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Application of laser-induced plasma spectroscopy to the measurement of transition probabilities of Ca I

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Abstract

We present improved experimental transition probabilities for the optical Ca I 4s4p-4s4d and 4s4p-4p^2 multiplets. The values were determined with an absolute uncertainty of 10%. Transition probabilities have been determined by the branching ratios from the measurement of relative line intensities emitted by laser-induced plasma (LIP). The line intensities were obtained with the target (lead-calcium) placed in argon atmosphere at 6 Torr, recorded at a 2.5 μs delay from the laser pulse, which provides appropriate measurement conditions, and analysed between 350.0 and 550.0 nm. They are measured when the plasma reaches local thermodynamic equilibrium (LTE). The plasma is characterized by electron temperature (T) of 11400 K and an electron number density (N_e) of 1.1 x 10^{16} cm^{-3}. The influence self-absorption has been estimated for every line, and plasma homogeneity has been checked. The values obtained were compared with previous experimental values in the literature. The method for measurement of transition probabilities using laser-induced plasma as spectroscopic source has been checked.

Keywords: Laser-induced plasma spectroscopy; Transition probabilities; Calcium; Plasma diagnostic

1. Introduction

Data on transition probabilities for spectral lines is a research field of continuous interest. The investigations in the fields of plasma physics, laser physics, astrophysics and earth atmosphere, require reliable spectroscopic data for atoms and ions. Such data are indispensable for monitoring various processes occurring in plasmas. The knowledge of transition probabilities is required e.g. for determination of the plasma temperature as well as atomic densities in plasmas. From the theoretical point of view, transition probabilities are very sensitive to the different interaction schemes used in studies of the atomic structure, allowing verification of their validity.

In astrophysics, calculations of stellar opacities, stellar atmospheres modelling and abundances determinations are dependent on an extensive list of parameters of different spectral lines of several atomic species. The abundance derived from a single spectral line is directly proportional to the oscillator strength, log *gf*- value, for the transition. It is therefore of the highest priority to find log *gf*- value as accurate as possible. Calcium lines are present in solar (see e.g. Moore et al., in 1966, [1], Holweger, in 1972, [2], Cayrel et al., in 2004, [3]) and stellar spectra (see e.g. Adelman and Davis Philip, in 1992, [4], Frebel et al., in 2005, [5]). Calcium is an important chemical element to study the history of α-process nucleosynthesis in the Galaxy.

The laser-induced breakdown spectroscopy (LIBS) has achieved great interest as spectroscopic source. LIBS technique, which uses a laser-induced plasma (LIP) as a spectroscopic source in emission experiments has already been used in previous work by this author to measure the transition probabilities of different atoms [6-12]. The method used was based on the determination of relative line intensities emitted by a LIP that were converted to absolute transition probabilities both by fitting to a Boltzmann plot and by the branching fraction method using experimental lifetimes. In 1997 Alonso-Medina [6] and Alonso-Medina et al., in 2001, [9], determined the transition probabilities of 30 Pb II lines and 39 Pb I lines and 1 Pb II line, respectively. In 1999 Colón et al. [7] and Alonso-Medina, in 2010, [11], determined the transition probabilities of 10 and 30 Pb III lines, respectively. In 2000 Alonso-Medina and Colón [8], determined the transition probabilities of 36 Sn II lines and Alonso-Medina, in 2003, [10], lines corresponding to several transitions from auto-ionized states of single-ionized tin were identified in a laser-produced plasma generated by 10640 Å irradiation of an Sn target at a flux of 2x10^{10} Wcm^{-2}. In 2010 Alonso-Medina [12], determined transition probabilities 97 of Sn I lines.

During the last 30 years many theoretical and experimental studies have been performed for Ca I to obtain the oscillator strengths and the transition probabilities for spectral lines [13-24]. In 1959, Olsen et al. [13] have measured relative gf-values for 107 lines in 34 multiplets of the Ca I spectrum. Lambert and Warner, in 1968, [14] also studied the lines of multiplet, 4s4p ^{3}P→4s4d ^{3}D, at about 445.0 nm though these are partially blended with lines of other elements. The most recent experimental oscillator strengths (f-value, gf) for the Ca I 4p-4d lines are the furnace absorption measurements by Smith and O'Neill in 1975 [15], who used radiative lifetimes from Gornik et al. [25], and Ostrovskii et al. [26] to put their measurements on an absolute scale. In Zajonc, in 1982, [16] a value is reported for the transition probability of Ca (4s6s ^{1}S→4s4p ^{1}P). Precise measurements of relative oscillator strengths for 37 lines (all lines have lower energy levels) were reported by Smith and Raggett in 1981 [17]. In 1988, precise relative oscillator strengths for seven lines of neutral calcium absorbed from the level 4s4p ^{1}P at 2.9 eV above the ground level have been measured using a carbon tube furnace, by Smith [18]. The measurements of oscillator strengths for the principal series of calcium 4s^2 $^1S_0$→4s np $^1P_1$

