A spectroscopic study of the plasma generated in a thallium arc. Transition probabilities for several lines of Tl I

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Abstract. The optical emission spectra (2000–15 000) Å of a plasma produced an a Tl arc lamp have been recorded and analysed; using the series nd ^{2}D$_{3/2,5/2}$ → 6p ^{2}P$^o_{3/2}$ and ns ^{2}S$_{1/2}$ → 6p ^{2}P$^o_{3/2}$ we have obtained that the electron density is of the order of 10^{14} cm^{-3} and the excitation temperature is (2880 ± 50) K. Relative transition probabilities for 26 lines from excited levels near the ionization limit of Tl I have been determined from line intensities.

1. Introduction

In this work we have obtained the spectrum of emission of Tl I in the range (2000–15 000) Å originated with an arc lamp of low current; all the lines arises from Rydberg levels. From the Inglis–Teller relation we have calculated the electron density of plasma, and we have also determined the excitation temperature of the levels in an energy interval of (4.24–5.82) eV; following Boltzmann's law we have also determined the transition probabilities for 26 lines of Tl I for transitions from levels P, D and S nearly ionization limit. The values obtained in this study are compared with existing experimental and theoretical values.

2. Experimental set-up and procedure

The experimental set-up is similar to that described in previous publications (Alonso-Medina 1996a, c, García and Campos 1988, 1989, Peraza *et al* 1991); emission intensities of lines with a common upper level have been measured by means of single-photon counting. The spectral source used was an ac Tl arc lamp, filled with argon, operating at 0.9 A and 1 Torr pressure; the light path was 1 cm. The transition wavelength range (2000–7500 Å) was isolated by using a 1.2 m Czerny–Turner monochromator with 0.36 Å resolution in the first order; photons were detected with an EMI 9558 QB (uv extended S20 response) photomultiplier cooled with dry ice.

The transition wavelength range (7000–15 000 Å) was isolated by using a 1 m Eagle monochromator (Martin *et al* 1989) having a 600 grooves mm^{-1} concave holographic grating, blazed at 9000 Å; the spectral resolution was 2 Å. Photons from 6000 to 11 000 Å were detected with an EMI 9808 B (S1 response) photomultiplier cooled with dry ice. Photons from 8000 to 15 000 Å, were detected with an InGaAs PIN photodiode operating in the photovoltaic mode; the photosensitive diameter was 3 mm.

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To eliminate noise signals, a phase-sensitive detection technique (Tanarro and Campos 1986, Meade 1982) was used; the light was chopped at a frequency of 450 Hz. The electronic system consisted of a passband amplifier, an analogue–digital converter and an analogue phase-sensitive circuit which subtracts the half-periods of noise from the signal plus noise half-periods; the output of this circuit feeds a strip-chart recorder. In this type of arc lamp only lines of Tl I and of Ar I are observed, and the resolution of the system avoids the interference between the lines of the two atoms.

Calibrated tungsten-strip and deuterium lamps were used to determine the spectral reponse in the 2000–15 000 Å range. The calibration was also verified by means of Ar I branching ratios which are well known (Alonso-Medina 1996c, Befeki 1976, Borge and Campos 1983, Wiese *et al* 1989), and which permit the comparison of the response selected in the spectrum regions centred in 3900, 6900, 8500 and 10 500 Å. The Ar I lines used were the transitions of wavelengths 3948.98, 4045.96, 4181.88 and 4335.34 Å arising from the $4s[3/2]^0 \rightarrow 5p'[1/2]$ transition, the lines 6965.4 and 7272.9 Å arising from the $4s[3/2]^0 \rightarrow 4p'[1/2]$ transition, the lines 8014.8 and 8424.6 Å from the $4s[3/2]^0 \rightarrow 4p[5/2]$ transition and the lines 10 470.0 and 11 488.1 Å from the $4s'[1/2] \rightarrow 4p[1/2]$ transition.

Appropriate cut-off optical filters were used to eliminate second-order radiation. Several emission spectra were recorded to obtain relative intensity with statistical uncertainties of 3%. The sensitivity of the detector systems allows measurements with optically thin sources, avoiding systematic errors due to self-absorption.

