Experimentally determined transition probabilities for lines of Pb I and the 2203.5 Å line of Pb II

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Abstract

Transition probability for the line 2203.53 A of Pb II and transition probabilities for 39 lines of Pb I have been determined from measurements of emission line intensities in an optically thin laser-produced plasma of Pb and Sn in an atmosphere of Ar. Lines for which transition probabilities have not been previously published are included. In order to establish this homogeneity and the existence of local thermodynamic equilibrium, plasma has been studied. A temperature of 11060 K and an electron density of 10^{16} cm^{-3} were found. The results were compared with the available experimental and theoretical data given by other authors.

1. Introduction

The energy levels of neutral and ionised atoms of lead have been the subject of a few experimental [1–4] and theoretical [5–7] studies. The most recent are Alonso-Medina [8–10]. The 2203.53 Å line of Pb II, corresponding to the $7s\,^2S_{1/2} \rightarrow 6p\,^2P^o_{3/2}$ transition has not been experimentally determined.

The experiment was carried out by emission of a plasma generated by focusing a laser beam on a sample of Sn–Pb alloy (with a Pb content of about 0.5%) in Ar atmosphere. Laser-produced plasmas (LPP) have proved to be a valuable and versatile source of spectroscopic data on ionised species [10–15].

The electron temperature was determined using the relative emission intensities of several Pb I, Pb II, Sn II and Ar II transitions. Stark broadening of some Pb II and Sn II emission lines were used to obtain the electron density.

In this work the local thermodynamic equilibrium (LTE) assumption is discussed, and the homogeneity, temperature and electron density of the plasma are studied. With the LTE assumption verified several transition probabilities were placed on an absolute scale from the Boltzmann plot of line intensities of Pb II and Pb I. Other relative transition probabilities for 11 lines were placed on an absolute scale by using mean value pondered of all the lifetimes of the states of Pb I found in the literature. The values obtained are compared with existing experimental and theoretical values. We will describe in Section 2 the experimental system used for LPP spectroscopy, and then in Section 3 the various results obtained are discussed.

2. Experimental set-up and procedure

The experimental system is similar to that described in previous publications [10,14,15]. A plasma was generated by focusing a Nd:YAG laser at the sample surface. The light emitted by the laser-produced plasma was transmitted through a sapphire window to the entrance slit of a 1 m monochromator; the resolution of the spectroscopic system is 0.3 Å in the first order. The characteristics of the apparatus employed are shown in Table 1.

The spectra were recorded by a time-resolved optical multi-channel analyser (EG&G OMA III), that allows recording of spectra at a given delay from the laser pulse and during a selected time window. As the plasma grows and disappears quickly it is necessary to have a time-resolved

Table 1
Experimental apparatus and characteristics

Q-switched Nd:YAG laser	Quantel YG 585
Pulsewidth	10 ns
Pulse energy	275 mJ
Wavelength	10640 Å
Repetition rate	20 Hz
Spectrometer	Spex 1704
Type	1 m, Czerny-Turner
Grating	2400 grooves/mm
Slit	50 μm
Detection system	EG&G OMA III (model 1461)
Number of channels	1024
Minimum gate width	100 ns
Fiber-optic cable	UV fused silica, incoherent bundle
Length	5 m
Diameter	1 mm

detection. The spectra were obtained with 1 μs exposure time and 2.5 μs after each laser light pulse. The detection was performed in a synchronised manner with an 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 of the line was determined with a precision of 97%, and the instrumental width (FWHM) was found to be 0.11 Å for a wavelength of 3000 Å. The laser beam was focused in a spot of about 0.5 mm diameter, so the average light flux was 1.4×10^{10} W cm^{-2}.

A chamber was used to generate the plasma in a vacuum or in a gas atmosphere. After a vacuum of 10^{-5} Torr had been attained inside the chamber, by means of a turbomolecular pump, it was filled with argon and maintained at a constant pressure of 6 Torr throughout the measurement, using a small continuous flow of gas to maintain the purity of the atmosphere. The buffer gas pressure value, 6 Torr, was chosen because it gives the best contrast between line emission and continuum emission.

