Experimental determination of the Stark widths of Pb I spectral lines in a laser-induced plasma

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ABSTRACT

Stark widths of 34 spectral lines of Pb I have been measured in a Laser Induced-Plasma (LIP). The optical emission spectroscopy from a LIP generated by a 10640 Å radiation, with an irradiance of 1.4×10^{10} W cm^{-2} on a Sn–Pb target in an atmosphere of argon was analyzed between 1900 and 7000 Å. The Local Thermodynamic Equilibrium (LTE) conditions and plasma homogeneity have been checked. The 34 spectral lines measured in this paper correspond to the transitions $n(n=7, 8)s \rightarrow 6p^2$, $n(n=6, 7)d \rightarrow 6p^2$. The population levels distribution and the corresponding temperatures were obtained using Boltzmann plots. The plasma electron densities were determined using well-known Stark broadening parameters of spectral lines. Special attention was dedicated to the possible self absorption of the different transitions. Stark broadening parameters of the spectral lines were measured at 2.5 μs after each laser light pulse, where the electron temperature was close to 11200 K and the electron density to 10^{16} cm^{-3}. The experimental results obtained have been compared with the experimental values given by other authors.

1. Introduction

Data on Stark widths of spectral lines are relevant not only for atomic structure research, but also for applications to astrophysics and analytical techniques for plasma diagnosis. A detailed investigation of high-resolution astrophysical spectra requires a large number of accurate atomic data. The combination of the Hubble Space Telescope and the Goddard High Resolution Spectrograph has allowed the discovery of a number of elements heavier than zinc in the interstellar gas. With $Z=82$, lead has the highest cosmic abundance among the elements heavier than barium. Lead neutral was detected in several stars: Gonzalez et al. [1] detected the 7228.9 Å Pb I line in FG Sge, whereas the 4057.82 Å Pb I line was reported in Ap stars by Guthrie [2] and in star CS 29497-030 by Sneden and Ivans [3]. Sneden et al. [4] attempted to detect the 3683.48 Å and 4057.82 Å Pb I lines in the ultrametal-poor star CS 2289-052.

Measured and calculated Stark broadening parameters have been reported for different neutral and singly ionized elements by Konjević et al. [5]. However, only a few authors have reported values for lead. A part of these values were obtained by Miller et al. [6] for only 4 Pb II lines and 8 Pb I lines, using a gas-driven shock tube. A pulsed capillary discharge was used for the Stark parameter measurements of Pb I spectral lines by Salakhov et al. [7] and Sarandaev and Salakhov [8]. Fishman et al. [9] used an impulsive capillary light-source for measuring the Stark parameter of 9 Pb I lines at 24000 K adjusted to an electron density of 10^{17} cm^{-3}, with estimated relative uncertainty of about 30%. Castle et al. [10] carried out time-resolved measurements of intensity variation of five lead atomic lines by using a laser-induced breakdown spectroscopy (LIBS) plasma on a solid target at standard atmospheric conditions.

Laser ablation of solid sample is one of the most important applications of Laser Induced Plasma Spectroscopy (LIPS) in science and technology by Radziemski and Cremers [11,12]. The emission spectrum of the plasma plume reveals important information regarding identification and quantification of the emitting species present in the ablated material. 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 it has been shown by Irons [13], Zhao et al. [14], Wolf [15], Blanco et al. [16], Castle et al. [10], Alonso-Medina [17], Colón et al. [18], Be Martínez and Blanco [19], Alonso-Medina and Colón [20], Alonso-Medina et al. [21], Alonso-Medina et al. [22], Harilal et al. [23], Colón and Alonso-Medina [24], Shaikh et al. [25], and Alonso-Medina and Colón [26].

In this paper, a plasma generated by focusing a laser beam on a sample of Sn–Pb alloy (with a Pb content of about 0.5%) in an argon atmosphere at 6 Torr and 2.5 μs after each laser light pulse has been used in order to provide Stark widths (FWHM, full width at half of the maximal intensity) of 34 Pb I spectral lines corresponding to the $6p^2$–ns ($n=7, 8$) and $6p^2$–nd ($n=6, 7$) of Pb I, between 1900 and 7000 Å. The obtained results have been compared with the experimental data published, but no experimental values of Stark widths for 24 of the emission lines considered in the present work appear reported in the literature. Experimental working conditions of stability and homogeneity of electron density and temperature in the plasma were determined by means of a study of the temporal evolution in different environmental conditions and target composition. The Local Thermodynamic Equilibrium (LTE) assumption has been also discussed by analysis of these experimental working conditions.