Self-absorption checks were made by placing a mirror behind the lamp so that the geometrical length of the emitting region was doubled; no change in intensity relations was observed. Thus, it was concluded that self-absorption corrections were unnecessary.

Light emissivity was proved to be practically constant in a central zone of width 6 mm and height 15 mm. Measurements made to test light intensity stability did not show variations greater than 8% during 90 min. Furthermore, line intensities were taken as an average of several up and down spectral scans, obtained in different days.

It has been checked that all the lines have a Gaussian profile with the same FWHM of 0.18 Å, and therefore the normalized ratios between the heights of lines are the relative intensities. In the lines arising from levels near the ionization limit, used only to evaluate the electronic density, the Stark broadening is important and to measure relative intensities it is necessary to make adjustments of the observed profiles by means of a convolution of the instrumental profile with the Voigt profiles obtained from the contributions selected (Brüggemann and Bollig 1992, Griem 1964).

3. Results and discussions

3.1. Emission spectrum

Of the emission spectrum obtained in this work there are few experimental values of the transition probabilities for lines corresponding to transitions from levels near the ionization limit. An example of the type of information obtainable from such a spectrum is given in figure 1, where lines of Rydberg levels are shown: $nd\,^2D_{3/2,5/2} \rightarrow 6p\,^2P^o_{3/2}$ with $n = 10$–23 and $ns\,^2S_{1/2} \rightarrow 6_p\,^2P^o_{3/2}$ with $n = 12$–20. Figure 2 depicts graphically the energy level diagram of Tl I, where it is possible to identify the correspondent transitions, and we can appreciate that the highest level number before the limit of ionization is 23; the table of Moore (1958) has been used to provide level energies for our diagram.

It is known that for the type of lamp utilized in this work, the absorption is appreciable in the resonance lines and in transitions from low-energy levels, and therefore it is not
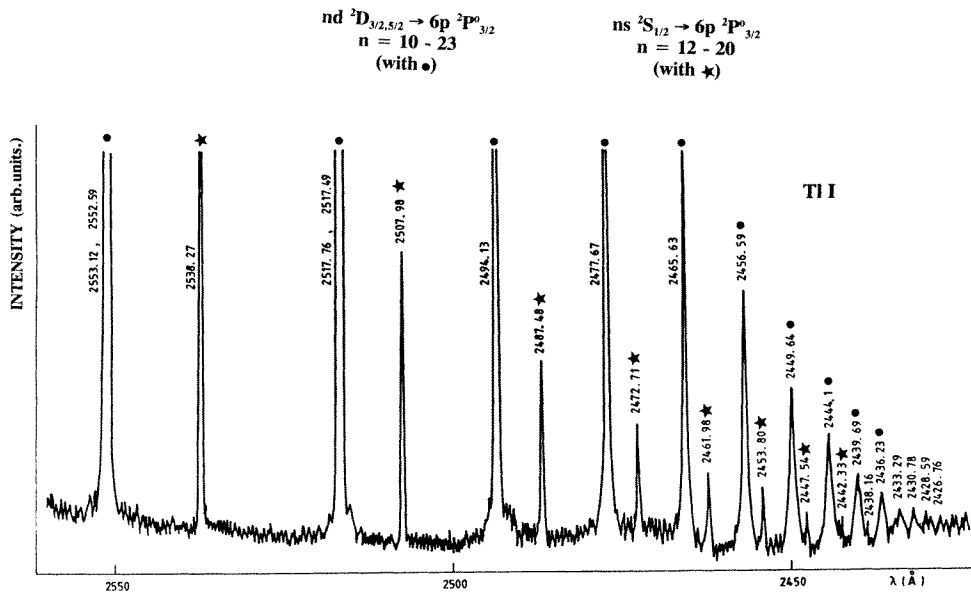
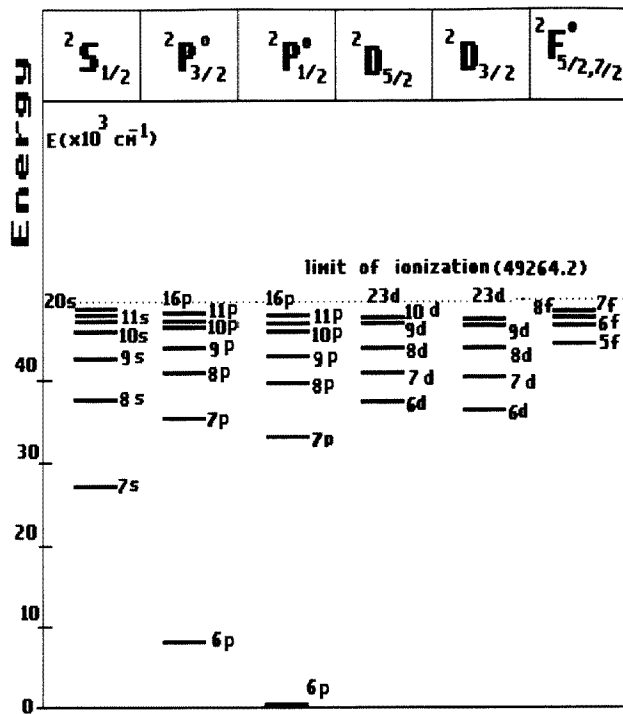Figure 1. Tl I spectrum in the range (2550–2400) Å.