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 to the entrance slit of the spectrometer, as can be seen in Fig. 1. In this way, it was possible to select 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 of the lead are located in the plasma and to determine the real values of the parameters of the plasma, Alonso-Medina [10].

The spectral response of the system was obtained in the 2000–7000 Å wavelength range by means of a previously calibrated deuterium lamp for the 2000–4000 Å range, and a tungsten lamp for the 3700–7000 Å range. Both the lamps were previously calibrated. The calibration was also verified by means of Ar I and Ar II branching ratios [16–19] to permit the comparison of the response selected in the spectral regions centred in 2500, 3800 and 6500 Å, Alonso-Medina [10]. As the system is more efficient in the range 4000–5000 Å the study of the line 2203.55 A of Pb II has been realised also in second order as test of the results.

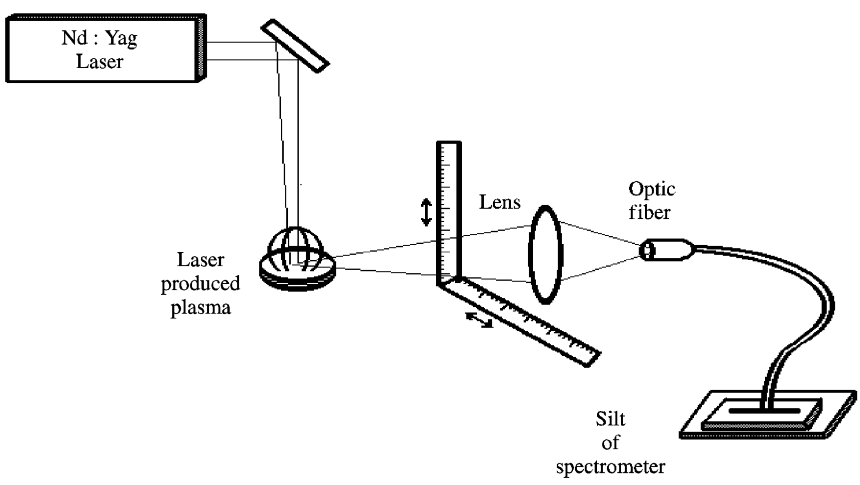

Fig. 1. Schematics of the experimental arrangement for the study of the plasma homogeneity.

Branching ratios have been determined by measuring the relative emission line intensities for lines arising from the same upper levels. As is well known, for these measurements optically thin light sources must be used. In the present work, to avoid self-absorption effects, we used Sn–Pb alloys with a lead content lower than 0.5%. For contents of this order of magnitude, a dependence of the branching ratios on concentration has not been observed. The obtained values are in agreement with the values from other authors, indicating that no significant self-absorption exists and no corrections are necessary.

3. Experimentals results and discussion

The LPP emission spectrum in the visible region was recorded for different delay times Alonso-Medina [10]. In our experimental conditions with a delay time of 2.5 μs after the laser pulse, in an atmosphere of Ar at 6 Torr, all the transitions of the Pb II spectrum can be observed as also can those of the Pb I as well as some of the Ar I, Ar II and Sn I and Sn II.

We used Sn–Pb alloy targets with a lead content lower than 0.5%. Figs. 2 and 3 display typical emission spectra obtained in the conditions described above; the lines studied range from 2000 to 7000 Å. Relative intensities have been measured for lines of Pb II, Pb I, Sn II and Ar II, evaluating the area under each one, for which purpose adjustments were made to the profiles observed of the lines by means of a convolution of the instrumental profile, known, with the Voigt profile obtained from the Lorentzian and Gaussian contributions selected [20,21].

The instrumental profile was pre-determined by the observation of various narrow lines emitted by hollow cathode lamps. The setting of the profiles allows us to safely obtain the total intensities of the lines, as well as the Lorentzian and Gaussian contribution in each line.

