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A spectroscopic study of laser-induced tin–lead plasma: Transition probabilities for spectral lines of Sn I

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ABSTRACT

In this paper, we present transition probabilities for 97 spectral lines of Sn I, corresponding to transitions n ($n=6,7,8$)s → 5p^2, n($n=5,6,7$)d → 5p^2, 5p^3 → 5p^2, n($n=7$)p → 6s, determined by measuring the intensities of the emission lines of a Laser-induced breakdown (emission) spectrometry (LIBS). The optical emission spectroscopy from a laser-induced plasma generated by a 10 640 Å radiation, with an irradiance of 1.4×10^{10} Wcm^{-2} on an Sn–Pb alloy (an Sn content of approximately 20%), in vacuum, was recorded at 0.8 μs, and analysed between 1900 and 7000 Å. The population-level distribution and corresponding temperature were obtained using Boltzmann plots. The electron density of the plasma was determined using well-known Stark broadening parameters of spectral lines. The plasma under study had an electron temperature of 13,200 K and an electron number density of 2×10^{16} cm^{-3}. The experimental relative transition probabilities were put on an absolute scale using the branching ratio method to calculate Sn I multiplet transition probabilities from available radiative lifetime data of their upper states and plotting the Sn I emission spectrum lines on a Boltzmann plot assuming local thermodynamic equilibrium (LTE) to be valid and following Boltzmann's law. The LTE conditions and plasma homogeneity have been checked. Special attention was paid to the possible self-absorption of the different transitions. The experimental results obtained have been compared with the experimental values given by other authors.

1. Introduction

The determination of the transition probabilities for spectral lines is a vast field of research on account of its considerable interest in atomic structure research, laser physics, plasma physics, thermonuclear fusion research and applications to astrophysics. A detailed investigation of high-resolution astrophysical spectra requires a large number of accurate atomic data. Tin is an important element in laboratory diagnostics, e.g. recently in semiconductor lithography tools [1,2] and in cosmic plasmas [3].

Tin neutral atom energy levels have been the subject of a few experimental and theoretical studies. Oscillator strengths of Sn I have been published previously by Corliss and Bozman [4], Penkin and Slavenas [5] (using the hook method) in 1962, have measured the absolute f-values of 29 Sn I lines in the spectral range of 2200–3200 Å, with an error of about 9%, except for resonance lines, with an estimated measurement error of 14%. In 1965 Lawrence et al. [6] used the atomic-been-technique to measure the absolute f-values of six lines for multiplet 5p^2 ^{3}P–6s ^{3}P in the spectrum Sn I. In 1967 Ovechkin et al. [7] determined transition probabilities for 11 spectral lines of Sn I. DeZafra and Marshall [8] have obtained experimental absolute oscillator strengths for 4 spectral lines of neutral tin. Lotrian et al. [9] (in arc discharge) have obtained transition probabilities in the spectral range of 2400–4000 Å for 17 spectral lines of Sn I. Wujec and Musielok [10] have measured absolute transition probabilities for 39 lines of Sn I for 26 lines, error 20–25%, and for the remaining lines 50%, using emission spectroscopy, in ultra-violet and visual spectra region. Wujec and Weniger, in 1977, [11] determined absolute transition probabilities from the emission spectra produced in a wall-stabilized arc for fifteen lines of Sn I in the spectral range od 5300–6850 Å, with estimated errors of about 40%. Miller et al. [12] have determined transition probabilities from 9 spectral lines in the range of 3100–6000 Å (errors, 35–50%). Muradov [13], in 1979, determined relative oscillator strengths of Sn I. A relativistic calculation of transition probabilities of the np(n+1)s and np^2 configurations for Sn I was performed by Holmgren and Garpman [14] in 1974. Migdalek [15], in 1979, calculated the relativistic oscillator strengths for the np^2 → np(n+1)s transition array as well in Sn I spectra in jj and intermediate coupling. Optical oscillator strengths for transitions 5p^2–ns, 5p^2–nd of Sn I have been calculated by Ganas [16] and for 14 lines of the 5p^2–6s transition for Gruzdev [17]. Bieron et al. [18] in 1991, have calculated, using the relativistic configuration interaction (CI) approach, the oscillator strengths and excitation energies for the np^2 → np(n+1)s transitions in Sn I. Energy levels and radiative transition probabilities for states within the 5p^k ($k=1$–5) configurations of atoms and ions in tin have been calculated by Biémont et al. [19]. In 1998 [20] and 2001 [21], Curtis estimated the branching fractions for the ns^2 np^2–ns^2 p(n+1)s

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transitions in Sn I, using intermediate coupling. Recently Yu et al. [22] have calculated oscillator strengths of neutral tin and Oliver and Hibbert [23] have calculated oscillator strengths using the atomic structure code CIV3 (Breit–Pauli configuration interaction) of transition in Sn I. Nadeen et al. [24–26] used two-step spectroscopy to investigate the even parity Rydberg levels of neutral tin.

Laser-induced breakdown spectrometry (LIBS) is a modern analytical technique based on emission spectroscopy that employs powerful laser pulses, focused on a sample, to attain representative vaporization and excitation, it has a fast response, as described recently in [27]. The analytical performance of the LIBS technique depends heavily on the choice of the experimental conditions. Laser ablation for analysis of solid sample is one of the most important applications of Laser-induced plasma spectroscopy (LIPs) in science and technology by Radziemski and Cremers [28,29]. LIBS use a low-energy pulsed laser (a few hundred mJ) to generate the plasma which vaporizes a small amount of sample. The interaction of a high-power laser beam with solid samples generates plasmas on the target surfaces with high temperatures and electron densities [30–32]. The emission spectrum of the plasma plume reveals important information regarding identification and quantification of the emitting species present in the ablated material. Plasma characteristics depend on laser intensity, wavelength and pulse duration, as well as on the physical and chemical characteristics of target material, and the surrounding atmosphere [33,34]. From the experimental point of view, LIP has proved to be a valuable and versatile source of spectroscopic data on neutral and ionized species as has been shown, specifically, in tin [35–41].