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($11 \leq n \leq 25$) are reported, by Ahmad et al., in 1994, [19] using the magneto-optical spectroscopic technique. Excitation energies and oscillator strengths of neutral calcium are calculated through third order using a variant of multi-reference many-body perturbation theory, known as the effective valence-shell Hamiltonian method, by Majumder et al., in 1999 [20]. In 2003, Froese Fischer and Tachiev [21], have determined transition probabilities and lifetimes for all levels of the Ca I spectrum up to 2d4p $^1F_3$ using the multiconfiguration Hartree-Fock method with lowest-order relativistic effects included through the Breit-Pauli Hamiltonian. Recently the $4s^2\ ^1S_0$-$4s4p\ ^1P_1$ radiative rate was measured by Vogt et al. (in 2007) [22]. Haq et al. (in 2008) [23] have determined the oscillator strengths of the 4s4p $^1P_1 \rightarrow$4snd $^1D_2$ ($30 \leq n \leq 70$) and the 4s4p $^3P_1 \rightarrow$4snd $^3D_2$ ($20 \leq n \leq 50$) Rydberg transitions and Aldenius et al. (in 2009) [24] have determined oscillator strengths for the 4p-5s triplet (610.27, 612.22, 616.22 nm) in Ca I and experimental radiative lifetimes for seven energy levels in the triplet system of Ca I.

The LIBS technique was used for the analysis of Ca in a soil, Bustamante et al. [27] and the ablation of calcium sample has been studied by the optical emission spectroscopy of the evolving plasma using the fundamental, second, and third harmonic of a Nd:YAG laser, which reveals numerous transition due to neutral and singly ionized calcium, Hafeez et al. [28].

In this paper, we present transition probabilities for 12 spectral lines of Ca I corresponding to transitions $4s^2$-4s4p, 4s4p-4s4d and 4s4p-$4p^2$. These values were determined with an absolute uncertainty of 10 % (~25% have the values given in the NIST for these lines). Intensity relative values have been obtained from measurements of all emission lines of laser-produced plasma carried out with a calcium-lead target (with 99.9% lead purity and 0.1% calcium purity) placed in an argon atmosphere at 6 Torr and 2.5 µs after each laser light pulse, which provides appropriate measurement conditions. We have used two different methods in order to place the data on an absolute scale: using experimental values, measured in literature [24,25,29], of the radiative lifetimes of corresponding states (Branching ratios method) and, with the local thermodynamic equilibrium (LTE) assumption, several transition probabilities were placed from the Boltzmann plot of Ca I line intensities. Uncertainties from different contributions are estimated. The results obtained for this work are compared with the experimental data present in the literature.

In this work one of the main difficulties in obtaining transition probabilities is the necessity of verifying that line intensities are measured in a plasma in optically thin, and as the self-absorption of the lines causes a systematic error in the values determined, the use of a small concentration of calcium in the sample allowed us to solve this problem. As it is well known, the optical depth for an emission line depends on its atomic features and on the density of the emitting species in the plasma, which is directly related to concentration of the element in the sample.

The classical approach in the study of LIP is based on the assumption of LTE. Under this assumption the temperature and electron density can be easily determined. In LTE the loss of radiative energy is small compared to energy exchange between material particles so that Maxwell and Boltzmann relations are still valid locally [30-33]. Recently, Cristoforetti et al [34] conducted a detailed study. In this paper the LTE is discussed, and the plasma parameters such as temperature and electron density are obtained. The self-absorption effects were calculated and also the homogeneity of the plasma is studied.

2. Experimental Details

The experimental system is similar to that described in previous papers [6-12,35-39], although more detailed description is presented in [12,36-38], so only a brief description is given here.

A Q-swith Nd:YAG laser generated 290 mJ pulses of 7 ns of duration at 1064.0 nm, with a frequency of 20 Hz, which were deflected by total reflection in a prism and is focused with a 12 cm focal length lens onto a calcium-lead target of 99.9% Pb and 0.1% Ca purity placed in a vacuum chamber evacuated with a turbo-molecular pump, and it was filled with argon and maintained at a constant pressure throughout the measurements, using a small continuous flow of gas to maintain the purity of the atmosphere. Measurements were carried out in argon at 6 Torr. The laser irradiance on the target was 2×10^{10} Wcm^{-2}. The diameter of a typical crater was of 0.5 mm. The laser energy was monitored using a calibrated power-meter.

The temperature, electron number density and time evolution of laser-produced plasma can be controlled. 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, which could influence the intensity of the spectral lines and could lead to the destruction of the sample.

The light emitted by the laser produced plasma was transmitted through a sapphire window on the entrance slit of a spectrometer, located 8 cm from the plasma. The spectrometer used was a Czerny-Turner (with a 1 m focal length and a 2400 grooves/mm holographic grating). The fist-order resolution, for a slit of 50 µm, is 0.3 Å which corresponds to 3 channels, and equipped with a gated optical multichannel analyser (OMA III, formed by 1024 silicon photodiodes), which can be used to record sections of the spectrum with a delay with respect to the laser pulse and for a selected interval of time. The minimum duration of the time window is 100-200 ns, and the spectra band detected by the device is about 100 Å. The instrumental function has been estimated for the 50 µm width entrance/exit slits.