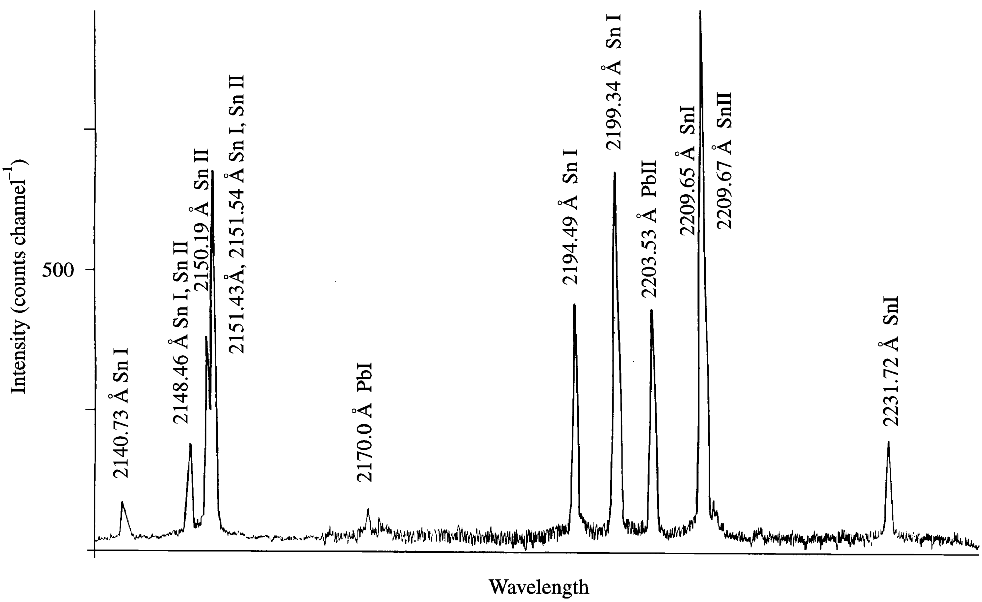

Fig. 2. Section of typical Pb I, Pb II, Sn I and Sn II spectra at 6 Torr (2.5 μs delay-time).

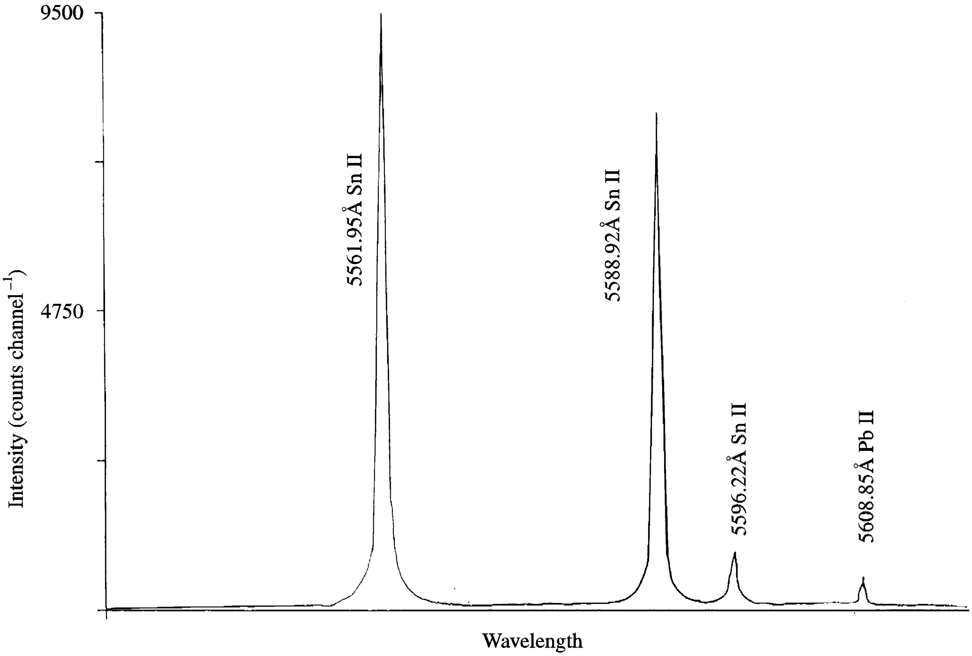

Fig. 3. Pb II and Sn II spectrum in the range (5550–5700) Å at 6 Torr atmosphere of Ar (2.5 μs delay-time).

As is well known 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

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

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 $-l/kT$, 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 [22,23].