The organization of this paper is as follows. In Section 2, the experimental system used for LIPS and the procedure appear as described. The results obtained related to the electron density and temperature as well as Stark widths of the Pb I spectra lines are given in Section 3, and conclusions in Section 4.

2. Description of the experimental setup and procedure

The experimental system is similar to that described in previous papers [17,18,20–22,24,26]. Schematic diagram of the experimental system (LIPS) is shown in Fig. 1.

The system constituted of a Q-switched Nd:YAG laser (Quantel YG585) operating at its fundamental wavelength of 10 640 Å, at a frequency of 20 Hz, generated pulses of 275 mJ and a duration of 7 ns and 1 m Czerny-Turner spectrometer with a 2400 grooves/mm holographic grating and a 50 μm external slit, equipped with a gated optical multichannel analyzer (OMA III EG&G), which allowed the detection of each spectrum and its digital recording for later numerical analysis. The resolution of the spectroscopic system was 0.3 Å in the first order.

The pulsed laser was used to evaporate the target of Sn–Pb alloy and excite the vapor plume. A chamber was used to generate the plasma in a gas atmosphere. A vacuum of 10^{-5} Torr was attained inside the chamber by means of a turbomolecular pump, and it was filled with argon and maintained at a constant pressure of 6 Torr throughout the measurements, using a small continuous flow of gas to maintain the purity of the atmosphere. In this way the temperature, the electron density and the temporal evolution of LIP could be controlled.

The laser beam was focused on the sample by a lens of focal distance of 12 cm. The laser irradiance on the blank was 1.4×10^{10} W cm^{-2}, producing craters with standard diameters of 0.5 mm. The spatial width of the focused laser beam was measured by recording its image with a 1024-element linear silicon diode array. The light emitted by the LIP was transmitted, through a sapphire window, to the input slit of the spectrometer. Samples were located inside the 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.

The spectra were recorded by a time-resolved optical multichannel analyzer (OMA III) system, which can be used to record sections of the spectrum with a delay with respect to the pulse and for a selected interval of time; to obtain the best signal to noise ratio the measurements were made with a delay of 2.5 μs and the recording interval was 0.1 μs. The detection was performed in a synchronized manner with the electronic device that regulates the laser Q-switch. In each data acquisition period a correction was made with regard to the dark signal in the absence of the laser plasma. The instrumental profile was determined previously from the observation of several narrow spectral lines from hollow-cathode lamps, with a precision of 97%, the instrumental full width at half maximum (FWHM) being 0.11 Å for a wavelength of 3000 Å.

The spectral response of the system was obtained in the 1900 to 7000 Å wavelength range by means of previously calibrated lamps. A deuterium lamp was used for the 1900–4000 Å range, and a tungsten lamp for the 3500–7000 Å range.

The analysis of each spectrum was made by fitting the observed line profiles by numerically generated ones calculated by the convolution of the known instrumental profile, with the Voigt profiles obtained from the contributions selected, Lorentz and Gaussian. Under our experimental conditions all the tabulated transitions for Pb I and Pb II spectrum can be observed as those of the Sn I and Sn II and some of Ar I and Ar II spectra were analyzed between 1900 and 7000 Å. In Fig. 2 we present the section of the typical spectra.

In the present experiments, to avoid self-absorption effects, a sample of Sn–Pb alloy with a lead content of about 0.5% was used. Self-absorption effects estimated by absorption coefficient calculations (Thorne [27] and Corney [28]), turned out to be lower than 3% for the most intense lines, and therefore the plasma can be considered optically thin.