In this paper, different plasmas (tin, lead and tin–lead alloy) are fully characterized, in terms of their appearance, emission spectra, electron temperature (T_e) and electron number density (N_e), in vacuum. This paper aims to provide new experimental values of transition probabilities for spectral lines of Sn I and provide experimental values from spectral lines in the range of 5000 to 7000 Å, with few estimated errors, while the values given in literature include uncertainties of up to 40%. To obtain transition probabilities of Sn I, the experiment was carried out by emission of a plasma generated by focusing a laser beam on a solid sample of Pb–Sn (with 80% lead purity and 20% tin purity), in vacuum, recorded with a 0.8 μs delay time and at a fixed gate time of 0.1 μs, and analysed between 1900 and 7000 Å.

In this paper, we present transition probabilities for 97 spectral lines involving the levels of Sn I corresponding to transitions $n(n=6, 7, 8)s \rightarrow 5p^2$, $n(n=5, 6, 7)d \rightarrow 5p^2$, $5p^3 \rightarrow 5p^2$, $n(n=7)p \rightarrow 6s$. Intensity relative values have been obtained from measurements of all emission line; we have used two different methods in order to place the data on an absolute scale. First, using experimental values, measured in literature, of the radiative lifetimes of the corresponding states (Branching ratios method). As far as we know, in the literature, radiative lifetime of only nine low-lying odd-parity levels in 5p6s and 5p5d have been measured using different technique (phase-shift, Hanle effect, the zero-field level-crossing technique, beam-foil, electron-excitation DCM) [8,42–46], and lifetimes for nine levels of the 5p7p configuration of neutral tin have been measured by the time-resolved fluorescence method for Zhang et al. [41] in 2008. Secondly, with the local thermodynamic equilibrium (LTE) assumption, several transition probabilities were placed on an absolute scale from the Boltzmann plot of Sn I line intensities. The values obtained are compared with existing experimental and theoretical values. Also, the state of local thermodynamic equilibrium (LTE) is evaluated and plasma homogeneity has been checked.

This paper is organized as follows. Section 2 describes the experimental system used for LIBS, the procedure for obtaining the plasma and the study of the emission spectrum. The results obtained regarding the electron density and temperature of plasma, the LTE conditions, homogeneity of plasma in study, as well as transition probabilities of the Sn I spectra lines and analysis of the possible self-absorption of the different transitions, are given in Section 3, and conclusions in Section 4.

2. Experimental setup and procedure

The experimental setup, has already been described in previous papers in detail [36,37,40,47–52], so only a brief description is given here. A schematic of our experimental setup is shown in reference [52]. The laser used in our experiment was a Q-switched laser Nd:YAG (Quantel YG585) of 7 ns pulse duration of 275 mJ at 10 640 Å with a frequency of 20 Hz. The laser energy was monitored using a calibrated power-meter.

The laser beam is deflected by total reflection in a prism and is focused, with a quartz lens of focal distance of 12 cm, the surface of the target placed horizontally, with a power density on the surface of 1.4×10^{10} Wcm^{-2}, producing craters with standard diameters of 0.5 mm.

A chamber was prepared to generate the plasma with the target in vacuum ($\sim 10^{-5}$ Torr). The chamber has a system for changing the target position, maintaining the vacuum, so the plasma is formed in each measurement on the smooth surface of the target and not on the crater formed in the previous measurement. It also features a quartz window through which the light is sent to the spectrometer entrance slit, located 8 cm from the plasma. The spectrometer used in the 1900–7000 Å range 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, a resolution that is hard to achieve and equipped with a gated optical multichannel analyser (OMA III EG&G) system, 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 200 ns, and the spectral band detected by the device is about 100 Å.

The measurements were repeated at several delay times of 0.15–9 μs and at a fixed gate time of 0.1 μs, and consisted in the accumulation of 20 laser pulses at a delay time. To obtain the best signal-to-noise ratio the measurements were made with a delay of 0.8 μs and a recording interval of 0.1 μs. The detection was performed in synchronized manner with the electronic device that regulates the laser Q-switch. The measurements were obtained, after ablative cleaning the target for 2 laser pulses, in order to remove impurities. 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 needed for the numerical analysis of each spectrum was determined from the observation of several narrow spectral lines from hollow-cathode lamps, with a precision of 97%. The distance for which two lines can be distinguished is 0.36 Å in first order.

The lines studied ranged from 1900 to 7000 Å. The system has been calibrated in wavelength by recording the well-known lines of Ar, Ne and Hg covering the wavelength range of 1900–7000 Å, the uncertainties in the measurement are $\approx$0.001 Å. To calibrate the spectral response of the system (efficiency) 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.

Also, light from the plasma is collected through a quartz lens in an optical fiber (UV fused silica, 1 mm diameter) which transmits it to the entrance slit of the spectrometer, see schematic in Fig. 1. The lens and optical fiber connector have been mounted on a telescopic spring that lets you vary their relative distance to coincide with the focus distance of the image of the plasma, keeping aligned plasma-lens-optical fiber. The support is mounted on an optical bench, allowing controlled horizontal and vertical movements, thereby varying the area of plasma whose image is detected in the optical fiber. The focal length of the lens and its distance from the plasma was chosen to produce an enlarged image ($f=5$ cm, located $s=17$ cm from the plasma and $s'=5.5$ cm from the entrance of the fiber). The fiber