The computer used has a card for communications, through which the communication is made with the central unit OMA. This computer has been programmed for the whole process of acquisition of data from the OMA throughout the measurement process.

The measurements were repeated at several delay times of 0.15-9 µs and a fixed gate time of 0.1 µs is used. The measurements consist of the accumulation of 20 laser pulses at a delay time and were obtained, after ablative cleaning of the target with 2 laser pulses in order to remove impurities. To obtain the best signal to noise ratio, the measurements of spectral lines of Ca I were made with a delay of 2.5 µs, and the recording interval was 0.1 µs. All emission spectra are recorded in the spectral range 350.0-550.0 nm and in argon atmosphere at 6 Torr. Figure 1 presents two sections of typical spectra, in the range 396.0-406.0 nm and 411.0-429.0 nm wavelength (a delay of 2.5 µs in a 6 Torr argon atmosphere), where some of the spectral lines of Ca I, Ca II, Pb

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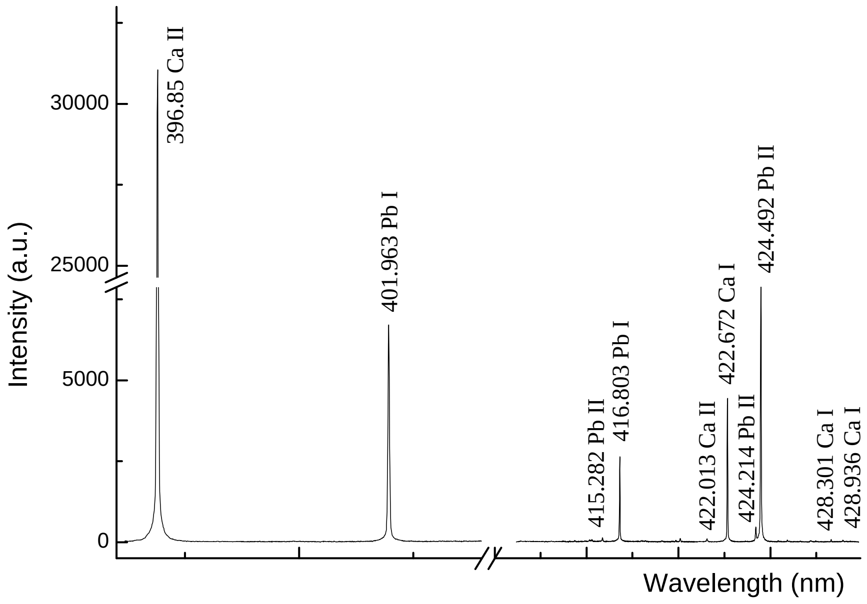

Figure 1. Emission spectra lines of lead-calcium plasma generated by laser (in an argon atmosphere at 6 Torr, delay time of 2.5 μs) covering the region of (396.0-406.0) nm and (411.0-429.0) nm.

I, Pb II can be observed. The break in the Y axis has been for the difference in the counts/channel between the resonance line of Ca II (396.847 nm) and resonance line of Ca I (422.673 nm). The possibility of detecting a wide spectral range is an advantage for LIP characterization, as it allows using a high number of spectra lines, increasing in this way the accuracy of the plasma temperature determination.

The calibration of the spectral response of the experimental system was made, before the experiment, using a standard tungsten lamp, in the 350.0-700.0 nm range. The system efficiency was measured five times, and the error was estimated to be around 3%.

The spectra were stored in a computer for further analysis and treated by software which is able to separate two close overlapping lines and to determine their relative intensities, with uncertainties ~3%. The line intensities were obtained by subtracting the background intensity. The final intensity of each line was the average of six different measures.

The relative intensities have been measured evaluating the area under one line, for which purpose the adjustments were made to the profiles observed from the lines by means of a convolution of the instrumental profile, known with Voigt profiles obtained from the contributions selected, Lorentz and Gaussian. The instrumental profile was determined from the observation of several narrow spectral lines emitted by hollow-cathode lamp (with a precision of 97%). This profile has been a Voigt profile (as an example, Gaussian FWHM=0.014 nm and Lorentz FWHM=0.012 nm for 350 nm). The setting of the profiles allows us to safely obtain the total intensities of the lines, as well as the Lorentz and Gaussian contribution in each line [37-39].

The same experimental system was used to study the homogeneity of the plasma, 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, keeping the plasma-lens-optical fiber aligned. 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 were taken by scanning the plasma emission in two perpendicular directions, through the axis of the plasma with a distance from the blank in the 0.25-2.75 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 0-1.12 mm, to determine where the different calcium and lead atomic species are located in the plasma and to determine the real values of the parameters of the plasma (temperature, electron number density) [12,36-38].

The value of the temperature and density of electrons is highly close to the target surface. In the first stage, the plume is much higher than at later times because energy is regained in the recombination of the ions. In the present work, it is shown that there is no temporal variation in the temperature and electron number density of the plume at different positions for long delay time (from 2 μs). A delay time of 2.5 μs with respect to the laser pulse is chosen as the best condition for this work.

3. Results and Discussion

As already mentioned above, the use of emission spectroscopy for the measurement of transition probabilities, temperature and electron number density of plasma, requires optically thin spectral lines. An estimation of the absorption coefficient of all the lines studied will be shown in a later discussion, in order to verify that self-absorption was negligible.