Figure 2. Partial diagram of energy levels of the Thallium atom.

possible to give values of relative transition probabilities; in Kirkhight and Sargent (1974) the description of the absorption of the line 3776.8 Å correspondent to the $7s\,^2S_{1/2} \rightarrow 6p\,^2P^o_{1/2}$

transition of Tl I is shown in detail, which is obtained with a lamp identical to that utilized in this work. The lines studied in this paper originate in levels near the ionization limit, and they have an absorption negligible in practice with regard to experimental errors.

3.2. Electron density

When the considered levels are near the limit of the $nd\,^2D_{3/2,5/2} \rightarrow 6p\,^2P^o_{3/2}$ series, the lines have a progressive broadening caused by the Stark effect, and when the Stark splitting is the same as the energy separation of the levels with different principal quantum numbers the spectral series of lines just end; above some maximum value, say n_{max}, the energy levels of the atom merge with the continuum, as is shown in the section of the emission spectrum of Tl I obtained with a multichannel analyser, see figure 3. The last lines of the series $nd\,^2D_{3/2,5/2} \rightarrow 6p\,^2P^o_{3/2}$ that are clearly different from the continuum are the 17d transition, with 2444.1 Å, and the 18d, with 2439.7 Å; in the series $ns\,^2S_{1/2} \rightarrow^2 P^o_{3/2}$ the last lines correspond to 16s, with 2461.9 Å, and 17s, with 2453.8 Å.
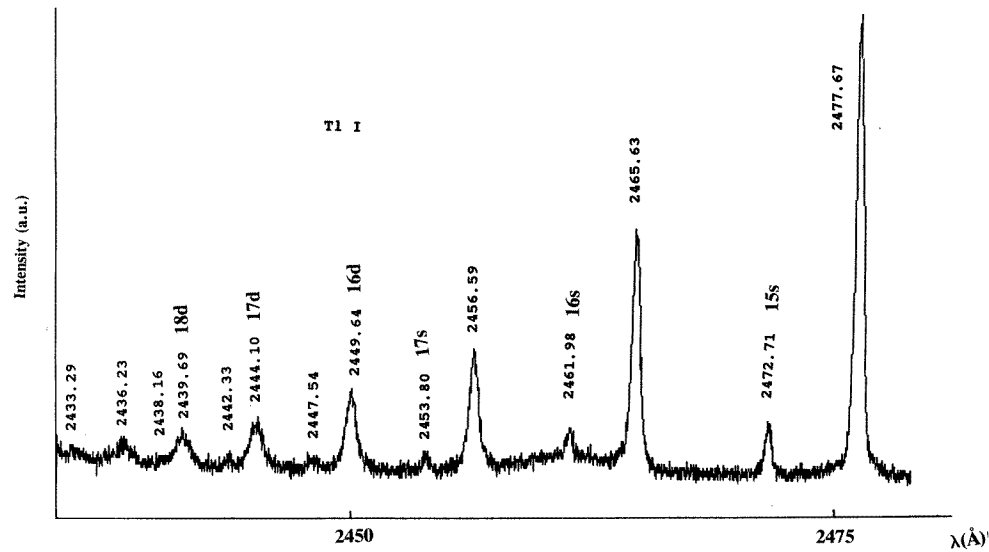

Figure 3. Section of the Tl I spectrum where the lines merge with the continuum.