Fig. 4 shows a partial energy-level diagram for Pb I including the lines in study, and Fig. 5 shows a partial Grotrian diagram for Pb II, showing transitions used for temperature calculation.

As a confirmation of the LTE assumption we also obtain the plasma temperature as deduced from lines of the buffer gas; the selected spectral lines from Pb I, Pb II, Sn II and Ar II are shown in Table 2 together with the relevant information needed. The transition probabilities for the Pb II and Pb I are those obtained in our previous study [8–10] for the Sn II line these data come from the work of Wujec and Weninger [24] and for the Ar II of Vujnovic and Wiese [18].

Fig. 6 displays a Boltzmann plot from which a value of (11060 ± 450) K for $\Delta E = 2.14$ eV was obtained for the electron temperature for Pb II. With the spectrum lines selected for Pb I — 3639.6,

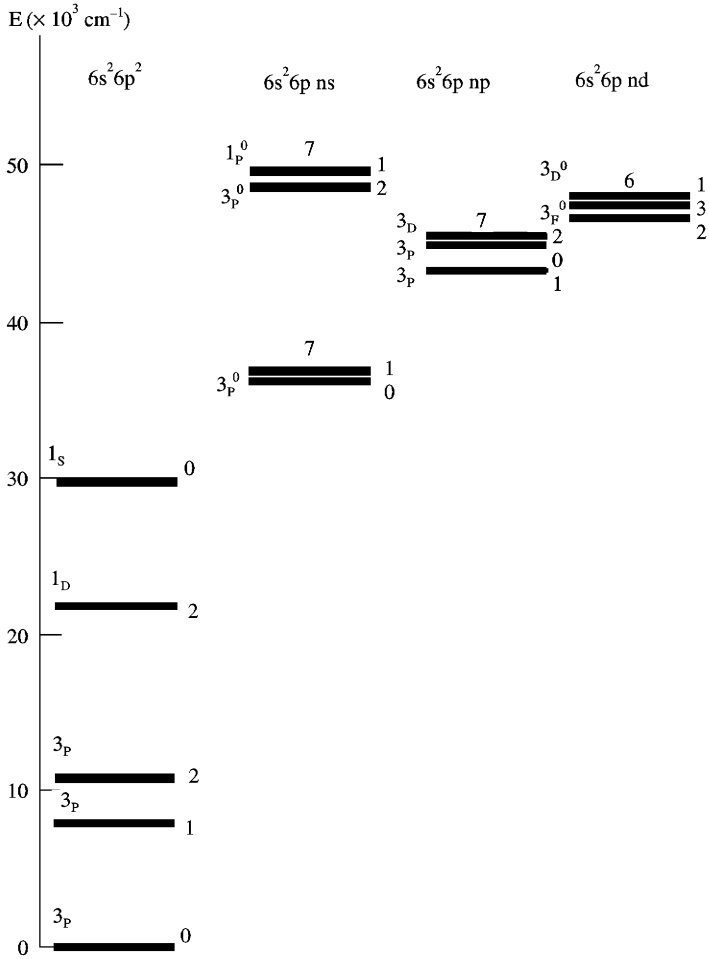

Fig. 4. Energy level diagram of Pb I showing transitions in study.

3572.8 and 2446.3 Å — the (11100 ± 1000) K value for $\Delta E = 1.77$ eV was obtained. The spectrum lines selected for Ar II were 3944.3, 3952.7, 3968.4 and 3979.4 Å, and resulted in a value of (11200 ± 600) K for $\Delta E = 3.55$ eV; and for Sn II were 6844.2, 6453.6 and 5562.0 Å, with a value of (11100 ± 500) K for $\Delta E = 2.55$ eV. These values are totally compatible with the values obtained from the lines of Pb II and totally compatible with the values obtained using all the samples.

