 Å, obtained at four different delay times (150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively). Figure 1(a) shows the emission spectra obtained at 150 ns after the laser pulse, at this very early stage of plasma the plume emits a strong continuum radiation (intensity ~ 70 counts channel⁻¹), as we have previously referred, due to mechanisms involving free electrons. Also, we highlight observe two molecular bands of N_2 , the N_2 (2,4) emission (at 3710.5 Å, head of band ~ 195 counts channel⁻¹), and the N_2 (1,3) emission (at 3755.4 Å, head of band ~ 456 counts channel⁻¹), an spectral line of Pb I, the line 3739.93 Å ($6s^2 6p ({}^2P_{1/2}) 7s {}^3P_2 \rightarrow 6p^2 {}^1D_2$), two spectral lines of Pb II, the line 3713.98 Å ($6s^2 ({}^1S) 8d {}^2D_{5/2} \rightarrow 6s^2 ({}^1S) 7p {}^2P_{3/2}$) and the line 3785.9 Å ($6s^2 ({}^1S) 5f {}^2F_{5/2} \rightarrow 6s 6p^2 {}^4P_{5/2}$) and two spectral lines of Pb III, the line 3728.69 Å ($6s ({}^2S) 8s {}^3S_1 \rightarrow 6s ({}^2S) 7p {}^3P_1$) and the line 3736.06 Å ($6s ({}^2S) 5g {}^1G_4 \rightarrow 6s ({}^2S) 5f {}^1F_3$). That is to say, first, a continuum emission, N_2 molecules are observed and atomic and ionic lines that they begin to be detectable. All the emission lines appear distorted, little intense, that warn us

Figure 2. Emission spectrum of laser-induced lead plasma, using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns in vacuum, at different delay times: 150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively. Observation of the time evolution of plasma in order to investigate the time evolution of excited plasma species showing predominantly the spectral lines of Pb III and Pb IV and band fragment of N_2^+ (0,0) of the spectral region from 3895 to 3995 Å.

of possible self-absorption (although there is nothing to distinguish a line, which is only moderately absorbed, from one line free from self-absorption; it is well known that self-absorption will have the effect of distorting and especially of broadening lines and will, therefore, produce an apparently large width) superposed on the continuous signal. We observe that continuum emission have intensity ~ 70 counts channel^{-1} as we have already mentioned, in front of the spectral lines that appear, see example the line more intense that it appears is 3736.06 Å of Pb III with intensity < 190 counts channel^{-1} . Interference of molecular bands with spectral lines may prevent accurate line intensity measurements. Line 3739.93 Å of Pb I has large upper state excited energy, $E_i = 5.974$ eV ($48,188.67$ cm^{-1}), 9.163 eV ($73,901$ cm^{-1}) ionization limit, that will experience a sharp decrease in population as the plasma cools, emerges over the band fragment of N_2 (1,3), being difficult to measure.

Figure 1(b) shows the emission spectra obtained at 200 ns after the laser pulse; it is observed that continuum emission decreases, pass to intensity ~ 35 counts channel^{-1} , in front of the spectral lines that appear. The two molecular bands of N_2 decreases and that all the spectral lines increase in intensity. Also, it is observed that the spectral line 3706.02 Å ($6s$ (2S) $8s$ $^3S_1 \rightarrow 6s$ (2S) $7p$ 3P_0) of Pb III and the spectral line 3718.03 Å ($6s^2$ (1S) $9s$ $^2S_{1/2} \rightarrow 6s^2$ (1S) $7p$ $^2P_{1/2}$) of Pb II.

Figure 1(c), shows the emission spectra obtained at 300 ns after the laser pulse; it is observed that continuum emission decreases, pass to ~ 10 counts channel^{-1} , in front of the spectral lines that appear, that is to say, the line profile becomes narrower with time. The two molecular bands of N_2 they have practically disappeared, see example the N_2 (1,3) emission (at 3755.4 Å head of band 13 counts channel^{-1}), on the continuum. Also, all the spectral lines of Pb III decrease in intensity, conversely the line intensities of Pb I and Pb II increase. Figure 1(d) shows the spectra obtained at 400 ns after the laser pulse; we observed that continuum emission decreases, ~ 8 counts channel^{-1} , in front of the spectral lines that appear. The two molecular bands of N_2 they have disappeared, the lines of Pb III continue to decrease and those lines of Pb I to Pb II increase in intensity are thin and well resolved strong and sharp. Therefore, it is noticed that the continuous signal is weakening quickly according to the plasma and getting colder, on the contrary, the peaks of lines persist for longer times.

In Figure 2, the emission spectrum of lead plasma is displayed for the spectral range of 3895–3995 Å, obtained at four different delay times (150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively). Figure 2(a) shows the emission spectra obtained at 150 ns after the laser pulse, continuum radiation (intensity ~ 50 counts channel^{-1}), it is observed a

Figure 3. Emission spectrum of laser-induced lead plasma, using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns in vacuum, at different delay times: 150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively. Observation of the time evolution of plasma in order to investigate the time evolution of excited plasma species showing predominantly the spectral lines of Pb II and Pb III and band fragment of N_2^+ (1,2) and of N_2^+ (0,1) of the spectral region from 4200 to 4300 Å.

spectral line of Pb III, the line 3951.92 Å ($6s\ (^2S)\ 7p\ ^1P_1 \rightarrow 6s\ (^2S)\ 6d\ ^1D_2$) and spectral line of Pb IV, the line 3962.48 Å ($5d^9\ 6s\ 6p\ [16^\circ]_{1/2} \rightarrow 5d^{10}\ (^1S)\ 6d\ ^2D_{3/2}$). From the observation of the figure, it is possible to see that ionic line Pb IV is evident. Observing this line is important since it allows us to measure its Stark width, also observed excited N_2^+ molecules, watch (0,0) band head intensity of N_2^+ at 3914.4 Å head of band, intensity ~ 1095 counts channel^{-1} . Figure 2(b) shows the spectra obtained at 200 ns after the laser pulse; it is observed that the emission of the continuum, the intensity of the molecular band of N_2^+ decreasing, and the line of Pb IV also. Figure 2(c,d) shows the emission spectra obtained at 300 ns and 400 ns after the laser pulse, respectively. The molecular band of N_2^+ continues to decrease (intensities ~ 80 counts channel^{-1} and ~ 25 counts channel^{-1} , respectively), that the spectral line 3951.92 Å of Pb III, at 400 ns after the laser pulse, and the spectral line 3962.48 Å of Pb IV they have disappeared and that the resonant lines of Ca II (impurities) begin to appear.