The same experimental system was used to study the homogeneity of the plasma but, in order to obtain spatial resolution, the light was focused by means of a lens on a 1 mm light guide, facilitating selection

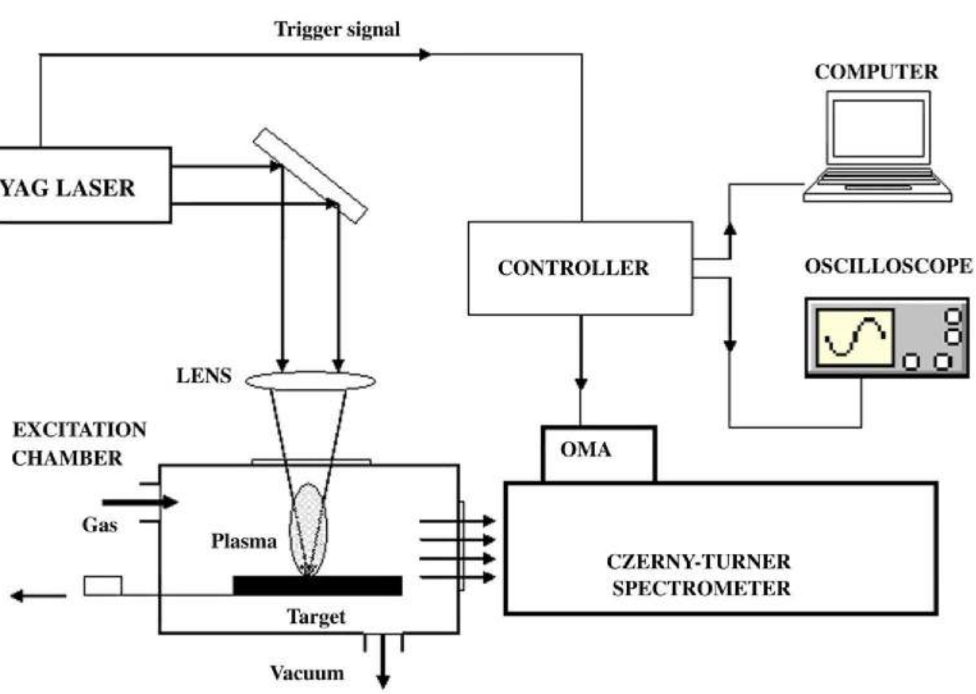

Fig. 1. Schematic diagram of the laser-induced plasma system.

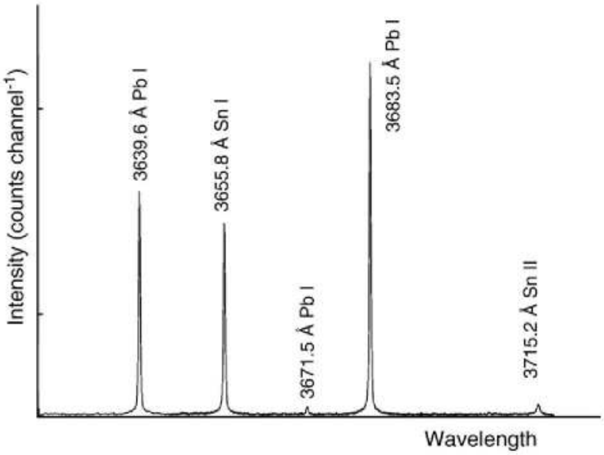

Fig. 2. Emission lines of Pb I at 6 Torr in argon atmosphere, 2.5 μs delay time from laser pulse.

of the point of the plasma from which the light emission was observed. The measurements were taken by scanning the plasma emission in two perpendicular directions, to determine where the different atomic species are located in the plasma and to determine the real values of the parameters of the plasma. Local profiles were obtained after Abel inversion of the integrated intensity. The fitting of the observed profiles provide the total intensity very accurately, as well as the broadening of the spectral lines.

3. Results

3.1. Values of the plasma temperature and electron density

In optically thin plasma the relative intensities, I_{ij} of the lines emitted from a given state of excitation can be used to calculate the electron temperature, if the A_{ij} transition probabilities are known, by the expression:

$$I_{ij} = \frac{A_{ij} g_i}{U(T)} N \exp\left(\frac{-E_i}{kT}\right) \tag{1}$$

for a transition from a higher state i to a lower state j, I_{ij} is the relative intensity, E_i and g_i are the energy and statistical weight of level i, $U(T)$ is the atomic species partition function, N the total density of emitting atoms, k the Boltzmann constant and T the temperature. If we were to plot $\ln(I_{ij}/g_i A_{ij})$ vs. E_i, the 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. The energies of the different levels are those of Moore [29].

The plasma temperature has been determined by means of several Boltzmann plots. The designations and the Pb I and Pb II transition probabilities selected for determination of the excitation temperature by Boltzmann plot are shown in Table 1. The relative intensities I_{ij} required for applying this method were obtained using a laser-induced plasma in this work and the transition probabilities were obtained in our previous study Alonso-Medina [17] and Alonso-Medina et al. [21].