The electron densities, N_e, of the plasma investigated have been obtained by comparisons the Stark broadening for several transitions with those of other authors; the value obtained is 10^{16} cm^{-3}. The values of the electron densities from very different spectrum lines are in good agreement. Table 3 displays the values obtained for the 4244.9, 5544.3 and 5608 Å of the Pb II, and for the 5562.0, 5334.4 and 5588.8 Å of Sn II, with the third column giving the Stark broadening obtained by Puric et al. [25] for the lines of Pb II, and those obtained by Miller et al. [4] for the lines of Sn II. Secondly, a result of (11100 ± 500) K was obtained by applying the Saha equation to

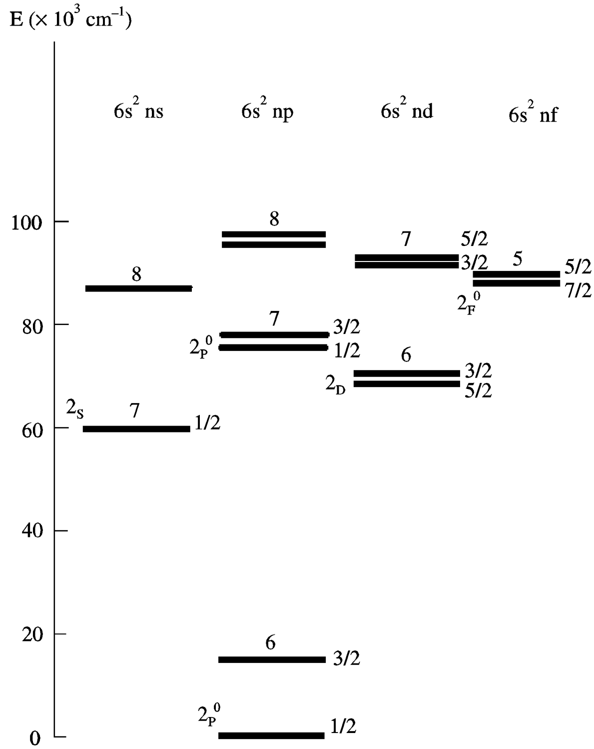

Fig. 5. Partial Grotrian diagram for Pb II showing transition used for temperature calculations.

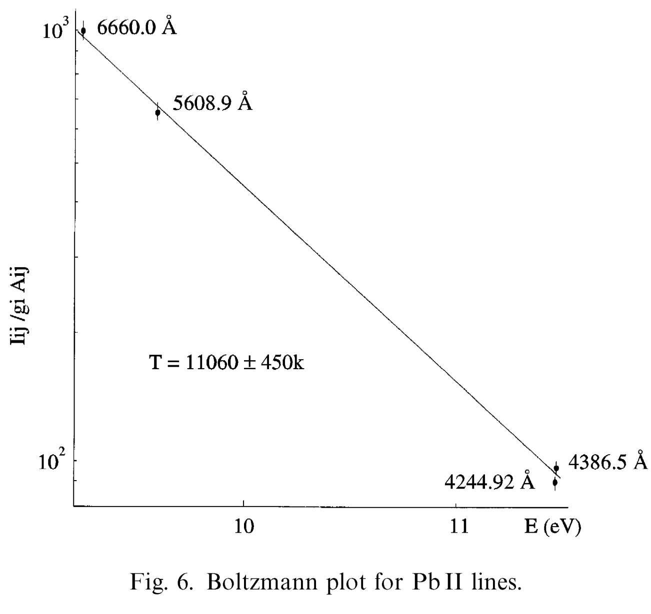

Fig. 6. Boltzmann plot for Pb II lines.

Table 2
Additional spectroscopic data of Pb I, Pb II, Sn II and Ar II employed for temperature determination

Atomic species	λ (Å)	Upper level (energies in eV)	g_i	A_{ij} ($\times 10^6$ s^{-1})
Pb I	3639.6[a]	4.37	2	32.0 ± 5.0
	3572.8[a]	6.13	2	102.9 ± 10.3
	2446.3[a]	6.04	2	22.6 ± 3.4
Pb II	6660.0[b]	9.33	2	57.2 ± 5.4
	5608.9[b]	9.58	4	84.8 ± 8.5
	4386.4[b]	11.47	6	155.7 ± 15.6
	4244.9[b]	11.47	8	115.0 ± 11.6
Sn II	6844.2[c]	8.65	2	66 ± 21
	6453.6[c]	8.97	4	121 ± 36
	5562.0[c]	11.2	6	118 ± 40
Ar II	3944.3[d]	19.55	6	4.1 ± 0.6
	3968.4[d]	19.55	6	4.8 ± 0.5
	3952.7[b]	23.10	4	20.8 ± 3.1
	3979.4[b]	23.04	2	98.0 ± 30.3

[a] Ref. [9].
[b] Ref. [10].
[c] Ref. [24].
[d] Ref. [18].