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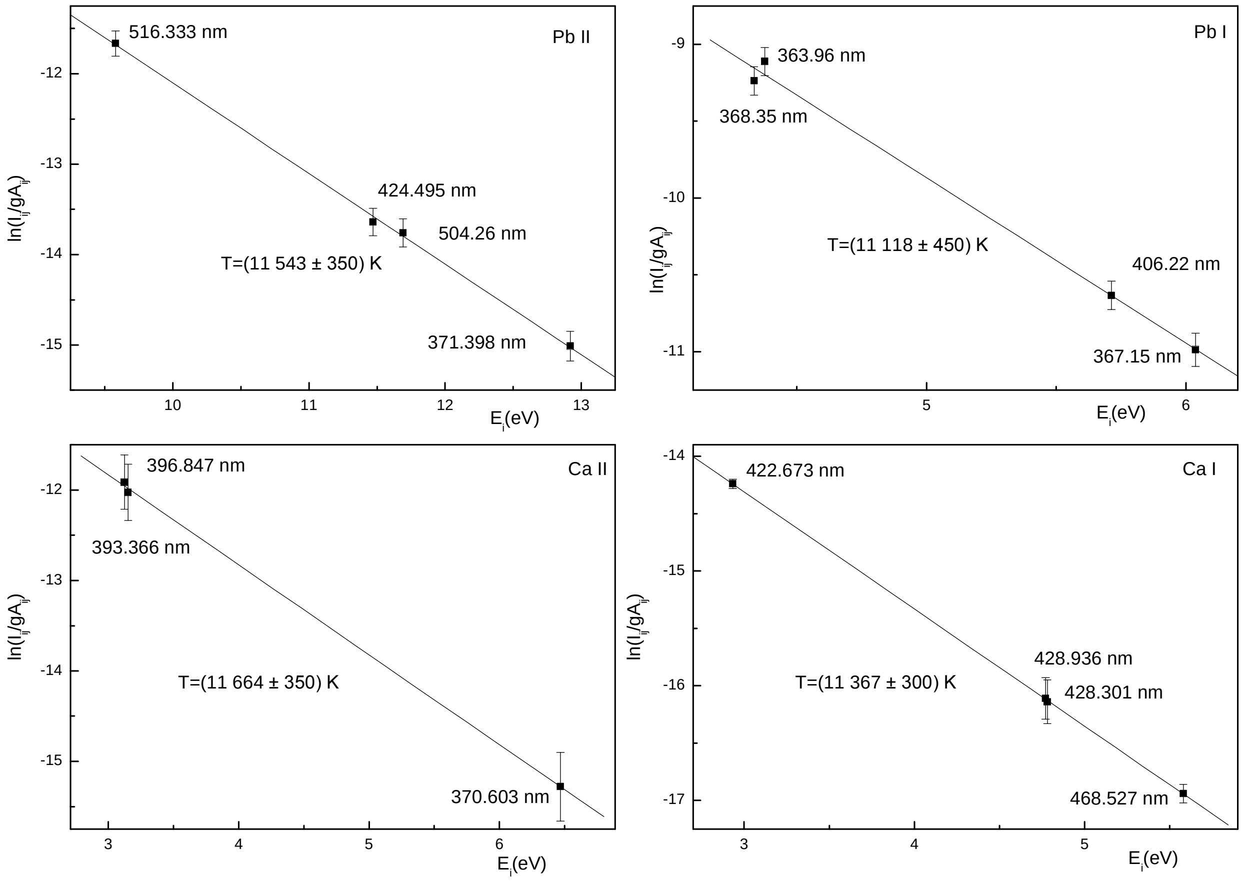

Figure 2. Experimental Boltzmann plots after 2.5 μs from the laser pulse in an argon atmosphere (a) for Ca I, (b) for Ca II, (c) for Pb I and (d) for Pb II.

A suitable choice of some spectral lines that are free from self-absorption allows the calculation of both temperature and density of the plasma.

3.1. Determination of the plasma temperature and the electron number density

The excitation temperature can be determined with the well-known Boltzmann method, from relative line intensities (I^{λ}_{ij}), provided that their transition probabilities (A_{ij}) from a given excitation state are known from the same element and ionization stage. The basic principle of the Boltzmann plot is described below (Griem, 1974 and 1997, [30,31] respectively, Lochte-Hotgreven [40], Bekefi [41]) by the expression:

$$A_{ij} = \left(\frac{U(T)}{Ng_i}\right) I^{\lambda}_{ij} e^{\frac{E_i}{kT}}$$

$$\ln\left(\frac{I^{\lambda}_{ij}}{A_{ij} g_i}\right) = \ln\left(\frac{N}{U(T)}\right) - \frac{E_i}{kT} \quad (1)$$

for a transition from a higher state i to a lower state j, I^{λ}_{ij} 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 (1.38 x 10^{-23} J/K) and *T* is the temperature in K.

If we were to plot $\ln(I^{\lambda}_{ij} / g_i A_{ij})$ 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.