This effect depends appreciably on the electron density of the plasma, and in a hydrogen plasma the splitting of the energy levels also increases as the square of the principle quantum number. Inglis and Teller (1939) give a relation in order to estimate the electron density from the last countable Balmer line of the hydrogen atom. From a simplified broadening theory for the Balmer lines, one finds that the highest quantum number n_{max} for which the energy levels are still separated is related to the electron density, N_e, by (Böhm–Vitense 1989)

$$\log N_e = 23.26 - 7.5 \log n_{max}. \tag{1}$$

This equation is valid for low temperatures, $T(K) < 10^5/n_{max}$, which is true in our case as is proved in the next section. Tl I is a hydrogenoid atom for the very excited levels and, assuming that high-n Tl levels approximate the Stark broadening of high-n Balmer lines,

expression (1) enables us to obtain a value for the electron density in the emission plasma generated in the lamp described previously.

The values calculated for N_e, in cm^{-3}, are 7×10^{13} for the 18d transition and 1.1×10^{14} for 17d; in the series ns the values are 1.7×10^{14} for the 16 s transition and again 1.1×10^{14} for the 17s. We can conclude that the electron density is of the order of 10^{14} cm^{-3}.

3.3. Temperature of plasma

When the conditions of an optically thin plasma are such that local thermodynamic equilibrium (LTE) is valid, the relative intensity (I_{ij}) of lines from a given state of excitation can be used to calculate the electron temperature but the transition probabilities (A_{ij}) must be known previously since the populations of the excited states are given by the Boltzmann distribution (Befeki 1976 and Griem 1964). We can apply the expression

$$\ln\left(\frac{I_{ij}}{g_i A_{ij}}\right) = \ln\frac{N}{Z(T)} - \frac{E_i}{kT}. \tag{2}$$

For a transition from upper state i to lower state j, I_{ij} is the intensity, N and $Z(T)$ are the population and the partition of the atomic species, respectively. E_i and g_i are the energy and the statistical weight of level i, k is the Boltzmann constant and T is the temperature. A plot of $\ln(I_{ij}/g_i A_{ij})$ against *a Boltzmann plot*, has a slope of $-1/kT$, and therefore the temperature can be obtained without a knowledge of N and $Z(T)$; the line intensities used (in photons s^{-1}) are normalized to the highest value.

Table 1. Parameters for electron temperature calculations.

Transition	λ (Å)	E_i (eV)	A_{ij} ($\times 10^6$ s^{-1})
$7p\,^2P^o_{1/2} \to 7s\,^2S_{1/2}$	13 013.2	4.236	17.1 ± 0.7[a]
$7p\,^2P^o_{3/2} \to 7s\,^2S_{1/2}$	11 512.8	4.360	23.7 ± 0.9[a]
$7d\,^2D_{3/2} \to 7p\,^2P^o_{1/2}$	12 732.9	5.209	7.35 ± 0.62[b]
$9s\,^2S_{1/2} \to 7p\,^2P^o_{1/2}$	11 100.3	5.352	1.15 ± 0.11[b]
$8d\,^2D_{3/2} \to 7p\,^2P^o_{1/2}$	9509.4	5.539	3.25 ± 0.23[b]
$10s\,^2S_{1/2} \to 7p\,^2P^o_{1/2}$	8976.7	5.616	0.38 ± 0.04[b]
$10p\,^2P^o_{3/2} \to 6d\,^2D_{3/2}$	10 072.1	5.709	0.059 ± 0.04[b]
$9d\,^2D_{3/2} \to 7p\,^2P^o_{1/2}$	8373.9	5.717	2.36 ± 0.16[b]
$11s\,^2S_{1/2} \to 7p\,^2P_{1/2}$	8129.9	5.760	0.34 ± 0.05[b]
$11p\,^2P^o_{3/2} \to 6d\,^2D_{3/2}$	9257.4	5.817	0.019 ± 0.006[b]
$10d\,^2D_{3/2} \to 7p\,^2P^o_{1/2}$	7816.5	5.821	1.68 ± 0.18[b]

[a] Hunter and Commins (1982).
[b] Alonso-Medina (1996c).