Fig. 3 displays a Boltzmann plot from which a value of 11200± 200 K ΔE=2.174 eV was obtained from the electron temperature for Pb I. As confirmation of the LTE hypothesis, we also obtained the temperature of the plasma deduced from lines 5608.9 Å, 4386.5 Å, 5042.6 Å, 4152.8 Å and 3455.1 Å of Pb II with a value of 11300±300 K for ΔE=12.819−9.581=3.238 eV the transition probabilities for the lines of Pb II are taken from the study by Alonso-Medina [17]. The value is totally compatible with the values obtained from the lines of Pb I.

The electron density, N_e, of the plasma investigated has been obtained by comparing the Stark broadenings for several transitions with those of others authors, using the expression by Befeki [30] and Milosavljevic and Poparic [31]:

$$\omega = 2\omega_p\left(\frac{N_e}{10^{16}}\right)\left[1 + 1.75A\left(\frac{N_e}{10^{16}}\right)^{1/4}\left(1 - 1.2N_D^{-1/3}\right)\right] \tag{2}$$

where ω (in Å) is the full width at half maximum (FWHM) of the transition considered and obtained at the density N_e expressed in cm^{-3}, ω_p is the Stark broadening parameter, A is the ion broadening parameter. The parameter 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 [15]. For the electron densities present in this study, the quasi-static ion broadening, take into account in the second term in the expression (2), is only approximately 5% of total width. In our measurements we have assumed that A is negligible (Konjevic´ [32]).

The electron densities obtained from the Stark broadening may be considered reliable, because the other broadening mechanism considered in this study accounts for 3% of the total broadening value. The value of the electron density was obtained using in the last equation the experimental values of the Stark broadening parameter, ω_p, for the 3683.5 Å Pb I transition the value of ω_p=(0.130±20%) Å was obtained for a temperature of 24000 K and $N_e = 1.0\times10^{17}$ cm^{-3} for

Table 1
Parameters of Pb I and Pb II spectra lines used for electron temperature determination (6 Torr of argon, delay time of 2.5 μs)

Transition	λ (Å)[a]	E_i (eV)	A_{ij} ($\times10^6$ s^{-1})
Pb I			
$6p^2\ ^3P_1$–$7s\ ^3P_0$	3683.5	4.335	167.6±10.6[b]
$6p^2\ ^3P_0$–$7s\ ^3P_1$	2833.1	4.375	55.7±3.3[b]
$6p^2\ ^3P_2$–$6d\ ^3F_2$	2873.3	5.635	33.3±2.0[b]
$6p^2\ ^3P_2$–$7s\ ^3P_2$	2663.2	5.975	90.5±5.5[b]
$6p^2\ ^1D_2$–$7s\ ^1P_1$	3572.7	6.130	95.3±6.0[b]
$6p^2\ ^1D_2$–$7d\ ^3D_1$	3220.5	6.437	82.7±5.8[b]
$6p^2\ ^3P_2$–$7d\ ^3D_1$	2388.9	6.509	50.8±2.5[b]
Pb II			
$7s\ ^2S_{1/2}$–$7p\ ^2P_{3/2}$	5608.9	9.581	84.8±8.5[c]
$6d\ ^2D_{3/2}$–$5f\ ^2F_{5/2}$	4386.5	11.473	155.7±15.6[c]
$7p\ ^2P_{1/2}$–$7d\ ^2D_{3/2}$	5042.6	11.690	90.0±8.9[c]
$7p\ ^2S_{3/2}$–$9s\ ^2S_{1/2}$	4152.8	12.566	22.3±2.8[c]
$7p\ ^2P_{1/2}$–$8d\ ^2D_{3/2}$	3455.1	12.819	42.1±6.1[c]

[a]Moore [29], [b]Alonso-Medina et al. [21], [c]Alonso-Medina [17].