In Figure 3, the emission spectrum of lead plasma are displayed for the spectral range of 4200–4300 Å, obtained at four different delay times (150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively). Figure 3(a) shows the emission spectra obtained at 150 ns after the laser pulse, continuum radiation (intensity ~ 50 counts channel^{-1}), it is observed a

two spectral lines of Pb II, the line 4242.14 Å ($6s^2\ (^1S)\ 5f\ ^2F_{5/2} \rightarrow 6s^2\ (^1S)\ 6d\ ^2D_{5/2}$) and the line 4244.92 Å ($6s^2\ (^1S)\ 5f\ ^2F_{7/2} \rightarrow 6s^2\ (^1S)\ 6d\ ^2D_{5/2}$) and an spectral line of Pb III, the line 4272.66 Å ($6s\ (^2S)\ 7p\ ^1P_1 \rightarrow 6s\ (^2S)\ 7s\ ^1S_0$), also observed two molecular band of N_2^+ , the N_2^+ (1,2) emission, 4236.5 Å, head of band 366 counts channel^{-1} , and the N_2^+ (0,1) emission (at 4278.13 Å, head band 1624 counts channel^{-1}). Figure 3(b) shows the emission spectra obtained at 200 ns after the laser pulse, it is observed that the molecular bands decrease in intensity while the intensities the lines of Pb II and Pb III grow. Figure 3(c,d) shows the emission spectra obtained at 300 ns and 400 ns after the laser pulse, respectively, it is observed that the intensities of the lines of Pb II continue to grow while the line 4272.66 Å of Pb III is decreasing.

In Figure 4, the emission spectrum of lead plasma are displayed for the spectral range of 2390–2490 Å, obtained at four different delay times (150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively). Figure 4(a) shows the spectra obtained at 150 ns after the laser pulse, it is observed a strong continuum emission that persists to 300 ns where several lines of Pb I begin to appear with little intensity, the line 2401.94 Å ($6s^2\ 6p\ (^2P_{1/2})\ 7s\ ^1P_1 \rightarrow 6p^2\ ^3P_1$) and the line 2476.77 Å ($6s^2\ 6p\ (^2P_{1/2})\ 8s\ ^3P_1 \rightarrow 6p^2\ ^3P_1$), see Figure 4(b). In Figure 4(c), at 400 ns after the laser pulse, and Figure

Figure 4. Emission spectrum of laser-induced lead plasma, using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns in vacuum, at different delay times: 150 ns (a), 200 ns (b), 300 ns (c), and 400 ns (d), respectively. Observation of the time evolution of plasma in order to investigate the time evolution of excited plasma species showing predominantly the spectral lines of Pb I of the spectral region from 2390 to 2490 Å.

4(d), at 600 ns after the laser pulse, it is observed that spectral lines of Pb I, the line 2393.79 Å ($6s^2 6p ({}^2P_{1/2}) 7d {}^3F_3 \rightarrow 6p^2 {}^3P_2$), the line 2401.94 Å ($6s^2 6p ({}^2P_{1/2}) 7s {}^1P_1 \rightarrow 6p^2 {}^3P_1$), the line 2443.82 Å ($6s^2 6p ({}^2P_{1/2}) 8s {}^3P_0 \rightarrow 6p^2 {}^3P_2$), the line 2446.18 Å ($6s^2 6p ({}^2P_{1/2}) 8s {}^3P_1 \rightarrow 6p^2 {}^3P_1$), and the line 2476.77 Å ($6s^2 6p ({}^2P_{1/2}) 8s {}^3P_1 \rightarrow 6p^2 {}^3P_1$) with low intensities due to poor spectral response of the experimental system used, in that spectral region.

It is noticed that the amount of energy radiated in form of the continuum emission is far greater than the energy radiated by the atomic/ionic spectral lines, at these short delay times and that during the expansion the energy emitted by the continuum gradually decreases. Ionic lines appear first, Pb III, and Pb IV because they have higher ionization energy. The intensity of the molecular bands decreases, and the intensities of the atomic/ionic lines present increase. Being the Pb III and Pb IV emission persistence the shortest among the atomic/ionic species. In Figures 1–4, it is observed that for short delay times (150–300 ns) as a consequence of the limitation in number of excited levels due to the high density effect, the population of the low energy levels is overestimated in comparison to that of the high energy levels along the optical path during the detection time, it is well known that after the pulse laser, the LIP is in

recombination stage.^[2,3,27,29] It is also possible to observe that during the expansion, when the electron number density decreases, emission lines stark rise up from the continuum radiation spectrum while the continuum exponentially decreases and that more lines appear. It is noticed that the lines obtained of neutral lead atoms are thin and well resolved strong and sharp, whereas those of the singly ionized lead ions are broad and variable-lived. It is noticed that the maximum intensity of the spectral lines is reached after a characteristic time, depending on the species and that the intensities of lines are decreasing at longer times after the pulse laser.

In this work, it is, especially important, noticed that the molecular bands of N_2 and N_2^+ molecules were essentially they present in early times, <100–400 ns, ceasing to be observed around the 400 ns and, decreasing in intensity, staying, for example (0,0) band head intensity of N_2^+ at 3914.4 Å head of band, ~ 29 counts channel⁻¹. From the 400 ns up to 9 000 ns, after the laser pulse, LIP can be considered an atomic plasma. When the plasma is disappearing, for long delay times, there is some molecular bands with very low intensity, as you can see at 9000 ns after laser pulse, whereas the several atomic and ions lines of lead were observed about him the continuum since the 100 ns and

Figure 5. Emission spectrum of laser-induced lead plasma, using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns in vacuum. Shown of typical spectrum of lead plasma, obtained at 9000 ns delay time covering the spectral regions (a) of 3690–3790 Å, (b) of 3895–3995 Å, and (c) of 4200–4300 Å. Observation of the time evolution of plasma in order to investigate the time evolution of excited plasma species.

lasting up to 9000 ns after laser pulse, where the plasma is already colder. In Figure 5, it is shown that the emission spectrum of lead plasma obtained at 9000 ns delay time covering the spectral regions (a) of 3690–3790 Å, (b) of 3895–3995 Å, and (c) of 4200–4300 Å. The line 3739.93 Å of Pb I that begins to appear above continuum emission from 100 ns time delay and it lasts until 9000 ns and the two molecular bands of N_2 not observed, seen in Figure 5(a). In Figure 5(b,c), the two molecular bands of N_2^+ if they observed with low intensity if along with the resonant lines of Ca I and Ca II (calcium is an impurity of the sample used). The resonant lines of Ca II appear at 400 ns of delay (with very little intensity) and remain until the 9000 ns of delay while the line 4226.7 Å of Ca I that appears from 800 ns remains until 9000 ns of delay, see Figure 5. The presence of impurities will influence the accuracy the measured temperature in the corresponding delay times; this has not been the subject of study in this work. The spectral lines of Pb II reach their maximum intensity at 400 ns, disappearing at 2500 ns. It is importantly noticed that alone some lines of Pb I and Pb II lasts until 9000 ns. In 9000 ns after the laser pulse, the already colder plasma, the lines of the different species have large upper state excited energies that will experience a sharp decrease in population as the plasma cools. The observation of the two molecular bands of N_2^+ , with low intensity, neither was not the subject of study in this work.