The energy and transition probabilities utilized for the determination of excitation temperature are given in table 1 (Alonso-Medina 1996c, Hunter and Commins 1982). The corresponding plot is shown in figure 4, which clearly has a linear design as in the Boltzmann plot; the value obtained is $T_{exc} = (2880 \pm 50)$ K.

To support the LTE hypothesis the MacWhirter's criterion to estimate the lower limit of the electron density has been used; it is given by the following expression (MacWhirter 1965):

$$N_e(cm^{-3}) \geqslant 1.6 \times 10^{12}\sqrt{T}(\Delta E)^3 \tag{3}$$

where ΔE, in eV, is the energy difference between the upper and lower states considered, and therefore the respective transition will have the line with smallest wavelength, T, in
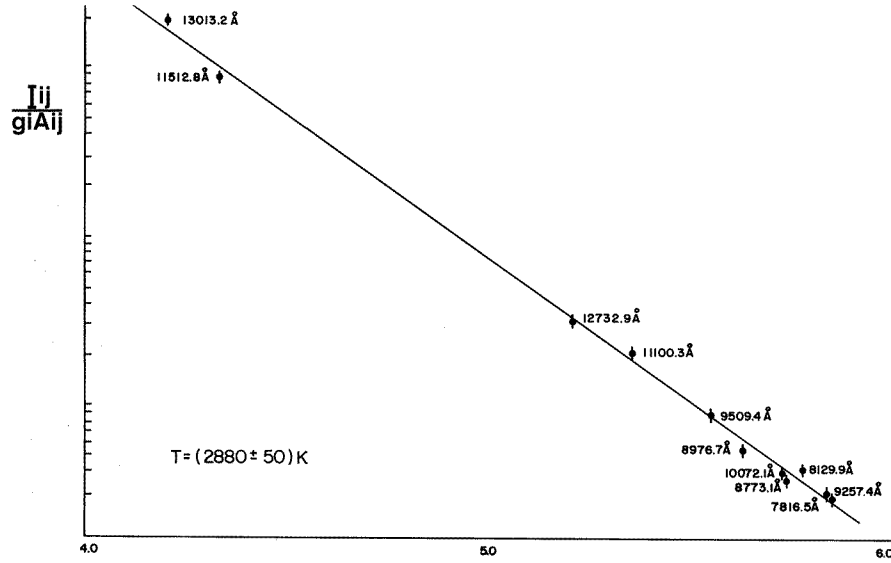
Figure 4. Boltzman plot for the calculation of the temperature.

K, is the temperature and N_e the lower limit of the electron density necessary to keep the populations of the energy levels at 10% of the LTE by collision (Wolf 1992), in competition with the radiative processes. In our case, $T = 2880$ K, the maximum value of ΔE is 1.6 eV, $\lambda = 7816.5$ Å and accordingly the lower limit given by expression (3) is 3.5×10^{14} cm^{-3}, which is the same order of magnitude as the N_e value obtained before. Consequently we can judge that the condition of LTE for transitions from high excited levels of Tl I is applicable.

3.4. Tl I transition probabilities obtained from the Boltzmann plot

If we generalized the existence of LTE to the complete spectral range obtained, we can build the Boltzmann plot to calculate the transition probabilities with wavelengths in the ultraviolet region. These parameters calculated for the 26 lines of Tl I, with wavelengths in the range (2200–4900) Å, are displayed in the third column of table 2, while columns one and two give the transitions and the corresponding wavelengths, respectively. The remaining columns give the experimental (Penkin and Slavenas 1963, Gallagher and Lurio 1964) and theoretical (Anderson et al 1967, Alonso-Medina 1996b) values of transition probabilities found in the references.

A good match is observed between the values obtained in this work and the experiment of the references; however, the existence of serious discrepancies with any theoretical values is notorious and they are not similar here. This disagreement may be due to a number of reasons, either experimental or theoretical, but it could be partly explained by the fact that the theoretical models do not adequately consider the interaction of the electronic configurations with similar energy (Alonso-Medina 1996b, Martínez et al 1996). In any case it is necessary to obtain more values with other conditions of excitation and with different theoretical approximations to delimit the correct order of magnitude of the transition probabilities.