The excitation temperature has been determined by means of a Boltzmann plot for several lines of Ca I, obtaining (11 376 ± 300) K for ΔE=2.65 eV, of a Boltzmann plot for several lines of Ca II, obtaining (11 664 ± 350) K for ΔE=3.35 eV, of a Boltzmann plot for several lines of Pb I, obtaining (11 118 ± 450) for ΔE=1.70 eV and of a Boltzmann plot for several lines of Pb II, obtaining (11 543 ± 350) K for ΔE=3.34 eV, as can be seen in Figure 2. These values were obtained, from the relative intensities (I^{λ}_{ij}), required for applying this method, emitted by laser-produced plasma in this paper, and the transition probabilities are as displayed in Table 1 (values which were obtained in our previous studies [6,9,18,22,42] respectively). The energies of the different levels are those of Moore [43]. The errors were estimated from the standard deviation of the slopes obtained in the least squares fittings. The uncertainties that are taken into

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Table 1. Spectroscopic parameters for selected Ca I, Ca II, Pb I and Pb II spectra lines used to calculate the excitation temperature (in an argon atmosphere at 6 Torr, delay time of 2.5 μs, the Pb-Ca target having a purity of 99.9% Pb and 0.1% Ca).

Species	Transition	λ (nm)[a]	E_i (eV)	A_{ij} (10^7 s^{-1})	Error %
Ca I	4s4p $^1P_1 \rightarrow 4s^2\ ^1S_0$	422.673	2.933	21.558[b]	0.04
	$4p^2\ ^3P_1 \rightarrow$ 4s4p $^3P_0$	428.936	4.770	6.0[c]	18
	$4p^2\ ^2P_2 \rightarrow$ 4s4p $^3P_1$	428.301	4.781	4.3[c]	18
	4s4p $^1P_1 \rightarrow$ 4s6d $^1D_2$	468.527	5.579	0.86[d]	2.3
Ca II	4p $^2P_{1/2} \rightarrow$ 4s $^2S_{1/2}$	396.847	3.124	14.6[c]	20
	4p $^2P_{3/2} \rightarrow$ 4s $^2S_{1/2}$	393.366	3.152	15.0[c]	20
	5s $^2S_{1/2} \rightarrow$ 4p $^2P_{1/2}$	370.603	6.469	8.4[c]	20
Pb I	6p7s $^3P_0 \rightarrow 6p^2\ ^3P_1$	368.35	4.335	16.8[e]	6.3
	6p7s $^3P_1 \rightarrow 6p^2\ ^3P_1$	363.96	4.376	3.08[e]	6.8
	6p6d $^3D_1 \rightarrow 6p^2\ ^1D_2$	406.22	5.713	7.81[e]	6.9
	6p8s $^3P_1 \rightarrow 6p^2\ ^1D_2$	367.15	6.037	3.03[e]	5.9
Pb II	7p $^2P_{3/2} \rightarrow 6p^{24}P_{1/2}$	516.333	9.581	0.099[f]	15
	5f $^2F_{7/2} \rightarrow$ 6d $^2D_{5/2}$	424.495	11.471	11.0[f]	10
	7d $^3D_{3/2} \rightarrow$ 7p $^2P_{1/2}$	504.260	11.692	9.0[f]	10
	8d $^3D_{5/2} \rightarrow$ 7p $^2P_{3/2}$	371.398	12.919	3.9[f]	10

[a] *Moore [43]*
[b] *Vogt et al. [22]*
[c] *NIST [42]*
[d] *Smith [18]*
[e] *Alonso-Medina et al [9]*
[f] *Alonso-Medina [6]*

account are: a) the line profile fitting procedure (~1%), b) the relative line intensity determination (~2%) and c) the transition probabilities (0.04-20%, depending on each line) see Table 1. All the data exhibited a linear fit with a correlation coefficient better than 0.999. The high uncertainty of the transition probabilities of the Ca I lines led to an uncertainty of temperature as high as ~20%. In Figure 2, the error of the temperature corresponds to the propagation of the error of the slope of the linear fitting. The linearity of the plots and the coincidence of the temperatures supported the existence of LTE.

The ionization temperature was calculated using the relative line intensity ratio method (in the electron density 1.1 x 10^{16} cm $^{-3}$), Saha´s equation [30,31,40], between Ca I (422.67 nm) and Ca II (396.85 nm) spectral lines; the necessary atomic data are taken from references [42,44,45]. The value obtained is 11700 K with an estimated error of ~ 12%.

These values, the excitation temperature and the ionization temperature, are totally compatible and are close to 11400 K (with an estimated error of ~10%), justifying the existence of LTE. It is well known that LTE plasmas are characterized by single temperature [34,41,46].