Table 3
Electron density of plasma (6 Torr Ar, delay time of 2.5 μs)

		λ (Å)	$T = 16{,}000$ K, $N_e = 10^{17}$ cm^{-3}, $\omega_{exp} \pm 15\%$	N_e (10^{16} cm^{-3})
Pb II transition	5f $^2F^o_{7/2} \rightarrow$ 6d $^2D_{5/2}$	4244.9	1.52[a]	0.99 ± 0.20
	7d $^2D_{5/2} \rightarrow$ 7p $^2P^o_{3/2}$	5544.3	3.18[a]	1.01 ± 0.19
	7p $^2P^o_{3/2} \rightarrow$ 7s $^2S_{1/2}$	5608.9	2.12[a]	1.00 ± 0.18
Sn II transition	6p $^2P^o_{3/2} \rightarrow$ 6d $^2D_{5/2}$	5562.0	5.1 ± 0.7[b]	1.10 ± 0.20
	6p $^2P^o_{1/2} \rightarrow$ 6d $^2D_{3/2}$	5332.4	5.3 ± 0.7[b]	0.99 ± 0.20
	5d $^2D_{5/2} \rightarrow$ 4f $^2F^o_{5/2}$	5588.8	3.8 ± 1.0[b]	1.12 ± 0.33

[a] Ref. [25].
[b] Ref. [4].

the Pb I line at 5005.5 Å and the 5042.6 and 5602.9 Å lines of Pb II, using the transition probabilities given by Alonso-Medina [9].

This value of N_e is sufficient to assume LTE for the population of the studied levels according to the criterion of Mc Whirters

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

where ΔE, in eV, is the energy difference between both configurations and T the plasma temperature, in K. In our case $\Delta E = 3.55$ eV and the lower limit given by this expression is 7.53×10^{15} cm^{-3} which justifies the assumption of LTE.

An estimate of the self-absorption of the plasma can be made once the temperature and electron density are known by absorption coefficient calculations [26]. In this experiment self-absorption effects turned out to be lower than 1% for the most intense lines; thus, the plasma can be considered optically thin.

In order to determine the change of the temperature and the electron density in different regions of the plasma had been used several Pb II and Ar II lines. These results indicate a satisfactory homogeneity for temperature and electron density. Deviations from the average are less than 10% for N_e and less than 5% for T in a region measuring approximately 2.5 mm in size corresponding to 95% of the emission of light; similar results have been obtained in other LPP experiments.

Table 4
Comparisons of experimentally determined transition probabilities (column 3) of Pb I with other results (in $\times 10^6$ s^{-1})

Transition levels		λ (Å)	This work	[a]	[b]	[c]	[d]
Upper	Lower						
6p 7s $^3P^o_2$	6p^2 $^3P_1$	2476.5	35.6 ± 6.1		38.0 ± 3.8	28.0	
	6p^2 $^3P_2$	2663.2	79.7 ± 16.0		101.0 ± 10.1	71.0	
	6p^2 $^1D_2$	3739.9	58.6 ± 10.2			73.0	
$\tau = (5.98 \pm 0.22)$ ns							
6p 7s $^1P^o_1$	6p^2 $^3P_0$	2022.1	7.1 ± 0.6	6.8 ± 0.6		5.2	11.0 ± 4.9
	6p^2 $^3P_1$	2402.0	26.4 ± 3.4	29.8 ± 3.0	28.0 ± 2.8	19.0	
	6p^2 $^3P_2$	2577.3	64.1 ± 6.8	55.2 ± 5.5	67.0 ± 6.7	50.0	
	6p^2 $^1D_2$	3572.8	99.5 ± 10.0	102.9 ± 10.3		99.0	
	6p^2 $^1S_0$	5005.5	10.4 ± 1.4	12.1 ± 1.2		27.0	
$\tau = (4.99 \pm 0.13)$ ns							
6p 6d $^3D_2$	6p^2 $^3P_1$	2614.3	206.0 ± 41.2		234.0 ± 50.0	187.0	
	6p^2 $^3P_2$	2823.3	26.0 ± 5.2		43.0 ± 4.3	25.5	
	6p^2 $^1D_2$	4063.4	0.0019 ± 0.0005				
$\tau = (4.34 \pm 0.23)$ ns							