There are authors^[30,31] who say that, for plasma to reach LTE, there is an important requirement, where atoms in the plasma only exist in significant populations for two

successive stages of ionization. In the spectra obtained in this work, see Figure 1(a) at 150 ns from the laser pulse, several spectral lines of Pb I, Pb II, and Pb III appear and in Figure 2(a) also spectral lines of Pb III and Pb IV. This requirement is met from 400 ns after the laser pulse where there are only lines of Pb I and Pb II, we will analyze and study all these later. The lines ions or atomic are mainly emitted from the hot plasma core, while molecular band emission originates from the cold plasma periphery, where the atomic emission is reabsorbed.^[2,4,27,29,30] There are several studies on the formation of molecules in laser plasma, see the previous works,^[27,32–34] for example; and, recently,^[35] studies suggested that a strong influence of chemical reactions on the angular distribution of species within the ablation plume and that in his analyses indicate that chemical reactions occur mostly in the plasma periphery where the temperature is low.^[33] Harilal et al.^[27] comment that the generation of molecular excitation and emission (N_2 , N_2^+) occur through various mechanisms, being one possible mechanism the heating of the ambient gas and corresponding excitation of molecular species by the shock wave propagating outward from the laser breakdown. Other mechanism is excitation of the surrounding medium via UV radiation produced by the spark. Also, it is assumed to be formed these molecules during spark cooling. Studies are beyond the scope of this work.

As we have already mentioned, the measurements were repeated at several delay times from the laser pulse 150 to 400 ns. The electron density and electron temperature have

Table 1. Spectral lines parameters of Pb I, Pb II, Pb III, and Pb IV used in the determination of the excitation temperature including wavelengths.

Specie	Transition	λ (Å)	E_i (eV)	E_j (eV)	A_{ij} ($\times 10^7$ s $^{-1}$)
Pb I	<i>Ionization Limit</i> 9.163 eV				
	5d ¹⁰ 6s ² 6p (² P _{1/2}) 7s ³ P ₁ → 5d ¹⁰ 6p ² ³ P ₁	3639.57	4.375	0.969	3.08 ± 0.20 ^a
	5d ¹⁰ 6s ² 6p (² P _{1/2}) 7s ³ P ₁ → 5d ¹⁰ 6p ² ³ P ₂	4057.90	4.375	1.320	10.80 ± 0.75 ^a
	5d ¹⁰ 6s ² 6p (² P _{1/2}) 7s ³ P ₂ → 5d ¹⁰ 6p ² ¹ D ₂	3739.93	5.974	2.660	5.33 ± 0.34 ^a
	5d ¹⁰ 6s ² 6p (² P _{1/2}) 7s ³ P ₂ → 5d ¹⁰ 6p ² ³ P ₁	2476.40	5.974	0.969	3.65 ± 0.23 ^a
	5d ¹⁰ 6s ² 6p (² P _{1/2}) 8s ³ P ₁ → 5d ¹⁰ 6p ² ³ P ₁	2446.18	6.037	0.969	2.45 ± 0.15 ^a
	5d ¹⁰ 6s ² 6p (² P _{1/2}) 7s ¹ P ₁ → 5d ¹⁰ 6p ² ³ P ₁	2401.94	6.130	0.969	3.01 ± 0.20 ^a
	5d ¹⁰ 6s ² 6p (² P _{1/2}) 7d ³ F ₃ → 5d ¹⁰ 6p ² ³ P ₂	2393.79	6.496	1.320	6.31 ± 0.38 ^a
Pb II	<i>Ionization Limit</i> 15.032 eV				
	5d ¹⁰ 6s ² (¹ S) 5f ² F _{5/2} → 5d ¹⁰ 6s ² (¹ S) 6d ² D _{5/2}	4242.14	11.472	8.550	0.98 ± 0.10 ^b 0.93 ± 0.09 ^c
	5d ¹⁰ 6s ² (¹ S) 5f ² F _{7/2} → 5d ¹⁰ 6s ² (¹ S) 6d ² D _{5/2}	4244.92	11.470	8.550	11.50 ± 1.16 ^b 11.21 ± 1.68 ^c
	5d ¹⁰ 6s ² (¹ S) 5f ² F _{5/2} → 5d ¹⁰ 6s ² (¹ S) 6p ² P _{3/2}	3785.90	11.472	8.198	1.01 ± 0.10 ^b 0.96 ± 0.14 ^c
	5d ¹⁰ 6s ² (¹ S) 9s ² S _{1/2} → 5d ¹⁰ 6s ² (¹ S) 7p ² P _{1/2}	3718.30	12.565	9.232	1.20 ± 0.20 ^b 1.75 ± 0.28 ^c
Pb III	5d ¹⁰ 6s ² (¹ S) 8d ² D _{5/2} → 5d ¹⁰ 6s ² (¹ S) 7p ² P _{1/2}	3713.98	12.918	9.232	4.19 ± 0.62 ^b
	<i>Ionization Limit</i> 31.937 eV				
	5d ¹⁰ 6s (² S) 7p ¹ P ₁ → 5d ¹⁰ 6s (² S) 6d ¹ D ₂	3951.92	21.968	18.831	0.88 ± 0.095 ^d
	5d ¹⁰ 6s (² S) 7p ¹ P ₁ → 5d ¹⁰ 6s (² S) 7s ¹ S ₀	4272.66	21.968	19.067	4.8 ± 0.55 ^d
	5d ¹⁰ 6s (² S) 8s ³ S ₁ → 5d ¹⁰ 6s (² S) 7p ³ P ₀	3706.02	24.536	21.191	6.9 ± 0.83 ^d
	5d ¹⁰ 6s (² S) 8s ³ S ₁ → 5d ¹⁰ 6s (² S) 7p ³ P ₁	3728.69	24.536	21.211	14.3 ± 1.5 ^d
	5d ¹⁰ 6s (² S) 5g ¹ G ₄ → 5d ¹⁰ 6s (² S) 5f ¹ F ₃	3736.02	26.986	23.669	28.6 ± 3.0 ^d
Pb IV	<i>Ionization Limit</i> 42.322 eV				
	5d ⁹ 6s 6p [¹⁶ °] _{1/2} → 5d ¹⁰ (¹ S) 6d ² D _{3/2}	3962.48	26.010	22.882	11.0 ^e
	5d ⁹ 6s 6p [¹⁶ °] _{1/2} → 5d ¹⁰ (¹ S) 7s ² S _{1/2}	4049.80	26.010	22.949	11.0 ^e

Kramida et al. NIST database,^[43] lower (E_j) and upper (E_i) energy levels, Moore,^[42] and transition probability (A_{ij}). All transition probabilities are collected from: (a) Alonso-Medina et al.,^[13] (b) Alonso-Medina,^[40] (c) Alonso-Medina,^[39] (d) Alonso-Medina,^[5] and (e) Alonso-Medina et al.^[41]

been measured at said delay times. The line profile becomes narrower with time and, that from 300 to 400 ns following the laser pulse, the emission lines show the excited level population in a Boltzmann form, in agreement with about the LTE.