The electron number density of the plasma was determined, as in other previous papers [6-12,35-39], by comparing the Stark broadening for some transitions with those of other authors. In this work the Stark broadening from collision of charged species, is the primary mechanism influencing these emission spectra together with the instrumental line broadening. The other mechanisms contributing to the line broadening (such as Doppler broadening, natural broadening and Van der Waals broadening) are negligible at the range of the electron densities in this study. As an example, at the temperature of plasma in study (11400 K), the Doppler width is estimated to be 5x10^{-5} nm for the transition at 393.366 nm of Ca II. The full width at half maximum (FWHM) of the Stark broadening profile lines is related to the electron number density N_e (cm^{-3}) by the following expression (Griem [30], Bekefi [41], Konjevic´ [46]):

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

where ω (in Å) is the 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, and 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 [47]. For the electron densities present in this study, the quasi-static ion broadening, taken into account in the second term in the expression (2), is only approximately 5% of total width. In our measurements, for ionic lines, we have assumed that A is negligible [46], therefore one obtains the following expression to determine the plasma electron number density, N_e,

$$N_e = \left(\frac{\omega}{2\omega_p}\right)\times 10^{16} \quad (3)$$

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Table 2. Electron number density of lead-calcium plasma (in an argon atmosphere at 6 Torr, delay time of 2.5 μs).

Species	Transition Array	Multiplet	λ (nm)^a	T (10^3 K)	ω_{exp} (Å)	N_e (10^{16} cm^{-3}) 11 400 K
Ca I	$4s^2 – 4s4p$	$^1S_0 – ^1P_1$	422.672	10.0	$N_e= 10^{15}$ cm^{-3} 0.124x10^{-2} ^{g}	1.19
Ca II	$4s – 4p^2$	$^2S_{1/2} – ^2P_{1/2}$	393.366	13.0	$N_e= 10^{17}$ cm^{-3} 0.10 ± 20% ^{h}	1.17 ± 22%
Pb I	$6p^2 – 6p6d$	$^1D_2 – ^3F_3$	401.963	11.2	$N_e= 10^{17}$ cm^{-3} 0.094 ± 10%^{i}	1.05 ± 15%
Pb II	6d – 5f	$^2D_{5/2} – ^3F_{7/2}$	424.492	11.3	$N_e= 10^{16}$ cm^{-3} 0.19 ± 10%^{j}	1.10 ± 15%

[a] Moore [44]
[g] Dimitrijevic´, Sahal-Bréchot [44]
[h] Goldbach et al. [45]
[i] Alonso-Medina [37]
[j] Colón, Alonso-Medina [35]

where ω_p, (in Å), is the Stark broadening parameter of the line, taken from literature.

The electron number density, N_e , of the plasma under study is about 1.1 x 10^{16} cm^{-3} with an estimated error of ~15%, and has been obtained by comparing the Stark broadenings for several transitions with those of others authors, see Table 2. The error comes from the statistical uncertainties of measured line widths and the Stark widths taken from the literature [35,37,44,45]. We have selected lines, 422.673 nm Ca I spectral line obtained by Dimitrijevic´and Sahal-Bréchot [44], for a temperature of 10 000 K and N_e = 10^{15} cm^{-3}, and 393.366 nm Ca II spectral line obtained by Goldbach el al. [45], for a temperature of 13 000 K and an electron density of 10^{17} cm^{-3}. The electron density was 1.19 x 10^{16} cm^{-3} and (1.17± 22%) x 10^{16} cm^{-3} respectively. Also, we have selected lines, from published broadening Stark widths, that present small uncertainties: 401.96 nm Pb I spectral line obtained in an previous work, for a temperature of 11 200 K and N_e = 10^{17} cm^{-3} obtained by Alonso-Medina [37] and 424.495 nm Pb II spectral line obtained by Colón and Alonso-Medina [35], for a temperature 11 300 K and N_e normalized 10^{16} cm^{-3}. The electron density was (1.05± 12%) x 10^{16} cm^{-3} and (1.10± 12%) x 10^{16} cm^{-3} respectively, see Table 2. The relative values of the electron densities obtained with such lines are in good agreement, and are totally compatible with the value 1.1 x 10^{16} cm^{-3} (~ 15% error). In case where the interest is in relative values of the electron densities for varying experimental conditions (in this work, argon atmosphere at 6 Torr), the errors can refer just to the uncertainties of the fitting of the line`s profile (~2%) and of the instrumental width (~3%), and not the uncertainty of the reference Stark parameter. Also, the value of the electron number density has been corroborated by Saha´s equation.

For the plasma to be in LTE, it requires that the density has to be high enough to ensure a high collision rate. The corresponding lower limit of electron density is given by the McWhirter criterion [48]:

$$N_e(cm^{-3}) \geq 1.6x10^{12}\sqrt{T}\,(\Delta E)^3 \tag{4}$$

where ΔE, (in eV), is the energy difference between the upper and lower strongly radiatively coupled states, and T (in K) the plasma temperature, and N_e is the lower limit of the electron density necessary to maintain the populations of the energy level at 10% of the LTE by collision, in completion with the radiative processes. Using the values obtained for the Ca I lines, the critical N_e is 1.08 x 10^{15} cm^{-3}, using the values obtained for the Ca II lines, the critical N_e is 6.38 x 10^{15} cm^{-3}, using the values obtained for Pb I lines, the critical N_e is 8.42 x 10^{14} cm^{-3} and using the values obtained for Pb II lines, the critical N_e is 6.36 x 10^{15} cm^{-3}, respectively.