[a] Ref. [9].
[b] Ref. [1].
[c] Ref. [24].
[d] Ref. [30].

The transition probabilities of lines with origin in the 6p 7s and 6p 6d configurations of Pb I, obtained from lifetime and branching-ratio measurements are shown in the third column of Table 4. The experimental errors for these values are the result of statistical uncertainties, errors in the lifetime measurements and uncertainties in the spectral response determination; data given by other authors have been included for comparison. There is a good agreement with the data of Penkin [1], Lotrian [3], and Alonso-Medina [9].

Table 5 contains a summary of the lifetimes of the $^3P^o_2$(6p 7s), $^1P^o_1$(6p 7s) and $^3D^o_2$(6p 6d) states of Pb I found in the literature [2,27–30]. The relative values of lines arising from these values were put on absolute scale by using mean value pondered of all the lifetime of these authors.

The transition probabilities obtained from the Boltzmann plot for the 2203.5 Å line of Pb II and for 30 lines of Pb I are displayed in column three of Tables 6 and 7. The remaining columns give the theoretical and experimental values to be found in the bibliography [6,8,31] in Table 6, [1–3,9] in Table 7. The values of column four are those calculated in studies previous to this work (Alonso-Medina [8,9]). The errors quoted in this table have been calculated as the quadratic addition of the statistical uncertainties. The error is due to the temperature estimate and systematic errors. It is notorious which there is a good agreement between the values.

Table 5
Lifetime for states of Pb I

State	Measurement lifetime (ns)		
6p 7s^3 P^o_2	5.85 ± 0.27^a	6.10 ± 0.50^b	6.60 ± 0.70^c
6p 7s^1 P^o_1	5.60 ± 0.50^c	4.99 ± 0.15^d	4.80 ± 0.30^e
6p 6d^3 D^o_2	4.14 ± 0.49^a 0.31	5.00 ± 0.50^c	

[a] Ref. [27] (Hanle method).
[b] Ref. [28] (Beam-foil).
[c] Ref. [29] (Delayed coincidences).
[d] Ref. [2] (Level-crossing effect).
[e] Ref. [30] (Level crossing).

Table 6
Pb II transition probability obtained by using the plasma temperature

Transition level	λ (Å)	Experimental This work	Absolute transition probabilities ($\times 10^8$ s^{-1}) Theory		
7s $^2S_{1/2} \rightarrow$ 6p $^2P_{3/2}$	2203.5	4.93 ± 0.74	4.92[a]	5.52[b]	4.97[c]

[a] Ref. [8].
[b] Ref. [6].
[c] Ref. [31].