The molecules can be used to obtain electron temperature and electron number density of the plasmas at delay times of 100–200 ns, the first negative system of N₂⁺ and second positive system of N₂ considerably dominate the spectrum from 3300 to 4800 Å, and there is extensive literature on its molecular parameters, has not been the aim of this work. In this work, we use lead spectral lines since the molecules are in the periphery of the plasma and would not be suitable for the characterization of the nucleus of the lead plasma. The presence of molecular species in the plasma depends on many factors as we have commented previously.

The self-absorption phenomenon can affect a emission lines in a spectrum and is larger around the peak of the emission the line intensity at the peak decreases while the full width at half maximum (FWHM) increases. A suitable choice of some spectral lines that are free from self-absorption they allow us the calculation of both temperature and density of the plasma. The effect of self-absorption depends on the population of the lower level of the transition and therefore is in general particularly evident for lines emitted by the major elements in the plasma and for transition ending at the fundamental level. Self-absorption occurs when the outermost cold layers of the plasma absorb part of the radiation emitted by the innermost layers and its effect is accentuated, as we have indicated, in the resonant transitions of atoms and ions. A way to verify that the lines used are not self-absorbed is to choose lines that do not end at the fundamental level, since if you study transitions whose

lower level has a high population density, the observed lines can present self-absorption. All spectral lines used in this study have high energies in the excited upper level; values are presented in Table 1.

Another way to verify is, for example, using two emission lines from a species that have the same level of higher energy and check that the ratio of their intensities does not change, in the different time delays, and be the same as the ratio of the corresponding transition probabilities. That is the known method, *two-line method*, of checking line intensity ratios within multiplets which are expected to adhere to LS-coupling.^[36] Technique is straight forward, very simple to apply, but it can be used only as an indicator whether self-absorption is present. This has been check in all possible cases, in this work, see as an example: (i) I_{3739.93 Å Pb I}/I_{2476.40 Å Pb I} = 1.45 at 200 ns delay time, I_{3739.93 Å Pb I}/I_{2476.40 Å Pb I} = 1.48 at 300 ns delay time, I_{3739.93 Å Pb I}/I_{2476.40 Å Pb I} = 1.46 at 400 ns delay time; (ii) I_{3785.99 Å Pb II}/I_{4242.14 Å Pb II} = 1.055 at 150 ns delay time, I_{3785.99 Å Pb II}/I_{4242.14 Å Pb II} = 1.06 at 200 ns delay time, I_{3785.99 Å Pb II}/I_{4242.14 Å Pb II} = 1.07 at 300 ns delay time, I_{3785.99 Å Pb II}/I_{4242.14 Å Pb II} = 1.06 at 400 ns delay time and, (iii) I_{4272.60 Å Pb III}/I_{3951.92 Å Pb III} = 5.199 at 150 ns delay time, I_{4272.60 Å Pb III}/I_{3951.92 Å Pb III} = 5.187 at 200 ns delay time, I_{4272.60 Å Pb III}/I_{3951.92 Å Pb III} = 5.190 at 300 ns delay time.

The absence of self-absorption effect on emission line intensities has been checked using a method described by Thorne.^[37] The degree of self-absorption can be explained by the self-absorption coefficient maximum for each line, $k(\lambda)$. With the obtained values of N_e in each plasma, we can calculate $k(\lambda)$ for the studied lines. The parameter that measures the importance of this effect is called the “optical thickness” of the line and is denoted a $k(\lambda)D$. In fact, the

ratio between the observed intensity and the one emitted by optically thin plasma was calculated (the condition being that the optical depth is much lower than 1).^[37,38]

$$k(\lambda) \times D(\text{cm}) \ll 1 \quad (1)$$

D is the physical length of the plasma, the value of the optical depth $k(\lambda)D$ are not in excess of 0.1. The lines studied in this work self-adsorption was negligible, we can consider that the experiment was carried out in optically thin plasma. For example, for the experimental plasma thickness of 1 mm, the aforementioned criterion was extensively fulfilled since the line 3962.48 Å of Pb IV, $k(\lambda)D=0.02$, the line 3951.92 Å of Pb III, $k(\lambda)D=0.018$, the line 4244.92 Å of Pb II, $k(\lambda)D=0.019$, and 4057.90 Å of Pb I, $k(\lambda)D=0.03$, at 200 ns delay time. Recall that the spectral line 4057.90 Å of Pb I corresponds to a transition whose lower level has a high population density.

Determination of the plasma temperatures and electron number densities

As mentioned previously, in order to get further details about the time evolution of the plasma obtained, in vacuum conditions, the temperature (T) and the electron number density (N_e) are very important parameters and their knowledge very useful for their characterization time. Temperature measurements are necessary during its entire useful life. When LTE conditions can be applied, the population of the linked states follow a Boltzmann distribution, which can be used as a first approximation to determine the temperature of the plasma in the different delays.^[16–20] The excitation temperature was measured using the Boltzmann plot is described below, and the Saha's equation for determining the ionization temperature. LTE plasmas are characterized by a single temperature the energy distribution of all species and degrees of freedom; in systems which are far from LTE, the use of increasingly higher excited levels ensures the assumption. Assuming the existence of LTE, electron number density, and temperature in LIP can be calculated by solving Saha's equation.

As is well known, in optically thin, the relative line intensities (I_{ij}^λ) of the lines emitted from a given state of excitation can be used to calculate the temperature, if the transition probabilities (A_{ij}) are known, using the following expression:^[16,17,19,20]

$$I_{ij}^\lambda = \frac{A_{ij}g_i}{U(T)} \text{Nexp}\left(\frac{-E_i}{kT}\right) \quad (1)$$

$$\ln\left(\frac{I_{ij}^\lambda}{A_{ij}g_i}\right) = \ln\left(\frac{N}{U(T)}\right) - \frac{E_i}{kT}, \quad (2)$$

for a transition from an upper state i to a lower state j , I_{ij}^λ represents the measured integral line intensity in counts s^{-1} , A_{ij} is the transition probability, λ is the wavelength of the transition, E_i is the excited level energy, and g_i is the energy and statistical weight of level i , $U(T)$ is the atomic species partition function, N is the total density of emitting atoms,

k is the Boltzmann constant, and T is the excitation temperature in K. If we were to plot $\ln(I_{ij}^\lambda/g_i A_{ij})$ vs. E_i , for lines of known transition probability (Boltzmann plot), the resulting straight line would have a slope $-1/kT$ and therefore the temperature can be obtained without having to know the total density of atoms or the atomic species partition function. For this purpose, the total intensity must be determined for each spectral line.