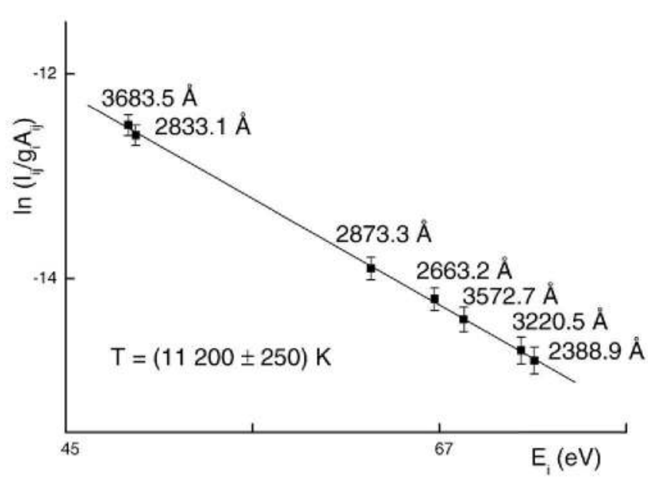

Fig. 3. Boltzmann plot for Pb I spectral lines from laser-induced plasma at 2.5 μs delay time from laser pulse.

Table 2
Experimental Stark width FWHM, ω (Å), of emission lines of Pb I at a given electron temperature, T ($\times 10^3$ K), and normalized at $N_e = 1.0 \times 10^{17}$ cm^{-3} (6 Torr of argon, delay time of 2.5 μs)

Transition array	Multiplet	λ (Å)[a]	T	ω (Å) This work	ω (Å) Other works
$6p^2$–7s	$^3P_0$–$^3P_1$	2833.1	11.2	0.069±0.006	
			24.0		0.077 $B^{f,g}$
	$^3P_1$–$^3P_0$	3683.5	11.2	0.131±0.010	
			24.0		0.130 $A^{e,g}$
	$^3P_1$–$^3P_1$	3639.5	11.2	0.153±0.015	
			24.0		0.130 $A^{e,g}$
	$^3P_1$–$^3P_2$	2476.5	11.2	0.092±0.009	
	$^3P_1$–$^1P_1$	2401.9	11.2	0.109±0.011	
	$^3P_2$–$^3P_1$	4057.9	11.6		0.062 C^d
			11.2	0.141±0.014	
			24.0		0.160 $A^{e,g}$
	$^3P_2$–$^3P_2$	2663.2	11.2	0.098±0.010	
			24.0		0.081 $B^{f,g}$
	$^3P_2$–$^1P_1$	2577.3		0.090±0.009	
	$^1D_2$–$^3P_2$	3739.9	11.2	0.113±0.011	
			24.0		0.140 $B^{e,f}$
	$^1D_2$–$^1P_1$	3572.8	11.2	0.072±0.007	
	$^1S_0$–$^1P_1$	5005.5	11.2	0.075±0.007	
$6p^2$–8s	$^3P_1$–$^3P_1$	2446.3	11.2	0.123±0.012	
	$^3P_1$–$^3P_0$	2443.8	11.2	0.118±0.012	
	$^3P_1$–$^3P_1$	2628.3	11.2	0.099±0.010	
	$^1D_2$–$^3P_1$	3671.5	11.2	0.107±0.011	
	$^1S_0$–$^3P_1$	5201.5	11.2	0.182±0.018	
$6p^2$–6d	$^3P_0$–$^3D_1$	2170.0	11.2	0.102±0.010	
	$^3P_1$–$^3D_1$	2613.7	11.2	0.111±0.011	
	$^3P_1$–$^3D_2$	2614.3	11.2	0.180±0.018	
			24.0		0.209 $A^{f,g}$
	$^3P_2$–$^3D_1$	2822.6	11.2	0.075±0.007	
	$^3P_2$–$^3D_2$	2823.3	11.2	0.138±0.012	
	$^3P_2$–$^3F_2$	2873.4	11.2	0.137±0.013	
			24.0		0.200 $C^{f,g}$
	$^3P_2$–$^3F_3$	2802.1	11.2	0.288±0.020	
			24.0		0.274 $A^{f,g}$
	$^1D_2$–$^3D_1$	4062.2	11.2	0.149±0.013	
	$^1D_2$–$^3F_2$	4168.1	11.2	0.195±0.019	
	$^1D_2$–$^3F_3$	4019.7	11.2	0.094±0.009	
$6p^2$–7d	$^3P_1$–$^3D_1$	2237.5	11.2	0.191±0.019	
	$^3P_2$–$^3D_1$	2388.9	11.2	0.260±0.025	
	$^3P_2$–$^3D_2$	2399.7	11.2	0.193±0.019	
	$^3P_2$–$^3F_2$	2441.8	11.2	0.161±0.016	
	$^3P_2$–$^3F_3$	2393.9	11.2	0.202±0.020	
	$^1D_2$–$^3D_1$	3220.5	11.2	0.199±0.019	
	$^1D_2$–$^3D_2$	3240.2	11.2	0.233±0.023	
	$^1D_2$–$^3F_3$	3229.7	11.2	0.103±0.010	