Table 7
Experimental Pb I transition probabilities obtained from Boltzmann plot

Transition levels			Experimental absolute transition probabilities ($\times 10^6$ s^{-1})				
Upper	Lower	λ (Å)	This work	Ref. [9]	Ref. [3]	Ref. [1]	Ref. [2]
7s $^2P^o_0$ →	6p^2 $^3P_1$	3683.5	167.6 ± 10.6		151.0	171.0 ± 17.1	
7s $^2P^o_1$ →	6p^2 $^3P_0$	2833.1	55.7 ± 3.3	43.0 ± 6.1	58.0	59.0 ± 5.9	47.0 ± 9.4
	6p^2 $^3P_1$	3639.6	30.8 ± 2.1	32.0 ± 5.0	33.5	32.0 ± 3.2	20.0 ± 7.0
	6p^2 $^3P_2$	4057.9	108.0 ± 7.5	93.1 ± 13.9	89.0	103.0 ± 10.3	105.4 ± 36.8
7s $^3P^o_2$ →	6p^2 $^3P_1$	2476.5	36.5 ± 2.3		28.0	37.8 ± 3.8	
	6p^2 $^3P_2$	2663.2	90.5 ± 5.5		71.0	100.6 ± 10.0	
	6p^2 $^1D_2$	3739.9	53.3 ± 3.4		73.0		
7s $^1P^o_1$ →	6p^2 $^3P_1$	2401.9	30.1 ± 2.0	29.8 ± 3.0	19.0	28.0 ± 2.8	
	6p^2 $^3P_2$	2577.3	59.3 ± 3.6	55.2 ± 5.5	50.0	67.0 ± 6.7	
	6p^2 $^1D_2$	3572.8	95.3 ± 6.0	102.9 ± 10.3	99.0		
	6p^2 $^1S_0$	5005.5	8.5 ± 0.5	12.1 ± 1.2	27.0		
8s $^3P^o_0$ →	6p^2 $^3P_2$	2443.82	49.3 ± 2.6				
8s $^3P^o_1$ →	6p^2 $^3P_1$	2446.3	24.5 ± 1.5	22.6 ± 3.4	24.5	14.9 ± 1.5	
	6p^2 $^3P_2$	2628.3	10.3 ± 0.8	7.0 ± 1.1	3.1		
	6p^2 $^1D_2$	3671.5	30.3 ± 1.8	34.4 ± 4.9	44.0		
	6p^2 $^1S_0$	5201.5	5.2 ± 0.3	5.8 ± 0.7	19.0		
9s $^3P^o_1$ →	6p^2 $^3P_2$	2332.5	36.0 ± 2.7				
	6p^2 $^1D_2$	3118.9	11.0 ± 0.8				
6d $^3D^o_2$ →	6p^2 $^3P_1$	2614.3	186.7 ± 11.2		187.0	234.0 ± 50.0	
	6p^2 $^3P_2$	2823.3	28.1 ± 1.9		25.5	43.0 ± 4.3	
6d $^3D^o_1$ →	6p^2 $^3P_0$	2170.0	172.9 ± 8.5	165.0 ± 16.3	149.0	184.0 ± 18.4	
	6p^2 $^3P_1$	2613.7	23.8 ± 1.4	21.2 ± 2.1	26.5	18.4 ± 8.3	
	6p^2 $^3P_2$	2822.6	2.0 ± 0.2				
	6p^2 $^1D_2$	4062.2	78.1 ± 5.4	70.1 ± 6.0	92.0		
6d $^3F^o_2$ →	6p^2 $^3P_2$	2873.4	33.3 ± 2.0		37.0	29.0 ± 3.0	
	6p^2 $^1D_2$	4168.1	1.3 ± 0.1		1.2		
6d $^3F^o_3$ →	6p^2 $^3P_2$	2802.1	193.1 ± 11.0		152.0	182.0 ± 18.2	
	6p^2 $^1D_2$	4019.7	2.1 ± 0.2		9.5		
7d $^3F^o_2$ →	6p^2 $^3P_2$	2411.8	27.6 ± 1.9				
7d $^3F^o_3$ →	6p^2 $^3P_2$	2393.9	63.1 ± 3.8			64.8 ± 6.5	
	6p^2 $^1D_2$	3229.7	6.0 ± 0.5				
7d $^3D_2$ →	6p^2 $^3P_2$	2399.7	22.4 ± 1.4				
	6p^2 $^1D_2$	3240.2	28.9 ± 2.0				
7d $^3D_1$ →	6p^2 $^3P_1$	2237.5	2.5 ± 0.2				
	6p^2 $^3P_2$	2388.9	50.8 ± 2.5				
	6p^2 $^1D_2$	3220.5	82.7 ± 5.8				
	6p^2 $^1S_0$	4340.5	27.4 ± 1.9				

4. Conclusions

In the present work we have obtained the transition probabilities values in 39 lines of the spectrum of emission of Pb I, and the transition probability for the 2203.5 A line of Pb II, first experimental data that are obtained. In the present study it is shown that laser-produced plasmas are a very interesting spectroscopic source, providing media with high temperature and density, but demanding time resolving spectroscopy for its study.

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