Measurement of the intensities of a series of lines from different excitation states of the same species allows evaluation of the plasma temperature, provided that the A_{ij} and g_i are known. The temperature has been estimated, in each delay time, using different spectral lines of Pb I, Pb II, and Pb III, tabulated in Table 1, which, as already mentioned, is not absorbed. Using being better to use spectral lines with transitions states involving upper-level states that which lie close to the ionization energy level (*ionization limit*). The use of several different lines instead of just one pair leads to greater precision of the plasma temperature determination. So, the estimates values of excitation temperatures have been obtained from the relative intensities, I_{ij}^λ , obtained in the measurements in the different delays, and the A_{ij} corresponding for this lines that have been taken from the bibliography.^[5,13,39–41] The spectral lines were selected according to the following criteria: (i) the overlapping of spectral lines has to be avoided, (ii) it is very important to use lines high A_{ij} values, (iii) the emission intensity must be large enough to ensure the observation with a sufficiently large signal-to-noise intensity ratio, (iv) self-absorption does not appear, and (v) that the lines must have a weak enough optical thickness to have a significant correlation between elemental concentration and line intensity. The accuracy of the temperature obtained is chiefly dependent upon the accuracy of the parameters used. The energies of the different levels are those of Moore^[42] and the wavelengths corresponding are those of NIST database.^[43] The ionic temperature gives a better estimate of the electron temperature while the atomic temperature underestimates it. Some authors argue that atomic lines should not be used for LIP diagnostic as they are affected by recombination processes.^[29] Boltzmann plots for temperatures, obtained in different delay times (150–400 ns), are presented in Figures 6–9, where the errors were estimated from the standard deviation of the slopes obtained in the least squares fittings, the uncertainties that are taken into account are (a) the line profile fitting procedure ($\leq 1\%$), (b) the relative line intensity determination ($\leq 2\%$), and (c) the transition probabilities (5–10%), depending on each line, see Table 1.

In Figure 6, at 150 ns delay time, the excitation temperature has been determined by means of a Boltzmann plot for several spectral lines. Studying the spectrum in Figure 6(a), three lines 3639.57 Å, 4057.29 Å and 3739.93 Å of Pb I, obtaining $(16,800 \pm 450)$ K for on small $\Delta E = 1.599$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99658. In Figure 6(b), four lines 4242.14 Å, 4244.92 Å, 3785.9 Å, and 3713.98 Å of Pb II, obtaining $(17,700 \pm 500)$ K for on small $\Delta E = 1.448$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than

Figure 6. Boltzmann plots for temperatures calculation of a laser-induced lead plasma using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns, in vacuum, obtained from spatially integrated measurements of the intensities of (a) Pb I lines, (b) Pb II lines, and (c) Pb III lines and delay time 150 ns.

Figure 7. Boltzmann plots for temperatures calculation of a laser-induced lead plasma using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns, in vacuum, obtained from spatially integrated measurements of the intensities of (a) Pb I lines, (b) Pb II lines, and (c) Pb III lines and delay time 200 ns.

0.99407. In Figure 6(c), four lines 3951.92 Å, 4272.66 Å, 3728.69 Å, and 3736.02 Å of Pb III, obtaining $(18,600 \pm 400)$ K for on small $\Delta E = 5.018$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99756. We observed that the excitation temperature obtained with the lines of Pb III is higher than those obtained with the lines of Pb II and is higher than that obtained with the lines of Pb I. The lines of Pb III are mainly emitted from the hot plasma core while the lines of Pb II and the lines of Pb I are emitted more towards from the cold plume periphery.

We do not have spectral lines of Pb IV to estimate the excitation temperature.

In Figure 7, at 200 ns delay time, the excitation temperature has been determined by means of a Boltzmann plot for several spectral lines. In Figure 7(a), four lines 3639.57 Å, 4057.29 Å, 3739.93 Å, and 2476.40 Å of Pb I, obtaining $(15\,000 \pm 150)$ K for on small $\Delta E = 1.599$ eV, all the data exhibited a linear fit with a correlation coefficient than 0.99981. In Figure 7(b), five lines 4242.14 Å, 4244.92 Å, 3785.9 Å, 3718.30 Å, and 3713.98 Å of Pb II, obtaining $(16,080 \pm 200)$ K

Figure 8. Boltzmann plots for temperatures calculation of a laser-induced lead plasma using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns, in vacuum, obtained from spatially integrated measurements of the intensities of (a) Pb I lines, (b) Pb II lines, and (c) Pb III lines and delay time 300 ns.

Figure 9. Boltzmann plots for temperatures calculation of a laser-induced lead plasma using the 10,640 Å laser, pulse energy 290 mJ, and pulse width 7 ns, in vacuum, obtained from spatially integrated measurements of the intensities of (a) Pb I lines, (b) Pb II lines, and (c) Pb III lines and delay time 400 ns.

for on small $\Delta E = 1.448$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99943. In Figure 7(c), four lines 3951.92 Å, 4272.66 Å, 3728.69 Å, and 3736.02 Å of Pb III, obtaining $(17,400 \pm 400)$ K for on small $\Delta E = 5.018$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99564. It has also been observed that the excitation temperature obtained with the lines of Pb III is higher than those obtained with the lines of Pb II and is higher than that obtained with the lines of Pb I.

In stage 150–200 ns expansion, the amount of energy radiated in the form of the continuous spectrum is far greater than the energy radiated by the line spectrum. The atomic and ionic excitation temperatures are different in different zones of the plasma. This indicates a change in temperature across the radial dimension. In some papers,^[29,31] this difference has been attributed to the inhomogeneity of LIP during the expansion. It maybe would be more appropriate to suggest that the LTE approximation may fail as a consequence of the strong radiative energy losses of LIP

expansion. This is why the importance of considering nonequilibrium effects in the initial stage of LIP expansion.

In Figure 8, at 300 ns delay time, the excitation temperature has been determined by means of a Boltzmann plot for several spectral lines. In Figure 8(a), the spectral lines 3639.57 Å, 4057.29 Å, 3739.93 Å, 2476.40 Å, and 2401.94 Å of Pb I, obtaining $(14,800 \pm 200)$ K for on small $\Delta E = 1.755$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99946. In Figure 8(b), the spectral lines 4242.14 Å, 4244.92 Å, 3785.9 Å, 3718.30 Å, and 3713.98 Å of Pb II, obtaining $(14,700 \pm 380)$ K for on small $\Delta E = 1.448$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99565. In Figure 8(c), the spectral lines 3951.92 Å, 4272.66 Å, 3728.69 Å, and 3736.02 Å of Pb III, obtaining $(14,900 \pm 250)$ K for on small $\Delta E = 5.018$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99903. The average temperature is about $\sim 14\,800$ K.