In this work, the values given for N_e and T correspond to the centre of the plasma. To determine the change of the N_e and T in different regions of the plasma, we have obtained their values at different points using various lines of Ca I, Ca II, Pb I and Pb II, and the result is that there is homogeneity for N_e and T; deviations from the average are less than 12% for N_e and 5% for T in a region measuring approximately 2 mm in size corresponding to 95% of the emission of light.

3.2. Analyses of the self-absorption of the emission lines

The problem of self-absorption in optical emission spectroscopy has been the subject of a number of papers [49-51], using several methods for evaluating the reduction in line intensity. Amamou et al. [49] proposed a method of determination of the ratios of transition probabilities and ratios of optical thicknesses for the case of Lorentzian profile of lines emitted by plasma in presence of self-absorption. El Sherbini et al. [50] proposed a method that relies on the quantification of the line width and on the evaluation of the electron density which are easily measurable from an experimental emission spectrum. Recently Bredice et al. [51] presented a new method for calculating the self-absorption coefficient of spectral lines obtained from laser-induced breakdown spectroscopy experiments.

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Table 3. Absolute transition probabilities of some lines of Ca I multiplets obtained by branching ratio method combined with experimental lifetimes (in an argon atmosphere at 6 Torr, delay time of 2.5 μs, (0.1%) Ca- (99.9%) Pb target).

Transition Levels	λ (nm) [a]	Absolute transition probabilities (10^7 s^{-1})		
		τ =13.6±1.0ns[k]	τ =12.3±1.8ns[l]	τ =12.2±0.5ns[m]
4s4d $^3D_1$→4s4p $^3P_0$	442.544	4.8 ± 0.6	5.3 ± 1.0	5.3 ± 0.5
4s4p $^3P_1$	443.568	2.2 ± 0.3	2.5 ± 1.0	2.5 ± 0.2
4s4p $^3P_2$	445.662	0.3 ± 0.04	0.3 ± 0.6	0.3 ± 0.3
		τ =4.6±0.5ns[k]		
4s4d $^3D_2$→4s4p $^3P_1$	443.496	5.1 ± 0.6		
4s4p $^3P_2$	445.589	2.1 ± 0.2		
		τ =6.9±0.4ns[n]		
$4p^2$ $^3P_1$→4s4p $^3P_0$	428.936	5.5 ± 0.5		
4s4p $^3P_1$	429.899	3. 0 ± 0.3		
4s4p $^3P_2$	431.865	6.2 ± 0.6		
		τ =6.9±0.4ns[n]		
$4p^2$ $^3P_2$→4s4p $^3P_1$	428.301	3.9 ± 0.4		
4s4p $^3P_2$	430.253	11.6 ± 1.1		

[a] Moore [43]
[k] Aldenius et al. [24]
[l] Gornik et al. [25]
[m] Ostrovskii, Penkin [26]
[n] Jönsson et al. [29]

In practice estimating the degree of self-absorption is a difficult task. The knowledge of the optical thicknesses allows evaluating the degree of self-absorption. In this work, without forgetting great care that has been taken to minimize the influence of self-absorption on emission line intensities determinations (a small concentration, ~0.1%, of calcium in the sample), the absence of self-absorption has been checked using a method described by Thorne [52]. With the aforementioned values of N_e and T we can calculate the absorption coefficient for the studied lines, expressed in m^{-1}:

$$k_\omega = \frac{\pi e^2}{2\varepsilon_0 mc} f_{ik} N_i \left[1 - \frac{N_k g_i}{N_i g_k} \right] g(\omega) \tag{5}$$

where f_{ik} is the oscillator strength (absorption), g_i and g_j are statistical weight of state 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. N_k and N_i are the population density of the lower-level energy and upper-level energy, respectively, was estimated at approximately equal to the electron density, which being an upper limit. A line may be considered optically thin if k_ω (cm^{-1}) x D(cm) <<1 [52, 53]. In this work, D ≈ 1 mm, the value of the optical depth k_ωD is not in excess of 0.01; for example 0.009 in 393.366 nm Ca II or 0.01 in the 422.673 nm Ca I. In the lines studied in present work, self-adsorption was negligible, so we can consider that the experiment was carried out in optically thin plasma.

3.3. Transition probabilities of Ca I spectral lines

In this work, the absolute transition probabilities can be determined, either from relative intensities measurements or branching ratio method using experimental lifetimes obtained from literature, and either from Boltzmann plot. The transition probabilities of lines with origin in the 4s4d $^3D_1$, 4s4d $^3D_2$, $4p^2$ $^3P_1$ and $4p^2$ $^3P_2$ states of Ca I are obtained using experimental lifetimes from the literature and line-strength sum rules are shown in the third column of Table 3. The experimental errors for these values are the results of statistical uncertainties, errors in the lifetime measurements [24-26,29] and uncertainties in the spectral response determination (~3%). It is significant that there is a good agreement between the values.