The accuracy estimates : 15%≤A≤25%≤B≤35%≤C≤50%.
[a]Moore [29], [d]Miller et al. [6], [e]Salakhov et al. [7], [f]Sarandaev and Salakhov [8], [g]Fishman et al. [9].

Fishman et al. [9] and Salakhov et al. [7]. The Stark broadening of this transition was obtained as the Lorentzian part, $\omega = (0.0131 \pm 0.0013)$ Å, of its Voigt profile. The electron density was $(1.0 \pm 0.1) \times 10^{16}$ cm^{-3}.

We have selected lines with published broadening Stark widths that present small uncertainties: 5042.6 Å, 5544.3 Å and 4386.5 Å Pb II spectral lines obtained in our previous work, for a temperature of 11300 K and $N_e = 0.8 \times 10^{16}$ cm^{-3}, Colón and Alonso-Medina [24]. The electron density was, $(0.99 \pm 0.09) \times 10^{16}$ cm^{-3}, $(1.09 \pm 0.10) \times 10^{16}$ cm^{-3} and $(1.1 \pm 0.1) \times 10^{16}$ cm^{-3} respectively. The values of the electron densities from very different spectrum lines are in good agreement.

McWhirter's criterion, for the lower limit of the electron density, has been used to support the LTE hypothesis and this is given by the following expression (McWhirter [33]):

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

where ΔE, (in eV), is the energy difference between the upper and lower strongly radiatively coupled states, and T, (in K), the temperature and N_e the lower limit of the electron density necessary to maintain the populations of the energy levels at 10% of the LTE by collision, in competition with the radiative processes.

Using the values obtained for the Pb I lines, the critical N_e is 1.75×10^{15} cm^{-3}, and using the values obtained for Pb II lines, the critical N_e is 5.77×10^{15} cm^{-3}.

With the aforementioned values of N_e and T we can calculate the absorption coefficient for the studied lines, using the following equation [27], expressed in m^{-1}:

$$k_\omega = \frac{\pi e^2}{2\varepsilon_0 mc} f_{ik} N_i \left[1 - \frac{N_k g_i}{N_i g_k}\right] g(\omega) \quad (4)$$

f_{ik} is the oscillator strength (absorption) and $g(\omega)$ is the normalized profile of the line. In the maximum, $\omega = 0$, and for a Lorentz profile, $g(o) = 2/\pi\Gamma$, where Γ is the FWHM of the line. A line may be considered optically thin if $k_\omega L \leq 0.05$ [28]. In our experimental conditions the value of the optical depth, $k_\omega L$, is not in excess of 0.02.

3.2. Stark broadening of several Pb I spectral lines

The spectroscopic analysis of the LIP emission has provided experimental Stark widths for 34 spectral lines of Pb I at temperature of 11200 K (Table 2). This data includes new values for 24 emission lines. The results of our experimental data of full width at half maximum (FWHM) parameters have been normalized to an electron density of 10^{17} cm^{-3}. The corresponding errors include uncertainties in the instrumental profile and statistical errors after an average of several spectra with a total of about 100 laser shots. The possible error due to the experimental uncertainty in the density of electrons in this study is also included. The first three columns denote the corresponding transition array, the multiplet and the wavelengths (in Å) for each studied transition. Electron temperatures are indicated in the fourth column. The fifth column compiles our experimental Stark width parameters. In the sixth column the experimental values of other authors are displayed.

4. Conclusions

The laser-induced plasma from a Sn–Pb target in an argon atmosphere has been studied under different conditions in order to assure if its results are optically thin and that thermodynamic equilibrium can be assumed. Spectroscopy analysis of the plasma light emission has been provided with the experimental Stark widths for 34 emission lines of Pb I. For 24 of these emission lines, no experimental values of Stark widths have been made by other authors. No significant self-absorptions exist and no corrections are necessary.

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