In Figure 9, at 400 ns delay time, the excitation temperature has been determined by means of a Boltzmann plot for several spectral lines. In Figure 9(a), the spectral lines 3639.57 Å, 4057.29 Å, 3739.93 Å, 2476.40 Å, 2446.18 Å, 2401.94 Å, and 2393.90 Å of Pb I, obtaining $(13,600 \pm 300)$ K for on small $\Delta E = 2.121$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99743. In Figure 9(b), the spectral lines 4242.14 Å, 4244.92 Å, 3785.9 Å, 3718.30 Å, and 3713.98 Å of Pb II, obtaining $(13,700 \pm 350)$ K for on small $\Delta E = 1.448$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99613. Figure 9(c), the spectral lines 3951.92 Å, 4272.66 Å, 3728.69 Å, and 3736.02 Å of Pb III, obtaining $(13,700 \pm 400)$ K for on small $\Delta E = 5.018$ eV, all the data exhibited a linear regression fit, with a correlation coefficient than 0.99635. The average temperature is about $\sim 13,700$ K.

During the expansion in stage 300–400 ns delay times, the energy emitted by the continuum gradually decreases, the coincidence of the excitation temperatures for the three species (Pb I, Pb II, and Pb III) supported, over this delay times, with the existence of LTE. At 400 ns delay time, only the resonant lines of Ca II appear (impurities), as mentioned above, with a very low intensity, affecting the temperature obtained within the estimated errors.

Figures 6–9 show that the temperature diminishes rapidly with time in the early phase of plasma life (150–400 ns). It then continues slows off (400–3000 ns) until it levels, which can be explained by the presence of a large difference entre the plasma temperature and ambient temperature.

Also, because emission lines from different ionization stages are present in the laser-induced lead plasma, a combination of the Saha ionization and Boltzman excitation distributions can be used to measure the electron temperature, but you need to know the N_e plasma.

To measurement the electron number density, N_e , it has been done using the Stark broadening (StB) method as well as using the Saha–Boltzmann equation (SBE). The StB is based on the Stark effect phenomenon in plasmas, which is due to collisions of the emitting atoms or ions which electrons and ions. The electric field generated by these fast-

moving electrons or ions in the plasma perturbs the energy levels of the individual atoms or ions, thereby broadening the resultant emission lines. The LTE assumption is based on the fact that the characteristic collision time is much less than the characteristic time of radioactive decay. Therefore, it is valid to assume that the Stark broadening is the dominant broadening mechanism when the density of plasma is above 10^{15} cm^{-3} , in the LIP. The other mechanisms contributing to the line broadening, such as natural broadening, resonance broadening, Van der Waals broadening and Doppler effects are negligible at the range the electron densities in this study.^[16,19]

Hence, the N_e of the plasma was determined by comparing the Stark broadening for some transitions with those of other authors. The experimental profiles were fitted by a Voigt profile. As aforementioned, the Voigt profile is the convolution of a Lorentzian curve and Gaussian curve; spectral lines have thus Lorentzian shape. The Gaussian in the measured line profile is due to the spectroscopic apparatus. In this way, convolution with the known instrumental profile can be taken into account, the spectral line intensity (area below profile) is obtained, the Lorentzian and Gaussian contributions to the full width at half maximum (FWHM) broadening can be separated, and lines with partial overlapping can be analyzed.

The theoretical FWHM of a Stark broadened line can be used for the determination of electron number density, N_e (cm^{-3}), using the following expression:^[16,18–20]

$$\Delta\lambda_{1/2} = 2\omega_{\text{exp}} \left(\frac{N_e}{10^{16}} \right) \left[1 + 1.75A \left(\frac{N_e}{10^{16}} \right)^{1/4} (1 - 1.2N_D^{-1/3}) \right], \quad (3)$$

where $\Delta\lambda_{1/2}$ (in Å units) is the FWHM of the transition considered and obtained at the density N_e expressed in cm^{-3} . The coefficients ω_{exp} and A , both independent of density and a weak function of temperature, are the electron the electron-impact hall width parameter and the ion-broadening parameter, respectively. N_D is the number of particles in the Debye sphere, which must be in excess of the lower limit $N_D = 2$ of the Debye approximation for correlation effects, Wolf.^[44] For the electron densities present in this study, the quasi-static ion broadening, taken into account in the second term in the expression (3), is only approximately 5% of total width. In our measurements, we have assumed that A is negligible.^[45]

The N_e of the plasmas investigated, has been extracted by compared the $\Delta\lambda_{1/2}$ of lines corresponding to species Pb I, Pb II, and Pb III obtained in this work with those ω_{exp} values from others authors, see Table 2.^[6,15,46] We have selected lines, with published broadening Stark widths, that present small uncertainties. The electron densities are been estimated to an accuracy of 10–15% error is essentially due to uncertainties of the used broadening parameters. In different stages and with the spectral lines 4057.29 Å of Pb I, 4244.92 Å of Pb II, and 4272.66 Å of Pb III, the values obtained have been (i) at delay time 150 ns, $5.45 \times 10^{16} \text{ cm}^{-3}$, $5.52 \times 10^{16} \text{ cm}^{-3}$, and $5.56 \times 10^{16} \text{ cm}^{-3}$, respectively, (ii) at delay time 200 ns, $4.24 \times 10^{17} \text{ cm}^{-3}$, $4.35 \times 10^{16} \text{ cm}^{-3}$,

Table 2. Stark full-width at half maximum, ω_{exp} (Å), of Pb I, Pb II, and Pb III spectra lines used in the determination of electron number densities.

Specie	Transition	λ (Å)	T ($\times 10^3$) K	N_e (cm^{-3})	ω_{exp} (Å)
Pb I	$5d^{10}6s^26p$ ($^2P_{1/2}$) $7s$ $^3P_1 \rightarrow 5d^{10}6p^2$ 3P_2	4057.90	11.2	1.0×10^{17}	0.141 ± 0.014^a
Pb II	$5d^{10}6s^2$ (1S) $5f$ $^2F_{7/2} \rightarrow 5d^{10}6s^2$ (1S) $6d$ $^2D_{5/2}$	4244.92	11.3	1.0×10^{16}	0.19 ± 0.02^b
Pb III	$5d^{10}6s(^2S)$ $7p$ $^1P_1 \rightarrow 5d^{10}6s(^2S)$ $7s$ 1S_0	4272.66	21.4	1.0×10^{17}	0.42 ± 0.07^c

(a) Alonso-Medina,^[15] (b) Colón and Alonso-Medina,^[46] and (c) Alonso-Medina.^[6] The wavelengths corresponding are those of Kramida et al. NIST database.^[43]

and $4.56 \times 10^{16} \text{ cm}^{-3}$, respectively; (iii) at delay time 300 ns, $2.59 \times 10^{16} \text{ cm}^{-3}$, $2.65 \times 10^{16} \text{ cm}^{-3}$, and $2.55 \times 10^{16} \text{ cm}^{-3}$, respectively and, (iv) at delay time 400 ns, $2.41 \times 10^{16} \text{ cm}^{-3}$, $2.40 \times 10^{16} \text{ cm}^{-3}$, and $2.42 \times 10^{16} \text{ cm}^{-3}$, respectively. It is noted that the densities obtained are slightly different according to the line used, differences that fall within the uncertainties.