For homogeneous and optically thin plasma in LTE with the temperature T = 11 400 ± 10% K, the electron number density N_e = 1.1 x 10^{16} ± 15% cm^{-3} and the relative line intensities measurements, the transition probabilities are obtained from Boltzmann plot, expression (1). Transition probabilities obtained from this method for 12 spectral lines of Ca I with wavelengths in the range of 350.0-550.0 nm, are displayed in column three of Table 4, while columns one and two give the transitions and corresponding wavelengths, respectively. The experimental errors for these values are the results of statistical uncertainties (~3%), the error in the temperature corresponds to the propagation of the error of the slope of the linear fitting (~3%), the self-absorption correction line errors (<1%) and uncertainties in the spectral response determination (~3%). The remaining columns data given by other authors [42,15,18] have been included for comparison. Smith and O`Neill [15] suggest that the absolute scale of transition probabilities presented in their work is probably correct to better than 15%. Besides, with this temperature and this electron number density and from relative lines strength measurements by comparison with the relative line strength of the 393.37 nm Ca II transition, the Saha´s equation has been confirmed. The uncertainties taken into account are: the line profile fitting procedure (≤1%), the maximum intensity stability (2%), the self-absorption correction line errors (<1%), dispersion of temperatures

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Table 4. Experimental transition probabilities of several lines of Ca I (in an argon atmosphere at 6 Torr, delay time of 2.5 μs, the Pb-Ca target having a purity of 99.9% Pb and 0.1% Ca) obtained from Boltzmann plot of temperature (11 400 ± 10 % K). Comparison of the obtained values with some published.

Transition levels			Absolute transition probabilities (10^7 s^{-1})		
Upper	**Lower**	**λ (nm)**[a]	**This work**	**Other authors**	
4s4d $^3D_1$	**4s4p $^3P_0$**	**442.544**	**5.04 ± 10%**	**4.68** [c]	**4.98 ± 15%**[ñ]
	4s4p $^3P_1$	**443.568**	**2.68 ± 10%**	**3.56** [c]	**3.43 ± 15%** [ñ]
	4s4p $^3P_2$	**445.662**	**0.28 ± 10%**	**0.24** [c]	**0.24 ± 15%** [ñ]
4s4d $^3D_2$	**4s4p $^3P_1$**	**443.496**	**5.86 ± 10%**	**6.30** [c]	**6.67 ± 15%** [ñ]
	4s4p $^3P_2$	**445.589**	**1.91 ± 10%**	**2.08** [c]	**2.03 ± 15%** [ñ]
4s4d $^3D_3$	**4s4p $^3P_2$**	**445.478**	**7.96 ± 10%**	**8.60** [c]	**8.70 ± 15%** [ñ]
$4p^2$ $^3P_1$	**4s4p $^3P_0$**	**428.936**	**6.03 ± 10%**	**6.00** [c]	
	4s4p $^3P_1$	**429.899**	**3.83 ± 10%**	**4.66** [c]	
	4s4p $^3P_2$	**431.865**	**6.91 ± 10%**	**7.40** [c]	
$4p^2$ $^3P_2$	**4s4p $^3P_1$**	**428.301**	**3.93 ± 10%**	**4.34** [c]	
	4s4p $^3P_2$	**430.253**	**12.9 ± 10%**	**13.6** [c]	**14.1 ± 2.3%**[d]
$4p^2$ $^3P_0$	**4s4p $^3P_1$**	**430.774**	**19.2 ± 10%**	**19.9** [c]	

[a] Moore [43]
[c] *NIST [42]*
[d] *Smith [18]*
[ñ] *Smith, O`Nell [15]*

obtained within the series of different diagnostics, dispersion of electron density obtained within the different lines, and dispersion of the transition probability of the 393.366 nm Ca II accuracy [42]. Values obtained by these two methods are fully compatible. Our results are in good agreement with experimental data reported in the literature. Moreover values that have been listed in NIST have uncertainties of 20-25%.

4. Conclusions

In the present work, optical emission spectra of the plasma produced by the 10 64.0 nm Nd:YAG laser of lead-calcium sample in an argon atmosphere at 6 Torr are recorded wih a delay with respect to the laser pulse and for a selected interval of time, 2.5 μs. Due to the transient nature of the laser induced plasma the spectra emitted by these types of discharges depend strongly on the observation time, at the best working conditions 2.5 μs after the laser pulse.

All the results presented in this work were obtained using a lead-calcium sample, having a purity of 0.1% Ca and 99.9% Pb. The emission spectrum of the plasma reveals transitions of neutral atoms and singly ionized calcium and lead ions. No self-absorption effects have been detected. The electron temperature of the plasma (11 400 K) has been determined from the Boltzmann plot method by using the relative emission line intensities of Ca I, Ca II, Pb I and Pb II and from Saha´s equation, where the electron number density (1.1 x 10^{16} cm^{-3}) is estimated from the Stark broadening profile of the spectral lines of Ca I, Ca II, Pb I and Pb II. The LTE conditions have been checked.

Spectroscopy analysis of the plasma light emission has provided the experimental transition probabilities for 12 emission lines of Ca I, which were determined with an absolute uncertainty of 10%. A good agreement with previously referenced data was found in almost all cases. In this work the transition probabilities for 428.936, 429.899, 431.865, 428.301 and 430.774 nm spectral lines of Ca I were determined with errors lower than those obtained by other authors. The method for measurement of transition probabilities using laser-induced plasmas as spectroscopic source has been checked.

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