Table 2. Tl I Transition probabilities obtained from the Boltzmann plot. (a) Penkin and Slavenas (1963); (b) Gallagher and Lurio (1964); (c) Anderson *et al* (1967); (d) Alonso-Medina (1996b).

		Absolute transition probabilities ($\times 10^6$ s^{-1})				
		Experimental			Theory	
Transition Levels Upper $\to$ lower	λ(Å)	This work	(a)	(b)	(c)	(d)
$10s\,^2S_{1/2} \to 6p\,^2P^o_{1/2}$	2207.1	13.5 ± 1.4	13.3		4.0	3.9
$6p\,^2P^o_{3/2}$	2665.7	6.0 ± 0.6	5.1	5.7 ± 0.6	5.4	5.0
$11s\,^2S_{1/2} \to 6p\,^2P^o_{1/2}$	2151.9	2.7 ± 0.3	2.9	3.1 ± 0.6	2.4	2.4
$6p\,^2P^o_{3/2}$	2585.7	2.8 ± 0.3			3.1	2.9
$12s\,^2S_{1/2} \to 6p\,^2P^o_{1/2}$	2119.0	1.7 ± 0.2	1.8	2.0 ± 0.5	1.5	1.5
$6p\,^2P^o_{3/2}$	2538.3	1.7 ± 0.2	1.5	1.6 ± 0.2	2.1	1.9
$13s\,^2S_{1/2} \to 6p\,^2P^o_{1/2}$	2097.9	1.1 ± 0.1				1.04
$6p\,^2P^o_{3/2}$	2508.0	1.0 ± 0.1	0.99	1.1 ± 0.1		1.25
$14s\,^2S_{1/2} \to 6p\,^2P^o_{1/2}$	2083.5	0.51 ± 0.05				
$6p\,^2P^o_{3/2}$	2487.5	0.54 ± 0.05				
$9d\,^2D_{3/2} \to 6p\,^2P^o_{1/2}$	2168.7	10.6 ± 1.1	9.9	9.8 ± 2.2	20.1	8.3
$6p\,^2P^o_{3/2}$	2609.9	2.0 ± 0.2	1.7	1.9 ± 0.2	2.9	1.2
$9d\,^2D_{5/2} \to 6p\,^2P^o_{3/2}$	2609.1	11.2 ± 1.1	9.1	10.0 ± 1.0	17.2	7.6
$10d\,^2D_{3/2} \to 6p\,^2P^o_{1/2}$	2129.3	5.4 ± 0.5	5.95	5.8 ± 1.5	12.5	4.9
$6p\,^2P^o_{3/2}$	2553.1	0.78 ± 0.08			1.75	0.70
$10d\,^2D_{5/2} \to 6p\,^2P^o_{3/2}$	2552.5	7.4 ± 0.7			10.6	4.4
$11d\,^2D_{3/2} \to 6p\,^2P^o_{1/2}$	2104.7	2.6 ± 0.3		4.0 ± 1.2		
$12d\,^2D_{5/2} \to 6p\,^2P^o_{3/2}$	2088.2	1.1 ± 0.1				
$8p\,^2P^o_{1/2} \to 7s\,^2S_{1/2}$	6713.8	3.7 ± 0.4			2.1	3.3
$8p\,^2P^o_{3/2} \to 7s\,^2S_{1/2}$	6549.9	6.2 ± 0.6			2.2	6.5
$9p\,^2P^o_{1/2} \to 7s\,^2S_{1/2}$	5584.0	0.45 ± 0.04			0.75	0.64
$9p\,^2P^o_{3/2} \to 7s\,^2S_{1/2}$	5527.9	1.3 ± 0.1			0.93	2.06
$10p\,^2P^o_{1/2} \to 7s\,^2S_{1/2}$	5136.9	0.21 ± 0.02			0.36	0.23
$10p\,^2P^o_{3/2} \to 7s\,^2S_{1/2}$	5109.5	0.52 ± 0.05			0.49	0.85
$11p\,^2P^o_{1/2} \to 7s\,^2S_{1/2}$	4906.3	0.0051 ± 0.0005			0.19	0.0072
$11p\,^2P^o_{3/2} \to 7s\,^2S_{1/2}$	4891.4	0.0035 ± 0.0004				

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