The overall equilibrium of ionization and recombination is described by SBE. When the plasma is sufficiently close to LTE conditions, the electron density can be derived from the intensity ratio of two lines corresponding to different ionization stages of the same element. The N_e determination based on the SBE, with the T determined by Boltzmann plot, is carried out using the following expression:

$$N_e = \frac{2I_{ij}^Z}{I_{ij}^{Z+1}} \frac{A_{ij}^{Z+1} g_i^{Z+1}}{A_{ij}^Z g_i^Z} \frac{\lambda_{ij}^Z}{\lambda_{ij}^{Z+1}} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \times \exp \left(\frac{E_i^{Z+1} - E_i^Z - E_\infty^Z}{k_B T} \right) \quad (4)$$

where ionization states of a species are represented by Z and $Z+1$, respectively, I_{ij}^Z and I_{ij}^{Z+1} are the integrated emission intensities of wavelengths λ_{ij}^Z and λ_{ij}^{Z+1} , respectively, g_i^Z and g_i^{Z+1} are statistical weight of upper level i , A_{ij}^Z and A_{ij}^{Z+1} are the transition probabilities, E_i^{Z+1} , E_i^Z , and E_∞^Z are the energy of the upper energy level and ionization energy, respectively, the species Z to $Z+1$ and h , c , m and k_B are the Planck constant, the speed of light in a vacuum, mass of electron, and Boltzmann's constant, respectively.

In this method, one only needs to know the intensity of two emission lines of the different ionization level (two-line method) and the T , the other parameters are constant and transition probabilities they are available in the bibliography, for the lines in study, see in Table 1. For example, using the lines 3951.92 Å of Pb III and 3962.48 Å of Pb IV the values obtained has been (i) at stage 150 ns and temperature $\sim 19,000$ K, $N_e = (4.8 \times 10^{16} \pm 30\%) \text{ cm}^{-3}$, and (ii) at stage 200 ns, and temperature $\sim 18,000$ K, $N_e = (3.6 \times 10^{16} \pm 30\%) \text{ cm}^{-3}$. But, a simple error propagation calculation reveals that, if the determined intensities, $\sim 3\%$, the transition probability of line Pb III all have $\sim 10\%$ the line Pb IV has been calculated by this author in previous work^[39] and $T \sim 10\%$. The N_e values obtained by the SBE method will have $\sim 25\text{--}30\%$ error, this shows the reason for the unpopularity of said method. This method also used for temperature determinations but you have to know electron number density.

In the phase under study, 150–400 ns from after the laser pulse, and with the results obtained, we can confirm that, as a consequence of the expansion and exchange of energy with the surrounding environment (in vacuum, $\approx 6.6 \text{ Pa}$), the excitation temperature and the electron number density strongly decrease. The temperature decreases from $\sim 18\,600$ to $13\,700$ K while the electron number density decreases from $\sim 5.5 \times 10^{16} \text{ cm}^{-3}$ to $\sim 2.4 \times 10^{16} \text{ cm}^{-3}$. All values for N_e and T measured in this work correspond to the center of the plasma. It should be noted LTE might also result in spatial decoupling, possibly leading to different plasma temperature and densities at different spatial positions.

To determine the change of these parameters in the different regions of the plasma, that is, to study the homogeneity of the plasmas measured in this work, we have obtained their values at different points, scanning the plasma in two perpendicular directions, using the lines of Pb I, Pb II and Pb III. The results indicate a satisfactory homogeneity for N_e and T in stage 300 to 400 ns. However, in stage 150 to 200 ns, not be said.

Evaluation of existence LTE

As already mentioned, LTE plasmas can be characterized by a single temperature that describes the distribution of species in energy levels the population of ionization stages or the kinetic energy of electrons and heavier particles. The excitation temperature which controls the population of the atomic and ionic energy levels should be the same as the ionization temperature, which determines the distribution of atoms of the same element in the different ionization stages. For the plasma to be in LTE, atomic and ionic states should be populated and depopulated predominantly by collisions rather than by radiation. This requires that the electron density has to be high enough to ensure a high collision rate.^[16,18]

In order to classify the thermodynamic status of the LIPs, the McWhirter's criterion^[47] can be applied to highlight the deviation from equilibrium. McWhirter's criterion establishes a minimum value of N_e for which the collisional excitation/de-excitation process is at least 10 times faster than radiative the processes be expressed with the following equation:

$$N_e (\text{cm}^{-3}) \geq 1.6 \times 10^{12} \sqrt{T} (\Delta E)^3, \quad (5)$$

where T (in K) is the plasma temperature, ΔE (in eV) is the energy difference between the upper and lower strongly radiative coupled states which are expected to be in LTE. It is important that the ΔE refers to two adjacent levels with

Table 3. Experimental Stark full-width at half maximum line intensity, ω_S (pm), and Doppler broadening, ω_D (pm), of two spectral lines of Pb IV, at different temperatures, T , and electron number density normalized to an $1 \times 10^{17} \text{ cm}^{-3}$, obtained in this work.

Transition array	Multiplet	λ (Å)	T ($\times 103$ K)	This work	ω_S (pm)	ω_D (pm)	Others work ^[24]
6d $^2D_{3/2}$	6s 6p [16°] $_{1/2}$	3962.48	18.5	46.1 ± 7.3	4.3		
			19.5	52.7 ± 8.4	5.0		
			22.6				47.0 ± 7.0
7s $^2S_{1/2}$	6s 6p [16°] $_{1/2}$	4049.80	18.5	47.8 ± 7.6	4.4		
			19.5	53.6 ± 8.6	5.1		
			23.8				61.5 ± 9.5

Values compared with Bukvić et al.^[24] The wavelengths corresponding are those of Kramida et al. NIST database.^[43]

the maximum difference in energy of the entire electronic configuration of the considered species. N_e is the lower limit in the electron density to collisional maintains the energy level populations to within 10%^[43] of LTE while competing with radiative processes, this typically fulfilled during the first stages of plasmas lifetime; for any Ne, it is possible to find high excitation levels where the states are close enough for Equation (5) to hold, and it is difficult to satisfy for the low-lying states, where ΔE is large.^[2,44,47] For example, using the values obtained of the spectral lines of Pb III, $\Delta E_i = 5.018 \text{ eV}$: (i) at delay time 400 ns, 13,700 K, the value N_e by McWhirter's criterion is $2.37 \times 10^{16} \text{ cm}^{-3}$ against the value obtained $2.42 \times 10^{16} \text{ cm}^{-3}$, (ii) at delay time 300 ns, 14 900 K, the value N_e by McWhirter's criterion is $2.47 \times 10^{16} \text{ cm}^{-3}$ against the value obtained $2.55 \times 10^{16} \text{ cm}^{-3}$, (iii) at delay time 200 ns, 17,400 K, the value N_e by McWhirter's criterion is $2.67 \times 10^{16} \text{ cm}^{-3}$ against the value obtained $4.56 \times 10^{16} \text{ cm}^{-3}$, and (iv) at delay time 150 ns, 18,600 K, the value N_e by McWhirter's criterion is $2.76 \times 10^{16} \text{ cm}^{-3}$ against the value obtained $5.56 \times 10^{16} \text{ cm}^{-3}$.

The McWhirter's criterion is a necessary though insufficient condition for LTE; this criterion was derived for homogenous and stationary plasmas but not sufficient condition when dealing with other types of plasmas that do not respond to these requisites. In the case of approximation to homogenous and stationary plasmas, it is important to check the equilibrium within different inelastic processes leading to the Boltzmann and Saha balances.^[48]

In this work, the existence of LTE, at stage 300–400 ns, it has been corroborated by comparing the electron number density directly measured with the Stark effect with the corresponding values obtained using the Saha equation. The use of Saha equation and the measurement of the Stark broadening of a suitable transition, in each case studied, has provided us with a reliable way to corroborate LTE. If was observed that with the Saha equation has been generated a smaller electron number density value than with the Stark effect but within the experimental uncertainty range. We can also say that stage 150–200 ns is close to LTE given the experimental uncertainty range.

Measurements of Stark width for 3962.48 Å and 4049.8 Å spectral lines of Pb IV

In this work, they have been measured Stark widths, ω_S , for 3962.48 Å and 4049.80 Å spectral lines of Pb IV, obtaining (once the instrumental width has been reduced) the

Figure 10. Stark width, ω_S (in pm), of Pb IV transitions vs. electron density (in cm^{-3}).

following values: (i) 29.5 pm and 30.0 pm, respectively, at stage 150 ns after the laser pulse and $5.6 \times 10^{16} \text{ cm}^{-3}$, and (ii) 21.2 pm and 22.0 pm, respectively, at stage 200 ns after the laser pulse and $4.6 \times 10^{16} \text{ cm}^{-3}$. The Doppler broadening, ω_D , for said spectral lines obtained are 2.7 pm and 2.8 pm, respectively, at stage 150 ns after the laser pulse and $5.6 \times 10^{16} \text{ cm}^{-3}$, and (ii) 2.6 pm and 2.7 pm, respectively, at stage 200 ns after the laser pulse and $4.6 \times 10^{16} \text{ cm}^{-3}$. This values they are presented in the columns 5 and 6, respectively, of Table 3, at the given temperature 19,500–18,500 K, respectively (values that we have extrapolated by not having spectral lines of Pb IV to estimate them) and normalized for N_e -value 10^{17} cm^{-3} . To estimate the uncertainty of the Stark widths obtained, we have taken into account different sources. The error due to the plasma inhomogeneity ($\sim 3\%$) has been estimated taking into account what expressed above, where we showed that a central region exists in the plasma at which the electron density is nearly constant, where are mainly emitted the ions lines. The error is due to the electron density ($\sim 10\%$) and also the typical statistical error ($\sim 3\%$). Doppler and Stark width that are the dominant mechanisms of spectral line broadening in strongly ionized laser-induced plasmas.

These two lines belonging a multiplet, the values of the Stark line width must be very close, as obtained in this work, and they are a good agreement with the experimental data were obtained existing.^[24] An important rule required for experimental data analysis within multiplet is “Line widths in multiplets are usually the same within a few per

cent. Rare exceptions are cases where some perturbing levels are accidentally extremely close to the perturbing levels of multiplet,^{»[36,45]} see Table 3.

In 2016, Burger and Hermann^[49] presented a method for the measurement of Stark broadening parameters, where it is carried out a detailed study about the assumption of a linear dependence of Stark width with electron density for all non-hydrogenic lines. In the present work, we have explored linear dependencies of Stark width with electron density for these transitions in the obtained temperature range, see values obtained in Figure 10. There is no linear dependence. The changes of Stark width with temperature cannot be neglected in this range.

Conclusions

This article focuses on the interpretation of the emission spectra in laser-induced lead plasma in vacuum. The evolution of the plasma has been studied by acquiring spectrum at 100–400 ns delay times. The understanding of the spectral peculiarities observed has been important in order to study the appearance and the disappearance of the different species and be able to extrapolate to the initial conditions of LIP, as a novelty two spectral lines of Pb IV have appeared in stage 100–200 ns expansion.

Measurements of plasma temperature and electron density of the produced plasmas at different delay times are performed in the present work, using the Boltzmann plot method, Stark broadening (StB) method and Saha-Boltzmann equation (SBE), respectively, and spectral lines of the different species that appear in each delay time. In the phase under study, 150–400 ns from after the laser pulse, the temperature decreases from $\sim 18,600$ to $13,700$ K while the electron number density decreases from $\sim 5.5 \times 10^{16} \text{ cm}^{-3}$ to $2.4 \times 10^{16} \text{ cm}^{-3}$. The absence of self-absorption was checked in the lines used.

The atomic and ionic excitation temperatures obtained differ more in the initial stage of the expansion than at later times. In stage 150–200 ns expansion, said temperatures are different in different zones of the plasma, see Figures 6 and 7. In some papers, previously made by other authors, this difference has been attributed to the inhomogeneity of the LIP during the expansion. It maybe would be more appropriate to suggest that the LTE approximation may fail as a consequence of the strong radiative energy losses of LIP expansion. This is why the importance of considering nonequilibrium effects in the initial stage of LIP expansion.

As a consequence of plasma expansion and recombination the electron number density and the plasma temperatures decreases, inducing recombination and decreasing the number of charged particles in the plasma and emission lines start to rise up from the continuum radiation spectrum, being news the presence of molecular species, in the initial stage up to ~ 300 ns after the laser pulse and in the final stage from $\sim 9\,000$ ns (see Figure 5), in the plasma.

In this work, we presented the results of measured Stark widths for $3962.48 \text{ \AA}$ and $4049.80 \text{ \AA}$ spectral lines of Pb IV of astrophysical interest and industrial, which have

uncertainties of $\pm 16\%$, what can be considered a quite tolerable agreement with respect to the accuracy of the experiment and the uncertainties, also a good agreement with the experimental data was obtained existing, contributing new measured values. The linear dependence of Stark widths with electron density for these lines obtained, 150–200 ns after the laser pulse ($19,500$ – $18,500$ K), it does not happen.

The species Pb III and Pb IV disappear in very shorts delay times, Pb IV ~ 200 ns and Pb III ~ 300 ns, after from the laser pulse, giving the possibility of using Pb III/Pb IV line-strength ratios and the Stark broadening to know the parameters of plasma the initial conditions.

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